BOOK OF ABSTRACTS

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Invited Talks

Accelerated Discovery of Novel Photovoltaic Materials – Prospects and Challenge

Authors

Dr. Thomas Unold - Department of Structure and Dynamics of Energy Materials, Helmholtz-Zentrum-Berlin, Berlin, Germany

Abstract

I will discuss the application of combinatorial methodologies and high-throughput characterization and its implications in the search of novel semiconductor materials suitable for optoelectronic applications.

Despite the undisputed success of photovoltaic technologies experienced during the last decades, there is clearly a strong drive towards discovering and optimizing earth-abundant, non-toxic, efficient and stable thin-film PV materials. Considering the size of the periodic table, and even limiting oneself to earth-abundant constituents, the compositional space that can and should be explored is vast, and undoubtedly may take an insurmountable amount of time to be fully covered, when relying on traditional experimentation.

In the last decades theory has managed to move far ahead of the experimenter's world with respect to high-throughput screening of possible semiconductor materials. Also, a number of open-access databases have been implemented, which now provide access to the results of millions of material computations, e.g. Materialsproject, NOMAD and many more.

Compared to the developments in theory, the experimental exploration of novel materials, that is synthesis, has been much slower, still mostly relying on the Edisonian approach of sequential processing and characterizing single composition/property samples. Unfortunately, this approach is very slow and easily leads to materials development cycles of about 10 years.

The exploration of novel materials could be significantly accelerated by pursuing a combinatorial approach, e.g. by studying libraries of multiple compositions, processing variations or absorber/functional layer variations on single substrates. Thus, hundreds of different samples can be processed in single synthesis runs, e.g. allowing to uncover full phase diagrams by employing only a few samples.

This approach leads to a very large amount of data, and eventually needs to rely on machine-learning techniques in order to aid in processing and analysis of results. In order for this approach to be successful, a proper metric has to be used in order to guide the exploration process, which is still currently under discussion. I also believe that fully accessible public domain databases of experimental data (that encompass dark data) will be needed, in order to reduce duplication of efforts, enable curation of results with respect to reproducibility and to accelerate learning.

Considering these aspects, I believe the acceleration of experimental materials design by more than a factor of 100 is possible and feasible. I will give examples of some recent work in our laboratory along these lines, which has allowed us to demonstrate accelerated exploration of novel chalcogenide and perovskite materials using combinatorial synthesis and high throughput characterization.

Antimony based solar cells for photovoltaic applications

Authors

Dr. Thomas Weiss - University of Luxembourg

Abstract

Chalcogenide antimony based absorbers is a material system with emerging interest as a photovoltaic material based on earth abundant elements. The bandgap of Sb_2Se_3 is approximately 1.2 eV and can be tailored from 0.9 eV by Bi-alloying, i.e. $(Sb,Bi)_2Se_3$, up to 1.7 eV for Sb_2S_3 and thus can even be utilized for tandem applications.

As will be shown, the major bottleneck for Sb_2Se_3 based solar cells is the deficit, for substrate and superstrate architectures. Here, we present sequentially processed substrate Sb_2Se_3 solar cells. We show that those solar cells are limited by interface recombination. It is demonstrated that a post-deposition annealing after CdS buffer layer deposition can mitigate those losses and that is improved (highest value of 485 mV in our study). However, at the same time reduces, which limits the beneficial effect on the efficiency for the post-deposition annealing. Simulations are used to explain the observed trend.

Interestingly, intermediate atomic layer deposited buffer layers can also mitigate (though by a lesser extent) interface recombination, while simultaneously improving. A combination of post-deposition annealing and ALD buffer layers might therefore pave the way for improved Sb_2Se_3 device efficiency with improved and .

In a second part, $(Sb_{1-x}Bi_x)_2Se_3$ absorber layers are presented. It is shown that the orthorhombic crystal structure of Sb_2Se_3 is maintained up to , which results in a bandgap of approximately 0.9 eV. A fist device is presented with an efficiency of 0.7 % and a bandgap of 0.93 eV – ideal for a 2-terminal bottom cell.

Bridging the computational-experimental divide to design new p-type transparent conductors for solar energy

Authors

Dr. Rachel Woods-Robinson - University of California, Berkeley

Dr. Andriy Zakutayev - National Renewable Energy Laboratory

Prof. Kristin A. Persson - University of California, Berkeley

Abstract

Despite increasing demand for renewable energy materials over the past decade, as well as recent advances in photovoltaics (PV), solar energy is still not widespread in society and real-world efficiencies still lag behind their theoretical limits. This lag is in part from energetic losses due to suboptimal solar cell contacts, and specifically contacts that have both p-type conductivity and optical transparency. A high performance p-type transparent conductor (TC) could enable advances in a wide range of PV applications, such as a junction partner to new thin film absorbers, as part of a top hole-selective contact stack, or as a window layer in tandem PV devices.

However, such materials with properties comparable to n-type TC have not yet been found, and nearly all TCs used in industry are still n-type. Although TCs are conventionally oxides, chalcogenide (S, Se, Te), pnictide (N, P, As), and mixed anion semiconductors show promise of higher hole transport and greater p-type doping propensity. Computational screenings offer a pathway to discover such materials, but so far no predicted p-type TC has high enough performance for devices, stemming from a disconnect between theory and experiment. How can we transform theoretical design principles into actual experimentally realizable materials?

This talk will synergize high-throughput computation, combinatorial experimental methodologies, and device integration to discover and optimize new p-type TCs. Various aspects of this design pipeline will be addressed, depicted graphically. First, computational approaches to materials discovery will be discussed. We define and evaluate descriptors currently used in computational screenings, showing several to have a remarkably high degree of false negatives and positives. Subsequently, we introduce new experimentally-guided metrics to assess high performance, and then use these metrics to perform various tiered computational searches and identify a set of promising p-type TC compounds that have not previously been grown as thin films.

Second, we synthesize these predicted semiconductors as thin films and focus on a few ternary case studies. Our approach uses combinatorial sputter deposition, which allows for varying stoichiometry, synthesis temperature, and thickness within a single sample to probe a wide array of phase space, followed by various structural, optical, and electronic characterization using both combinatorial and in-depth techniques. Some successes will be discussed and also

challenges encountered in the laboratory, and how we can learn from setbacks in transforming predictions to experimentally synthesizable thin films.

Ultimately, the next step after synthesis and characterization is incorporating these new p-type TC materials into solar cell devices. We have fabricated both silicon heterojunction (SHJ) and cadmium telluride (CdTe) solar cells using a novel p-type contact to explore the challenges bringing predicted materials to actual highly-optimized device stacks. This understanding, coupled with simulations, has then led to the development of additional new computational descriptors and screening criteria. Thus, each phase of this process continues to inform subsequent phases. With this combined theoretical and experimental framework, we have discovered new p-type TC materials and developed infrastructure and insight to inform future strategies for materials discovery.

Cation and anion mutations in kesterites: a way to flexible band gap energy tuning

Authors

Prof. Susan Schorr - Helmholtz-Zentrum Berlin für Materialien und Energie, 14109 Berlin, Germany, Freie Universität Berlin, Institute of Geological Sciences, 12249 Berlin, Germany

Abstract

Solar cells based on Kesterites (Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$) absorber layers is the only critical raw material (CRM) free thin film PV technology with tunable band gap energy, an excellent long-term stability and efficiencies already at 14-15 % level [1].

Most of the current commercial PV devices are exclusively formed by a single junction, independently on the used technology. This device configuration permit only achieve maximum theoretical efficiencies in the range of 30-33% depending on the band-gap of the absorber [2]. To achieve further cost reductions in thin film solar cell technologies, devise efficiencies must be increased beyond the single-junction limit. Therefore, there is an increasing interest in semiconductor materials which are potentially suitable for wide bandgap applications such as top cell absorber layers in tandem solar cells.

Quaternary chalcogenide semiconductors, like Cu_2ZnGeS_4, $Cu_2ZnGeSe_4$ or $Cu_2ZnSiSe_4$ contain only earth abundant, non-toxic elements and have band gap energies between 1.5 eV and 2.2 eV. Cation and anion mutation is an established method for flexible band gap energy tuning in compound semiconductors applied in our research. In doing so the materials optimization requires knowledge of the structure-property relationships as a key feature.

The presentation will give an overview of the following challenges which have to been tackled working with these wide gap quaternary chalcogenides:

(i) End members of solid solution series adopt often different crystal structures, thus within a series a structural transition in dependence on chemical composition occurs, e. g. [3]. This goes often along with the formation of a 2-phase region (miscibility gap) in which two quaternary phases with different crystal structures but the same chemical composition coexist.

(ii) Quaternary Cu-base chalcogenide semiconductors often show an off-stoichiometric composition which goes along with the formation of intrinsic point defects [4] and influences the band gap energy [4]. The formation of secondary phases is very likely, e. g. [5].

(iii) These materials can show a structural disorder [6] which may have consequences for the device performance, e. g. [7].

The presentation will give an overview of our research results based on systematic studies of powder materials by different diffraction techniques (X-ray and neutron).

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Development of ZnSnP2 solar cells -bandgap control of bulk crystals and thin films

Authors

Prof. Nose Yoshitaro - Department of Materials Science and Engineering, Kyoto University

Mr. Taro Kuwano - Department of Materials Science and Engineering, Kyoto University

Abstract

$ZnSnP_2$ (ZTP) is an earth-abundant material for promising absorbers of thin film solar cells. We have investigated optoelectronic properties of ZTP using bulk crystals and reported the best efficiency of 3.87 % in ZTP solar cells with the structure of Al/ITO/CdS/ZTP/Cu_3P/Cu. In particular, it is a unique that bandgap of ZTP can be varied from 1.2 to 1.7 eV, which comes from arrangement of cations, Sn and Zn, in ZTP without no composition change. The crystal structure of ZTP is known to be chalcopyrite, while it is also suggested that sphalerite should be considered as seen in $CuInSe_2$. Such structure change can be recognized as order-disorder phenomena in cation sublattice due to arrangement of Zn and Sn.

In this talk, our progress of development of ZTP solar cells with focusing on bandgap control. First, the previous results on the relationship between bandgap and order-disorder phenomena will be reviewed and then bandgap control in ZTP thin films will be presented.

In the previous work by our group, the order-disorder phenomena in ZTP was investigated using bulk crystals grown by flux method. The crystals with the bandgap of around 1.6 eV were obtained at slow cooling rates conventionally adopted for crystal growth, and it was revealed that the bandgap decreases with increasing cooling rate. The long-range order parameter due to Sn and Zn arrangement evaluated from powder XRD profiles continuously decreases from 0.94 to 0.54 with the increase of the cooling rate. These two results mean that the bandgap decreases with decreasing the long-range order parameter. In other words, the bandgap can be controlled by ordering behavior. This was also suggested by first principle calculation.

Recently, ZTP thin films were prepared on glass substrate by MBE in our group. The conditions such as cell temperatures to obtain films without secondary phases were determined with machine-learning assisted. Interestingly, the bandgap continuously increases with substrate temperatures. As previously described, the bandgap shows a one-to-one correspondence with the long-range order parameter, which is difficult to evaluate from XRD profiles of thin films, unlike powder specimens. We thus discuss the mechanism of bandgap variation from the viewpoint of cation ordering kinetics in the talk.

Future of PV: holy grail for the industry

Authors

Dr. Veronica Bermudez - QEERI

Abstract

Net- Zero Emission targets by 2050 are being announced by governments all around the world. The acceleration in the achievement of this target will determine our capacity to mitigate the anthropogenic induced Climate Change. Solar PV will be a key element to achieve those targets and pivotal in the energy transition.

The question is not only achieving the targets, but doing it in a timely and affective way. This challenge needs having available new materials able to go through current silicon limitations and increase the conversion efficiency. The development and implementation of highly efficient new materials and concepts for sustainable energy conversion is one of the biggest industrial challenges. However, for the industrial challenge, efficiency is a must, but it is far from being enough for a success story, and many other parameters need to be, sooner or later, considered.

A continuous improvement following a the Japanese business philosophy "kaizen" has been demonstrated today as effective for Si based technology. It has allowed to reach the levels of PV penetration we know today and the amazing cost reductions during the last 20 years. However, Silicon technologies have a physical limitation in the Schockley-Queisser limit, which can be a limiting factor for the PV production capacity to reach the Net-Zero targets.

New breakthrough technologies are needed, which however, should be aligned and comply with industry standards and requirements in terms of: raw materials availability and the associated geopolitics, scalability, suitability of the technology transfer,.. Other elements associated with regulatory framework, as toxicity, environmental considerations, carbon footprint should also be considered within the "winners".

The long term reliability associated to energy solutions is also a challenge to be addressed, as without a long-term understanding about performance and reliability new technologies can be a risk not only for the industry, but also for our climatic challenges.

The recyclability is an important element that will increase in importance. The IEA forecasts an increase of close 40% of the PV capacity production, which will generate an important environmental footprint: fabrication, transportation and recycling will produce close to 8 millions tons of waste. By 2050 this can be number can be multiplied by 10and account for more than 10% of the world electronic waste. The LCA of the new technologies (considering in particular the future carbon border taxes and carbon credit mechanisms) can make the different between new technologies.

Added to all the elements above, the PV module of the future will attract the interest of the industry if it is fabricated with materials 100% recyclable (from an environmentally friendly recycling process), with a high efficiency, multipurpose (electricity production, hot water, heating and cooling) and with extended lifetime. All of this keeping in mind that the economy is key and the governing element is the return on investment.

Heteroepitaxy to Expand Materials Selection for PV Devices

Authors

Dr. Kirstin Alberi - National Renewable Energy Laboratory

Abstract

Expanding the selection of electronic materials used in photovoltaic devices to a wider range of existing and emerging materials has the potential to support improvements in device performance, design flexibility and the use of earth abundant elements. The attached figure highlights just a few semiconductors and semimetals that could be potentially used for PV devices. Integration of dissimilar materials is a key requirement in this endeavor. In particular, mismatches in lattice constant, crystal structure and/or valence across an interface can lead to unwanted defects and properties. Additional methods, tools and insights for controlling heterointerface formation are needed to address these limitations. In this presentation, I will discuss two aspects of heterointerface formation in material systems with relevance to PV applications. The first is controlling the chemical properties at the nearly lattice-matched heterovalent ZnSe/GaAs interface [1,2], with a potential application toward window layers in III-V solar cells. The second is the epitaxy of tetragonal $(Cd,Zn)_3As_2$ thin films on zinc blende substrates [3]. This alloy system ranges from a Dirac semimetal (Cd_3As_2) to a semiconductor (Zn_3As_2, bandgap ~ 1 eV) and has potential uses as both a low resistance contact layer and a narrow bandgap absorber. Mastering heterointerface formation in epitaxial systems can lay the foundation for extending materials integration techniques to a variety of thin film combinations.

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Hunt for the next perovskite

Authors

Prof. Aron Walsh - Imperial College London

Abstract

The design criteria for sustainable thin-film photovoltaic devices includes the chemical (e.g. abundance, toxicity, stability, scalability) and physical (e.g. band gap, absorption, doping density, contact behaviour) properties of the underlying materials. Many non-conventional inorganic materials are being investigated including metal oxides (e.g. Cu_2O) and sulphides (e.g. SnS); however, none are close to reaching their theoretical potential as defined by the detailed-balance limit [1].

I will discuss how the success of metal halide perovskites and the latest advances in materials modelling [2] can assist in the discovery of new materials for solar energy conversion. The role of predictive simulations can vary from high-throughput screening of candidate compounds, assessment of physical responses, to the optimisation of device architectures. Particular attention will be paid to origins of non-radiative electron-hole recombination that is avoided in perovskites, but limits the performance of newer technologies. Examples will be taken from our exploration of kesterite (e.g. Cu_2ZnSnS_4), herzenbergite (SnS), and antimonselite (Sb_2Se_3) systems [3,4].

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Materials design for photovoltaics: from bulk systems to interfaces

Authors

Prof. Silvana Botti - Friedrich Schiller University Jena

Dr. Pedro Borlido - Friedrich Schiller University Jena

Dr. Tomáš Rauch - Fri

Prof. Miguel Marques - Martin Luther University Halle

Abstract

How can new functional materials be designed using supercomputers?

In this talk I will show that extensive first-principles calculations, combined with crystal structure prediction and machine learning, can efficiently speed up the discovery of new materials. As an example, I will focus on the search of materials for photovoltaics.

Characterizing the electronic properties of crystalline bulk materials can however be insufficient. Interfaces are in fact at the heart of electronic devices: transistors, light-emitting diodes and solar cells, all exploit quantum processes involving electrons in tailored multilayers. The ability to shape potential gradients at interfaces opens up the possibility to manipulate electrons and develop new functionalities. The design of interfaces, as well as the deep understanding and control of their properties, is still a challenge beyond the current state of the art. I will discuss some recent progresses in this direction. In particular, I will present two *ab initio* density functionals that we have developed for accurate calculations of band diagrams at interfaces and surfaces (see figure).

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Spectroscopic combinational analysis and AI for materials research acceleration

Authors

Dr. Victor Izquierdo-Roca - Institut de Recerca en Energia de Catalunya (IREC)

Abstract

The fast development of the modern world leads to the permanently increasing need of complex materials. This includes the new generations of thin film photovoltaic (PV) materials and device technologies that aim at higher efficiencies, lower costs, lower carbon footprint, and high customizability (shape, colour transparency, flexibility…) for ubiquitous integration in different scenarios (BIPV, VIPV, IoT, APV …). This type of thin film optoelectronic devices are multilayer, multiprocess and multiscale with a high degree of complexity. This high complexity requires the use of several characterization techniques in a combinatorial way in order to obtain relevant information that provides an advanced understanding of their physicochemical properties. Their deep physicochemical comprehension is fundamental to study their impact on the optoelectronic properties of the final solar cell devices since under such a high complexity even minor physicochemical variation can lead to great performance differences. Likewise, this understanding is also necessary to enable the optimization of the synthesis process to achieve devices with finely-tuned properties that allow reaching the highest possible power conversion efficiencies. In this regard, the use of spectroscopic techniques for combinatorial analysis represents a very valuable asset since it can provide deep physicochemical information such as composition, crystal structure, defect formation, secondary phases or doping in a fast and non-destructive way that can be combined with optoelectronic characterization for obtaining a very complete picture covering the full complexity of new generations of thin film PV materials.

The use of combinatorial analysis is still an unexplored topic in optoelectronic research which commonly focus on very specific techniques and parameters that only provide partial information of the devices. The main reason for the non-implantation of combinatorial analysis is the necessity of using several complex techniques in parallel, the high amount of data generated and the lack of methodologies that can deal with this kind of high dimensionality information. This high scientific effort for characterization, understanding and optimization usually results in very long lab-to-market times.

In this context, the present work shows the potential of combining spectroscopic combinatorial analysis and artificial intelligence (AI) for accelerating materials research and reduce lab-to-market times. We present practical examples in which semi-automatized combinatorial characterization is combined with AI machine learning algorithms applied to the research in emergent PV devices allowing the fast analysis of large amounts of spectroscopic and optoelectronic data and the creation of methodologies for performance prediction. Furthermore, the combination of AI-driven and analytical approaches shows how AI can provide deep scientific knowledge about complex materials which opens the way to new forms of fast research for high potential to improving photovoltaic technologies in a short time.

Step into a solar cell: a roadmap of the material and societal challenges to achieving a solar-powered world

Authors

Dr. Rachel Woods-Robinson - University of California, Berkeley

Abstract

Climate change is one of the greatest existential threats facing society and we urgently need to scale up solar energy technology, however solar currently accounts for only a tiny fraction (less than 1%) of global energy generation. In this talk I will discuss how we can bridge this divide, I'll reflect on the role of scientists in confronting climate change, and contextualize how my own path into a science career intersects with this story.

First, our journey will begin zooming out to look at our planet, and the status quo of our energy generation and consumption. In principle, the sun could deliver over 1,000 times more energy than the planet needs, way more than any other energy source, and this is what first motivated me to study science. We have made significant progress in research and deployment of renewable energy generation and storage technologies in recent years, but solar is still much less efficient than predicted theoretical limits. The reasons why have to do with "materials", in particular the tiny crystals that solar panels are made of.

Next, to investigate this, we'll shrink down to the size of a single hair and step *inside* a solar cell to meet these different crystal layers –– absorber layers, contact layers, encapsulation layers, etc. –– and learn how they work together to convert sunlight into electricity. I will highlight the most important materials challenges that scientists face in making solar more efficient, more reliable, and more sustainable. These challenges range from developing new materials and playing clever tricks to absorb more sunlight, to ensuring that solar panels are reliable and recyclable. My own research, a tiny subset of a research challenge within solar technology, focuses on designing a special kind of "contact" material for solar panels to make sure all of the sunlight-powered electricity can efficiently get transported from the cell out into the external circuit.

Lastly, we'll zoom out of the solar cell and back to our human size to discuss challenges scientists face beyond the lab in bringing solar to society, including materials supply chains, environmental justice, and science communication. I will discuss my work with my science outreach organization, Cycle for Science, which sends scientists on sustainable bicycle tours around the world to stop in classrooms and teach hands-on lessons about renewable energy and climate change to inspire the next generation of scientists.

Solving complex challenges like climate change involves working together and thinking across different length-scales and time-scales. The goal of this talk is that you leave with an understanding of why materials are important in solar cells, with some wonders and excitement about the crystals that make up our world, and with an idea of something *you* can do to work towards a renewable energy powered future.

Systematic Efficiency Improvement for Kesterite Solar Cells by Synergetic Alloying/Doping

Authors

Prof. Xiaojing Hao - University of New South Wales

Abstract

Increasing the diversity of viable photovoltaic materials is critical to allow greater adaptability as the technology continues to expand and develop not only for further increasing the efficiency but also fulfill various application areas for everywhere PV. Kesterite is such a green energy material to capitalize this opportunity, utilizing equally sustainable energy materials for efficient energy conversion. There has been a significant research effort on developing secret recipes to solve the key obstacles to further improve the kesterite solar cell efficiency. The performance of kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cell is known to be severely limited by the nonradiative recombination near the heterojunction interface and within the bulk of the CZTSSe absorber resulting from abundant recombination centers and limited carrier collection efficiency. Nonradiative recombination is simultaneously reduced by incorporating small amounts of Ge and Cd into the CZTSSe absorber. Incorporation of Ge is known effectively increases the p-type doping, thus successfully improving the bulk conductance and reducing the recombination in the CZTSSe bulk via enhanced quasi-Fermi level splitting, while the incorporation of Cd greatly reduces defects near the junction region, enabling larger depletion region width and better carrier collection efficiency. The combined effects of Cd and Ge incorporation give rise to systematic improvement in open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), and fill factor (FF), enabling an efficiency of 11.6%. The synergetic multiple cation doping/alloying strategy for systematically manipulating the opto-electronic properties of kesterite materials may provide a viable way for further efficiency improvement of earth-abundant kesterite solar cells.

The environmental impact of PV power production: Materials, Energy and Use

Authors

Dr. Stephan Pfister - ETH Zurich, Institue of Evirnmental Engineering

Abstract

Solar Power and especially photovoltaics will have a major role in future electricity provision. Therefore sustainability of large-scale expansion needs to be considered also from an environmental perspective. Production of pholtovoltaics involves energy and various meterials, which might become scarce, or are at least considered critical materials in the short and medium term. This includes for instance silicon but also absorber and electrodes materials. Earth-abundant materials might offer alternastives for large sclae application of PV power production. However, alternative materials might require more energy for production or have lower efficiencies (leading to larger area demand per kWh produced). Therefore, material availability and energy requriements need to be included in the assessment of new designs.

This presentation will evaluate current life cycle assessment Life cycle assessment (LCA) of existing and emerging PV technology. LCA is a standardized approach to assess impacts throughout the entire value chain of products or services (ISO 14040). It is therefore suitable to compare different products or to develop more environmentally friendly products. LCA of specific semiconductors is still limited. More specifically, various PV systems have been analyzed by LCAs over the last two decades, but often with limited focus on the production details, due to the lack of underlying detailed LCA data, such as for mining and processing of materials, as well as lacking details on processes of PV compound production. In ecoinvent, the largest LCA database, PV panels for a few types of PV cells are available, but generally outdated.

This talk will give an overview on the limitations of current assessments with a special focus on material and energy consumption, and address the aspect of the use phase.

Transition metal based ternary nitride semiconductors

Authors

Dr. Andriy Zakutayev - National Renewable Energy Laboratory

Abstract

Ternary nitride semiconductors is an interesting class of materials studied for their diverse optoelectronic properties that are predicted to be tunable by cation ordering. For example, $ZnSnN_2$ has been extensively studied as an earth-abundant absorber for future photovoltaics, whereas wider-gap $ZnGeN_2$ has been recently investigated for light emitting diodes. However, the actively studied ternary nitride semiconductors are mostly limited to Zn-IV-N_2 composition with main-group metallic elements (IV=Sn,Ge,Si) closely related to their parent III-N compounds such as InN and GaN.

This presentation will focus on transition metal based ternary nitride semiconductors beyond the main-group Zn-IV-N_2 compounds. First, chemical trends in predicted crystal structure and calculated thermodynamic stability of ternary nitrides containing main-group metals (II=Mg,Zn), and closed-shell transition metals (IV= Ti, Zr; V=Nb, Ta; VI=Mo, W) will be presented. Second, experimental results will be shown for optoelectronic properties of Zn_2NbN_3 and $ZnTiN_2$ thin films, as well as for bulk powder synthesis of $MgZrN_2$ and Mg_2NbN_3. Finally, kinetically controlled synthesis methods of metastable ternary nitrides, including two-step synthesis reaction and various protection layers, will be discussed.

Zn1-xSnxOy by atomic layer deposition as buffer layer in kesterite solar cells

Authors

Prof. Charlotte Platzer Björkman - Uppsala University

Dr. Natalia Martin - Uppsala University

Dr. Jes Larsen - Uppsala University

Mr. Nishant Saini - Uppsala University

Dr. Tobias Törndahl - Uppsala University

Abstract

Kesterite solar cells, based on Cu_2ZnSnS_4 (CZTS), or compounds with partial or full exchange of elements in CZTS, are interesting for solar cells made from only earth abundant and non-toxic elements. The record lab efficiency is however limited to 12.6%, and extensive studies have been performed on limitations from bulk recombination and contact formation. One of the most successful buffer layers used to replace the standard CdS is $Zn_{1-x}Sn_xO_y$ (ZTO), deposited by atomic layer deposition (ALD). The benefits of this material are reduced parasitic absorption in the short wavelength region, tunable band gap energy allowing improved matching of the conduction band offset to the absorber layer and excellent conformal coverage even for very thin films. Efficiencies comparable to, or exceeding those of, devices with CdS have been reported for kesterite solar cells with ALD-ZTO buffer layers from several groups.

In this contribution, we discuss some of the remaining open questions in applying ZTO as buffer layer regarding interface formation, stability and applicability of ZTO for different compositions of kesterite absorbers. We have previously shown that the heating up of the substrate in the ALD reactor, prior to buffer layer growth, has a positive impact on open circuit voltage, in addition to the positive impact from the ZTO material itself. Studies of this part of the ALD process, using ambient pressure x-ray photoelectron spectroscopy, with nitrogen, oxygen and water atmospheres has therefore been performed. We have also studied the buried CZTS/ZTO interface using hard x-ray photoelectron spectroscopy, where initial results will be discussed. Regarding device stability, we have examined the effect from dark storage, where larger degradation in fill factor could be observed as compared to devices with CdS. Finally, we discuss the applicability of ZTO to various compositions of kesterite absorbers, in particular for wider band gap solar cells.

Oral presentations

A Comparative Study on The Environmental Performance of Monograin Vs. Thin Film CZTS Solar Cells

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Abstract

Kesterite-based structures are being extensively studied for solar cell productions due to their earth abundant and nontoxic nature, high absorption coefficient, and wide variety of scalable deposition methods, among other benefits. Kesterite solar cells are primarily manufactured using thin-film technology. The monograin approach however, in the last decade gained further attention for solar cell production, providing a third alternative to mono-crystalline wafer and thin film methods. The monograin membrane approach combines the advantages of high throughput, low-cost deposition techniques primarily from the printing industry with the versatility of a flexible, light weight, thin film solar module. In this context, studies showed that the production of CZTS powders with an improved crystal structure is comparatively simple, inexpensive and a convenient method. This enables significantly more cost-effective and energy efficient material production with negligible waste production in the manufacturing process.

This paper, for the first time, presents a comparative cradle to gate environmental performance assessment of monograin vs thin film CZTS solar cell methods. Life cycle impact assessment methods CML 2001, IMPACT 2002+, and ILCD 2011 were utilised allowing for a full range of indicators to be included in the analysis. The analysis is designed to identify the environmental hotspots associated with materials and manufacturing processes for 1m^2 panel as the functional unit. Global Warming Potential (GWP) and Cumulative Energy Demand (CED) have been used as proxies to demonstrate the associated environmental impacts. Results demonstrated that the monograin powder production ranged between 23.5 and 29 kg $CO_{2\,eq}$/m^2 and 130 and 160 CED kWh/m^2 for the GWP and CED respectively. The powder production process had a higher impact than the roll-to-roll process being responsible for 64% and 58% of the GWP and CED, respectively. The production of semiconductor powder was responsible for the most emissions (72%) and CED (60%) in powder production process with the encapsulation process in the roll-to-roll module production the highest contributor to the GWP and CED. Overall, the materials used were the major contributors to the GWP and CED impacts of the production of monograin CZTS in comparison to process energy. The estimated GWP (82.1 kg $CO_{2\,eq}$/m^2) and CED (618.4 kWh/m^2) impacts of thin film CZTS production were higher than of the monograin method. In contrary to monograin solar cell production, the GWP and CED impacts were mainly attributed to the energy process (97%) rather than the material usage. The overall material usage of thin-film CZTS (0.007 kg/m^2) solar cell production was about 93% lower than the material use of the

monograin method (0.12 kg/m^2). This paper demonstrates considerable environmental benefits associated with the monograin technology as a promising alternative technique to the thin-film method.

A Path Forward for Bismuth Based Inorganic Solar Photovoltaics

Authors

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Abstract

Integrated photovoltaics (PV) technologies are the next big emerging market as appropriate for an urbanised world with limited resources. Silicon PV is likely to continue dominating utility-scale in the near-term future given its maturity and investments. However, silicon PV, because of its rigid architecture, opaque design and high-temperature processing, is not best suited for semi-transparent and flexible configurations and have limited configurability for 'system integration'. Affordable system-integrated PV requires new designs based on earth-abundant, low-cost and non-toxic materials; and based on scalable and low-cost processing.

With relevance to system-integrated PV, the performances of solution-processed lead hybrid perovskites PV have skyrocketed. The critical material properties such as benign defects, long minority carrier lifetimes, large dielectric constants and fast charge-mobilities leading to such impressive device efficiencies originate from a unique electronic structure manifested due to the presence of a heavy polarisable Pb^{+2} ion. In principle, the Bi^{+3} ion with similar characteristics can instil similar charge transport and optical absorption properties. Therefore, purely inorganic Bi-absorbers could serve as non-toxic and thermodynamically more stable alternatives. Learnings from the photophysical, transport and electronic structure of Pb-hybrid perovskites have ushered a path for the discovery and development of new inorganic absorbers based on bismuth. Despite this, there remains a clear gap between the performances of the state-of-the-art PV devices based on bismuth and lead.

This presentation will exhibit our results on three different Bi-absorbers – BiI_3, BiSI and $BiFeO_3$. In all three cases, the phase-pure films as analysed using quantitative analysis based on diffraction and Raman spectroscopy, as well as complete devices, are processed using molecular-precursor based solution processing. Using gold-standard G_0W_0 electronic structure calculations complemented by photophysical measurements, we demonstrate that both BiI_3 and BiSI have several desirable characteristics of strong absorption, large dielectric constants and low effective masses. Based on the band alignments calculated using the capacitance measurements, we construct solid-state p-i-n devices with superstrate configuration of FTO/TiO_2 (SnO_2)/BiI_3 (BiSI)/ F8 - poly(9,9-di-n-octylfluorenyl-2,7-diyl)/Au. We have achieved some of the best-in-class results efficiencies of 1.12% and 1.32% for BiI_3 and BiSI, respectively. In particular, we find our deposition route of sulphide-to-iodide replacement results in compact, homogenous and out-of-plane grain texturing for superior charge-transport and overall performance metrics with large open-circuit voltages of >600 mV for BiI_3. In the third case, we investigate, $BiFeO_3$, a popular multiferroic material for PV devices. Getting phase-pure $BiFeO_3$ has been reported a challenge; while using our solution processing approach, we could achieve high-level compositional and phase purity as well as fabricate the entire device of ITO/ZnO/$BiFeO_3$/Graphite. The all-solution processed $BiFeO_3$ represents one of the highest performing all-oxide devices with an device efficiency of 4% and 70% quantum efficiency in the

visible spectrum. We also evaluate the performance-limiting factors based on low-temperature device measurements and transient photoluminescence.

Lastly, based on our results and literature, we propose a few recommendations on the development of future Bi-based PV, including contrasting the electronic, structural and device features of Pb and Bi absorbers and how to optimise the screening, material growth, and devices further.

Anisotropic luminophore emission for enhanced light trapping in luminescent solar concentrators

Authors

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Abstract

Building-integrated photovoltaic (BIPV) technologies integrate photovoltaic energy generation into the design of semi-transparent and opaque building envelopes. The photovoltaic luminescent solar concentrator (LSC) is an example of such a technology and offers the potential for low-cost, passive concentration of direct and diffuse light. An LSC consists of a glass or plastic waveguide with embedded luminophores and integrated solar cells along the edges or in a matrix.

Even though the LSC concentrates sunlight in the waveguide and guides it to solar cells smaller than the top surface area, it cannot surpass the detailed balance limit for a single-junction solar cell. In short, the LSC remains at 1-sun illumination intensity, and the potential V_{OC} increase due to increased J_{SC} (concentration factor) is offset by the coincident increase in the J_0. Thus, the power conversion efficiency (PCE) of the LSC is limited to the typical 34%, while the world record remains at 7.1%, indicating both the poor performance of LSCs so far, but also the significant potential gain. One of the main loss mechanisms in an LSC is the emission of photons through the escape-cone, accounting for about 25% of all lost photons. This is a direct consequence of isotropic luminophore emission and the escape-cone angle of a glass/plastic waveguide in air.

Recent advances in the emission efficiency of semiconductor luminophores could significantly reduce parasitic losses, but efficient light trapping remains elusive to achieve high conversion efficiency LSCs. Here, we demonstrate anisotropic luminophore emission to enhance light trapping in the LSC waveguide. By embedding semiconductor CdSe-CdZnS core-shell nanoplatelet emitters into high-index TiO_2 nanocylinders, we alter their angular emission profile to increase emission into total internal reflection (TIR) angles. The emission direction can be controlled by tweaking Mie-like multipolar resonances in the individual nanocylinders (form factor) and the interaction with the lattice (structure factor). We use FDTD simulations to find the optimal nanostructure, and RCWA simulations to optimize the array dimensions. By optimizing the cylinder shape and lattice spacing, we show an increase in light trapping from 75% (isotropic emission) to 83.5%.

Arrays of TiO_2 nanocylinders were fabricated on top of a glass substrate. First, a multilayer stack of TiO2, CdSe-CdZnS core-shell nanoplatelets, and TiO_2 was created. Using e-beam lithography and subsequent reactive ion etching of the multilayer, we obtained an array of TiO_2 cylinders with 500 nm diameter, 120 nm height, and 1400 nm pitch, with an embedded nanoplatelet layer of 30 nm thick. SEM images and spatially resolved photoluminescence measurements show that the luminophores are only located inside the cylinders as designed. To demonstrate the directional emission, we measure angle-resolved luminophore emission in a Fourier-microscopy setup. To emulate the incorporation of the cylinder array inside the waveguide, we

used an immersion-oil objective, which also enables the collection of luminophore emission under grazing angles. This novel approach to the integration of nanoscale photonic structures and emitters paves the way for enhanced emission control in photovoltaic systems, as well as in solid-state lighting and smart displays.

Bottom-up Filling of Nanosized Trenches with Silver to Fabricate Transparent Conducting Electrodes

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Abstract

Transparent conducting electrodes (TCEs) are essential in many optoelectronic devices including solar cells, LEDs, sensors and displays. The most common approach for TCEs is the use of transparent metal oxide layers, in particular Indium tin oxide (ITO). However, ITO comes with numerous drawbacks such as the relatively high cost, fragility, rarity of Indium, strong UV absorption and relatively high sheet resistance. An exciting TCE alternative is the use of interconnected metallic nanowires, where their sub-wavelength cross-sections makes them transparent to visible light [1,2,3].

In this work, we show a promising cost-effective method to fabricate metal nanowire structures using selective-area electrochemical deposition (SAEC). SAEC is based on electrochemical deposition through an insulating template onto a conductive substrate. Next to the low fabrication cost, electrochemical depositions is a bottom-up method with numerous advantages such as scalability, ambient operation conditions, control over nucleation and high purity. While submicron sized features have been already demonstrated by SAEC [4,5], obtaining homogeneous void free filling of features below 100 nm using direct plating is a major challenge because of the terminal effect and the poor control of nucleation of the seed layer.

Here, we have explored the SAEC fabrication of silver nanowire grids over a large area by using soft-conformal imprint lithography as means to fabricate the template on ITO substrates. Electrodeposition of silver was performed by making use of the double pulse technique [6]. The particle density is found to be an important parameters for the void-free homogeneous filling of the trenches, which can be tuned by varying the duration and height of the nucleation pulse and the concentration of free silver ions in the electrolyte. Furthermore, at a low overpotential nucleation pulse the particle density is also influenced by the preferred crystal orientation of the ITO substrate. Although, the influence of the ITO substrates becomes negligible for a large enough overpotential, in which the nucleation is fully determined by mass transport instead of electron kinetics. We found that homogenous void-free filling of the trenches could only be obtained when the nucleation density is larger than 10^{10} particles per cm^2, corresponding to approximately 20 particles within one pitch of 2 μm.

Finally, we compare the optical and electrical properties of the SAEC-fabricated metal grids with those fabricated using conventional thermal or e-beam evaporation followed by lift-off. This work represents a low-cost and scalable strategy to fabricate sub 100 nm predefined metal structures, enabling the commercial viable fabrication of nanowire based transparent conductive electrodes for optoelectronic devices.

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Effects of work function and electron affinity on the performance of carrier-selective contacts in silicon solar cells using ZnSn(x)Ge(1-x)N2 as a case study

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Abstract

The search for new Earth-abundant and low-cost materials for photovoltaic (PV) applications has led to a recent interest in II-IV-N_2 semiconductors. Among these, $Zn_xSn_{1-x}N_2$ (ZTN) is an interesting candidate due to a tunable direct bandgap depending on stoichiometry ($0 < x < 1$) with values ranging from 0.7 to 2.8 eV and strong optical absorption in the solar spectrum. Alloying $ZnSnN_2$ with $ZnGeN_2$, another direct bandgap semiconductor but with wider energy gaps in the range 2.7-3.4 eV, results in $ZnSn_xGe_{1-x}N_2$ (ZTGN) compounds that can extend the bandgap range further up, encompassing the full visible spectrum, while maintaining a II/IV ratio of 1.

Yet, the accomplishment of PV devices with this family of semiconductors remains a largely unexplored research topic, with few works reporting PV devices with ZTN as absorber or electron-selective contact for silicon solar cells. Nevertheless, the wide ranges of values for bandgap and conductivity of ZTGN alloys makes them interesting materials to study as electron-selective contact for silicon heterojunction (SHJ) solar cells.

In this context, we fabricated by combinatorial sputtering $ZnSn_xGe_{1-x}N_2$ (ZTGN) layers ($10\% < x < 90\%$) on glass for material characterization and further assessed the performance SHJ solar cells featuring ZTGN as electron-selective contact using various complementary contact

structures. In the investigated composition range, bandgap was shown to be tunable between 1.6 eV and 2.3 eV, while conductivity and activation energy changed from 7 S/cm and 17 meV, for the Sn-rich composition, to 10^{-10} S/cm and 610 meV, respectively, for the Ge-rich composition.

Nevertheless, for all compositions, ZTGN performs similarly as electron-selective contact, with low V_{oc} in the range 450-580 mV and low FF. Comparing the use of p-type and n-type wafers, we evidenced that strong Fermi-level pinning at the c-Si interface occurred when the ZTGN layer was in direct contact with the silicon wafer, which was effectively suppressed when inserting an intrinsic a-Si:H passivating layer.

Fitting of the current-voltage curves of solar cells using various Sn and Ge content, with an exchange-current model, we could show that the work function of all ZTGN layers lies around 4.3 eV, i.e., within the silicon bandgap, independently of the Sn and Ge contents. Combining this work-function value with bandgap and activation energy extracted from ellipsometry and temperature-dependent conductivity measurements, we obtained the position of the conduction and valence bands for each composition. The Sn-rich composition therefore has a relatively high electron affinity (~4.3 eV), whereas the Ge-rich composition combines a too low electron affinity (3.7 eV) with a too low doping (too high activation energy).

This causes two different barriers for electron extraction, one being intrinsic to the selectivity of the contact and originating from unfavorable band bending in the silicon itself, and the other being external and due to the resistivity of the layer itself. Since electron affinity cannot be tuned, doping of Ge-rich ZTGN layers is suggested as the best option to make efficient electron-selective contacts with ZTGN layers.

Efficient ultrathin AgBiS2 solar cells via cation disorder engineering

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Abstract

High-performance, lightweight solar cells with low-cost and non-toxic substituents are a major target in the field of solar photovoltaics.[1–5] Ultrathin solar cells can reduce material consumption, weight and manufacturing demand, directly lowering the cost, in addition to benefitting quantum efficiency and photovoltaic (PV) performance. To enable ultrathin architectures, however, strong optical absorption is an absolute necessity.

Here, we demonstrate that engineering the cation distribution and disorder in an emerging ternary chalcogenide absorber can lead to major absorption enhancement, enabling ultrathin PV devices with short circuit current density of 27 $mA \cdot cm^{-2}$ and a record power conversion efficiency of >9%,[1] at a film thickness of only 30 nm.[1] We rationalise this behaviour through in-depth modelling of the thermodynamics of cation interactions in this disordered system, alongside simulations of the electronic structure and optical properties as functions of cation distribution. We show that cation-disorder-engineered $AgBiS_2$ nanocrystals offer an absorption coefficient that is higher than other PV material, and results in the best performing bismuth-based solar cell to date, giving hope that high-efficiency earth-abundant devices can be achieved via intelligent materials design strategies.

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Electrical properties of Zn3P2 grown on InP

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Abstract

Zinc phosphide (Zn_3P_2) is a promising earth-abundant solar cell material due to its direct band gap transition of 1.5 eV [1], which is close to the optimum solar energy conversion range. The large optical absorption coefficient of $>10^4$ cm^{-1} in the visible range [2], and the long minority carrier diffusion length reported (~10 µm) [1, 3] make it perfectly suited for thin film technology. Nonetheless, epitaxial growth of high-quality Zn_3P_2 is inherently challenging, due to the large lattice parameter (a= 8.089 Å and c = 11.45 Å) and the high coefficient of thermal expansion of Zn_3P_2. Both factors strongly limit the choice of commercially available substrate for the epitaxial growth of Zn_3P_2. One way to circumvent this is to use InP substrates for the growth of Zn_3P_2, as the phosphorous sub-lattice of the Zn_3P_2 exhibits a low lattice mismatch (~2.4%) with the group V element of InP [4]. We have demonstrated the benefit of using InP substrates on the growth of monocrystalline and polycrystalline Zn_3P_2 thin films as well as ordered arrays of nanopyramids [4,5].

In this work, we discuss the electrical properties of Zn_3P_2 with different morphologies grown by molecular beam epitaxy on intrinsic and doped InP substrates. Selective area epitaxy (SAE) is used to grow ordered arrays of nanopyramids. The electrical response of the nanopyramids has been investigated by conductive atomic force microscopy (C-AFM). A strong influence of the substrate can be observed even without illumination. Additionally, the electric response of these nanostrucutres is also affected by the geometrical parameters of the array (opening size, pitch). The I(V) curves obtained from the C-AFM measurements shows a clear non linear behavior which is enhanced with increasing opening size. This variation in electrical behaviour with

increasing opening size is attributed to the change in the composition of the grown Zn_3P_2, which is corroborated by STEM-EDX measurements [5]. The voltage-current characteristics of both mono-crystalline and polycrystalline thin-films indicate a strong correlation with the microstructure of the film. Spectral photocurrent measurements were performed to observe the contribution of the InP substrate to the overall photoconduction. Finally, charge mobility has been measured by terahertz spectroscopy and Hall effect measurements. Hall bars were fabricated on thin films with a characteristic size ranging from a few hundreds of microns down to a few microns. Mobility in Zn_3P_2 nanostructures is measured by growing nanoHall bars by SAE. This approach is key to shine light on the impact of the epitaxial growth and crystal quality on the material's transport properties.

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Extrinsic n- and p-type absorber doping for Sb2Se3-based solar cells

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Abstract

Antimony selenide (Sb_2Se_3) is a promising emerging material for use in photovoltaics (PV). It has excellent optical properties, cheap and earth abundant materials and has improved rapidly in the last 7 years, from 2% to over 9% efficient. While device efficiencies have developed rapidly during this time, certain fundamental aspects of Sb_2Se_3 remain a matter of some debate.

One example is the matter of doping. Early studies reported Sb_2Se_3 to be a natively p-type material and the device architectures used for Sb_2Se_3 solar cells mostly used it as the p-type material in a planar p-n heterojunction. Theoretical studies have since reported Sb_2Se_3 to be natively insulating due to compensating native defects, with limited capacity to be doped either p- or n-type through native defects. The discovery by our group that the Sb_2Se_3 used in our devices was n-type, due to unintentional Cl doping of the source material, and that these devices were competitive with the best reported efficiencies (7.3%), has opened the door to the potential of using extrinsic dopants to control the conductivity of Sb_2Se_3 [1].

In this study, bulk crystals of both Cl and Sn doped Sb_2Se_3 were fabricated for investigation of their electronic properties. A combination of ultraviolet, x-ray, and hard x-ray photoemission spectroscopy was used to obtain a depth profile of the energy separation between the Fermi level and the valence band maximum. A solution to Poisson’s equation was then found to fit the data, obtaining an estimate for bulk carrier density as well as a profile of the surface space

charge layer. These results are then compared to carrier densities measured by capacitance-voltage and Hall effect measurements.

The Cl doped crystal was found to be strongly n-type and the results of the Poisson's equation solution were consistent with the Hall effect and C-V results (10^{17}-10^{18-} cm^{-3}). 280 meV of surface band bending was observed with a depletion layer extending ~20 nm into the surface. The Sn doped crystal was more weakly doped (10^{16} cm^{-3}) and had significantly more band bending (500 meV) over a greater depth (~100 nm). The solution for the Sn doped crystal indicates a surface inversion layer, with the near surface region exhibiting slightly n-type conductivity with p-type behaviour further into the bulk. This is in agreement with density functional theory calculations of the defect level formation energies, which predicts self-compensation of the Sn_{Sb} antisites by Sn interstitials at a relatively low doping level.

This study provides an in-depth investigation of the impact of Cl and Sn doping on the electronic properties of Sb_2Se_3, combining a range of photoemission techniques, electronic characterisation and theoretical calculations on one of PV's most exciting emerging absorbers.

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Feasibility and growth mechanism of BaZrS3 chalcogenide perovskite from oxide precursors

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Abstract

In recent years, $BaZrS_3$ chalcogenide perovskite has emerged as a promising material for photovoltaic application. A direct bandgap of 1.8 eV coupled with strong light absorption coefficients and good carrier transport makes $BaZrS_3$ an ideal candidate for top cell materials in tandem solar cell technology. In addition, $BaZrS_3$ is also an earth-abundant and non-toxic semiconductor material, with excellent air stability in difference to inorganic-halide perovskites. In order to bring this material to the forefront of PV, it is necessary to deepen the knowledge of its fundamental properties, as well as find pathways for low-cost and affordable synthesis.

In this work, we explore the feasibility of synthesizing high-crystal quality $BaZrS_3$ thin films from $BaZrO_3$ precursors, with a special focus on investigating the mechanism of sulfide formation.

For this purpose, amorphous Ba-Zr-O precursor films were deposited on a quartz substrate using pulsed laser deposition and sulfurized at various temperatures (ranging from 700°C to 1000°C) under the H_2S atmosphere. This has resulted in a series of thin films with varying concentrations of S, from S-poor (S/(S+O) = 0.2) to S-rich (S/(S+O)=0.8). All films exhibit constant composition of Ba/Zr = 0.8, making them slightly Zr-rich. Detailed morphological and compositional assessment of thin films was performed by transmission electron microscopy (TEM) coupled with energy dispersive x-ray spectroscopy (EDX) and selective area electron diffraction (SAED) measurements on cross-sections of the thin films. The results have shown that at lower annealing temperatures (< 800 °C), the grown layers are mostly in nanocrystalline form, characterized by a homogenous mixture of nanodomains belonging to $BaZrS_3$ or $BaZrO_3$. With an increase in the annealing temperature (at 900 °C), further phase separation is observed with $BaZrS_3$ grains mostly located in the top region of the film, while ZrO_2 in addition to $BaZrO_3$

is observed at the back. Finally, the thin film synthesized at 1000°C is mostly constituted of high-crystal quality $BaZrS_3$ grains, with small nanometric ZrO_2 crystals observed at the back of the film. Grazing incidence wide angle X-ray scattering (GIWAXS) with various incidence angles (from 0.3 to 2°) has allowed structural assessment of the surface, sub-surface, and bulk region of thin films. These results have shown that: (i) there is no formation of $BaZr(O, S)_3$ solid solution, and (ii) $BaZrS_3$

is always synthesized in stoichiometric composition (Ba: Zr:S = 1:1:3). Rutherford Backscattering Spectrometry (RBS) has additionally confirmed the formation of stoichiometric $BaZrS_3$ compound. This is in difference to many other chalcogenide compounds, such as $Cu(In, Ga)Se_2$ and kesterites, which structures allow high variation in stoichiometry. The presence of highly intense and narrow peaks in the Raman spectra measured with 488, 532 and 785 nm confirm the formation of high crystal quality $BaZrS_3$ phase at higher annealing temperatures. Minor contributions from ZrO_2 and $BaZrO_3$

have also been observed in the Raman spectra. Based on these results, a detailed mechanism of S-incorporation and sulfide formation is proposed and discussed.

Highly efficient ultrathin Sb2S3 solar cells by confined crystallization and interface engineering

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Abstract

A general preparative method based on atomic layer deposition (ALD) is presented to overcome the poor chemical compatibility between classical n-type metal oxides and the sulfide or a heavier chalcogenide used as the light absorber layer in thin film solar cells. A sacrificial layer utilized as a scaffold is deposited on top of the Sb_2S_3 with the purpose of overcoming the well-known material mobility of highly pure Sb_2S_3 caused by the chemical incompatibility with TiO_2. The sacrificial layer is selectively removed once the Sb_2S_3 has been annealed and converted to stibnite phase while keeping the characteristic conformality of ALD layers. An exhaustive study of the Sb_2S_3/sacrificial layer (or top-interface) subjected to different physico-chemical treatments is carried out to further enhance the opto-electronic properties and therefore the performance of the solar cells. The photovoltaic characterization reveals that devices in which Sb_2S_3 interfaces have been treated are superior to the non-treated ones, reaching efficiencies of up to 5.5%. The generality of this approach is demonstrated for different nanostructures and has the potential to be applied in Sb_2Se_3 to solve the chemical incompatibility in the absence of CdS.

High-throughput investigation of ZnGeP2 thin films via reactive phosphine co-sputtering

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Abstract

There remains a strong interest in the discovery of new materials for optoelectronic devices, such as photovoltaics, using high-throughput synthesis. Phosphides have been largely overlooked for high-throughput synthesis due to challenges associated with their synthesis. In this work, we present the use of a high-throughput phosphide synthesis technique, reactive combinatorial co-sputtering with PH_3, to deposit $ZnGeP_2$ thin films. $ZnGeP_2$ is a promising material for tandem PV on silicon because it is lattice-matched to Si and has a wider band gap of 2.2 eV that can be tuned down to 1.7 eV and lower by controlling cation site disorder. In this study, we first grew amorphous films over a wide range of compositions and found an upper limit in growth temperature determined by Zn and P volatility. We found that deposition in a Ge-limited regime could be utilized to slow the growth rate and thereby compensate for the desorption of the Zn and P. Crystalline $ZnGeP_2$ films were then achieved by depositing the films at higher temperatures in this Ge-limited regime with a reduced deposition rate. X-ray diffraction revealed that the films had crystallized in the zincblende cation disordered structure. The crystalline films exhibited absorption energy threshold values ranging from 0.8 to 1.3 eV, significantly lower than the 2.2 eV band gap of ordered $ZnGeP_2$. Increased Ge content was found in films that exhibited a decreased absorption onset energy. Defect formation energy diagrams were used to gain an understanding of the off-stoichiometry seen in these films. These results illustrate the wide range of available band gaps in this material depending on composition and cation disorder. The absorption onset energies found in this work are near the optimal band gap for a single junction solar cell, however if increased cation order can be realized that would widen the band gap making it more suitable for a tandem device. This work provides the first high-throughput investigation of $ZnGeP_2$, demonstrating how off-stoichiometry can serve as a useful handle that can controllably tune properties in cation disordered $ZnGeP_2$.

Impact of Ge incorporation on the opto-electronic properties and the physics of deep defects in kesterites

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Abstract

To boost the efficiency of kesterite-based solar cells, cationic substitution has been widely investigated. Specifically, a growing interest has developed for the Germanium which leads to an improvement of the solar cell V_{OC} value, considered as the weak characteristic of kesterite material for PV applications. To obtain a comprehensive view of the relevance of Ge substitution in the Sn-based kesterite, using an *ab initio* approach, we studied the opto-electronic properties as well as the physical behaviour of points defects in Sn- and Ge-based kesterites. Controlling the nature of defects appears as a crucial requirement for an optimal tuning of the physical properties of kesterite absorber layers.

First, we highlight the high absorption coefficients (10^4 cm^{-1}) and the band gap values of 1.32 and 1.89 eV obtained respectively for the Sn- and Ge-based compounds. Then, using an improved version of the Shockley-Queisser model allowing a fine tuning of the recombination rate, we highlight the possible efficiency improvements of both CZTS and CZGS based solar cells while promoting their use as top cell for tandem approach.

Additionally, to gather a full picture of the impact of Ge incorporation in kesterite, we explored in detail the physical behaviour of point defects following both Ge doping and alloying of the Sn-based material. In both CZTS and CZGS, we highlight the net Cu/Zn disorder as well as the intrinsic p-type conductivity. More significantly for PV applications, we report on recombination centres that reduce the performances of kesterite-based solar cells. Upon Ge incorporation, in the both the Sn-based (doped) and the Ge-based (alloyed) kesterite, we observe a reduction of the lattice distortion following the formation of the Ge_{Zn} substitutional defect that leads, in comparison to its Sn_{Zn} parent, to a reduction of its carrier capture cross section, which we report as a possible explanation for the experimentally reported V_{OC} enhancement.

These works have received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 952982 (Custom-Art).

Ratz, Thomas, et al. "Opto-electronic properties and solar cell efficiency modelling of Cu_2ZnXS_4 (X= Sn, Ge, Si) kesterites." *Journal of Physics: Energy* 3.3 (2021): 035005.

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Innovative quasi-1D SbSeI micro-columnar semiconductors for defect-tolerant, optically tuneable solar cells

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Abstract

Emerging quasi-1D van der Waals chalco-halide semiconductors are attracting a lot of interest as photovoltaic absorbers, constituting an innovative and revolutionary approach to boost up the photovoltaic performance of thin-film-based devices, owing to their unique capacity to exhibit enhanced anisotropic electrical properties when they are correctly oriented. Also, it has been reported that the large spin-orbit coupling and mixing of antibonding s-orbitals at the top of the valence band might enable defect-tolerant features. So far, the mixed chalco-halide compound SbSeI has demonstrated efficiencies exceeding 4%, with a bandgap of 1.80eV, and a synthesis temperature below 300ºC.

In this work, SbSeI micro-columnar solar cells have been obtained by an innovative methodology based on the selective iodination of Sb_2Se_3 thin films at pressures higher than 1 atmosphere, using SbI_3 as the iodine source. The formation process of SbSeI has been studied by investigating the effect of different annealing parameters such as temperature, time and pressure. Accordingly, it is shown that under pressures above 1 atm, at temperatures below 250ºC, the SbSeI phase is not formed and the Sb_2Se_3 layer remains unaffected. At 250ºC, disordered SbSeI micro-columnar structures clearly appear with 2-3um height and 50-200nm thickness, however, the Sb_2Se_3 precursor is still clearly seen in the cross-sectional image with slightly reduced thickness. By increasing the annealing T under SbI_3 atmosphere, the height and density of the micro-columnar structures monotonically increases, achieving columns of around 20um height at 450ºC, see SEM images in **Figure 1**. Hence, we demonstrate a procedure to tune the height and thickness of SbSeI columns. In addition, **Figure 2** shows the X-ray diffractograms for a series of samples annealed at different T, times and pressures, confirming the almost full conversion of Sb_2Se_3 into SbSeI at 450ºC, exhibiting very good crystalline quality, albeit random orientation.

Selected samples were converted into functional solar cells using the Glass/Mo/SbSeI/CdS/ZnO/ITO structure. **Figure 3** shows the conversion efficiency and open

circuit voltage (V_{OC}) obtained for two samples annealed at 275ºC and 300ºC. For the 275ºC sample, efficiency up to ~1% is obtained with a V_{OC} around 350 mV. Interestingly, from the external quantum efficiency (EQE) it is observed that a low bandgap material (~1.25eV) and a wider bandgap material (~1.6-1.7eV) are contributing to the EQE, correlating with the SEM and XRD analysis where the presence of both Sb_2Se_3 and SbSeI were detected, see **Figure 4**. On the other hand, for the sample annealed at 300ºC, efficiencies higher than 0.3% are reached with V_{OC} values up to 550 mV, among the highest reported for the SbSeI. Indeed, EQE confirms that this is the dominant phase (a bandgap of 1.8 eV is extracted).

To sum up, in this work we demonstrate the potential of a novel emerging photovoltaic technology based on SbSeI micro-column absorbers. A detailed morphological, structural and compositional characterization study (including SEM, TEM and XRD analysis) has been carried out. Accordingly, we present a possible formation mechanism based on a self-catalyzed solid-liquid-vapor transformation; indicating new strategies to improve the morphology and carrier collection of the devices.

Interface passivation in textured perovskite/silicon tandem solar cells

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Abstract

Crystalline silicon (c-Si) solar cells are approaching their practical efficiency limits, which hinders their capacity to continue their learning curve. The most promising approach to overcome this efficiency limit and to continue lowering electricity prices consists in stacking a metal halide perovskite solar cell on c-Si to form a tandem device. Record monolithic perovskite/c-Si tandem solar now deliver an efficiency above 29% (compared to 26.7% for c-Si alone). Still, high-efficiency tandems often feature a solution-processed perovskite absorber, meaning that the pyramidal texture of the c-Si subcell needs to be completely flattened or at least significantly reduced [1]. This pyramidal texture is however beneficial in terms of optics: it promises higher photocurrents as it reduces reflection losses and promotes light trapping.

In this contribution, we discuss our latest progress in the processing of high-efficiency tandems featuring perovskite solar cells deposited on textured silicon heterojunction solar cells. For compatibility with micrometer-sized pyramids, the perovskite absorber is deposited here using an “hybrid” evaporation/spin coating process developed in-house. This method is notable for past demonstrations of perovskite/silicon tandem with efficiencies >25% thanks to a high short circuit current approaching 20 mA/cm^2 (certified efficiency of 25.2% [2]). To improve upon these numbers and especially the device open circuit voltage (V_{oc} < 1.8 V), we first identified the critical interfaces of the stack by extracting quasi-Fermi level splitting (QFLS) data from photoluminescence measurements [3]. Based on this knowledge, we modified processes and materials to improve our layer stack, notably the quality of its interfaces. As it will be discussed

at the conference, these efforts resulted in the demonstration of tandem devices with efficiencies equivalent to the state-of-the-art.

As shown in Figure 1A, the interfaces with each contact layer (either the hole transport layer, HTL, or the electron transport layer, ETL) are particularly detrimental to the QFLS. Treating the top surface with a passivating additive decreases significantly the losses in QFLS that are introduced when adding the C_{60} ETL. Our surface passivation treatment (SPT) reduces the density of recombination pathways on the top surface by binding to undercoordinated Pb^{2+} defects, which is reflected in halves of QFLS losses. Regarding the HTL/perovskite interface, losses are reduced to almost zero when changing from a spiro-TTB HTL to alternative materials, namely TaTM or self-assembled monolayers, implying more favorable interfacial properties with the latter materials. Combined with the SPT, the improved bottom interface enabled single junction cells with V_{oc} of 1.2 V (for a bandgap of 1.68 eV) and tandem cell V_{oc}'s of >1.9 V (Figure 1B). Together with the inherited good optics of textured silicon cells (Fig 1C), these advancements enabled us to fabricate devices with a total current > 40 mA/cm^2 and an efficiency >28% on >1 cm^2, one step towards achieving 30%-efficient monolithic perovskite-silicon tandems featuring textured wafers.

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Investigating Local Disorder in ZnSnN2-ZnO with X-ray Absorption Spectroscopy

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Abstract

$ZnSnN_2$ has recently shown promise for photovoltaic applications, offering potentially groundbreaking optoelectronic properties with the use of cation site disorder to tune the bandgap. However, questions remain about the connection between local coordination environment and long-range disorder in $ZnSnN_2$. In particular, it has been predicted that different types of local disorder may exist, but these are difficult to distinguish. Oxygen incorporation has also been observed to impact optoelectronic properties, but its bonding structure has not been studied. In this work, we investigate the local bonding environment in combinatorial sputtered $(ZnSnN_2)_{1-x}(ZnO)_{2x}$ thin films using X-ray absorption near-edge spectroscopy (XANES). N and O K-edge XANES results are consistent with FEFF10 simulations of cation-disordered structures, and reveal that $(ZnSnN_2)_{1-x}(ZnO)_{2x}$ films exhibit octet-rule-violating motifs around both anions. Upon annealing at $x = 0.25$, the local motif structure shifts toward octet-rule-conserving while long-range disorder is maintained. Spectroscopic ellipsometry reveals that local ordering increases the absorption edge energy at constant composition and long-range disorder. Additionally, alloy-induced absorption edge tuning from 1.0 to 1.7 eV is demonstrated. Finally, the interplay between off-stoichiometry, structure and

optical properties is discussed. This work provides a new understanding of the local environment in $(ZnSnN_2)_{1-x}(ZnO)_{2x}$ and demonstrates the use of XANES to probe disorder in II-IV-Ns.

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Kesterite based monograin photovoltaics: the ideal solution for sustainable power supply

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Abstract

In 2020 Photovoltaics became the cheapest electricity source in most countries of the world and will together with wind turbines have to take over most of the power production from fossil fuels-based technologies before 2050 in order to limit the CO_2-based climate change to less than 2 K as agreed in the 2015 Paris Agreement. Thereby the cost of electricity will drop far below today's cost allowing to also finance power storage and grid extension as needed for a renewables-based energy system [1].

Whereas the growth of PV installations is well under way in highly developed countries mainly by installing highly efficient monocrystalline silicon modules in larger and larger PV installations, the progress of electrification especially in poor countries providing access to electricity grids stays far behind the targets agreed on when accepting the UN Sustainable Development Goals (SDGs). Still more than 40 % of the world population (3 billion people) have no possibility to use clean fuels and technologies for clean cooking. Low cost decentralized and flexible PV may here provide a fast solution allowing also to harvest solar energy in building facades and on rooftops in densely populated regions. Here the monograin technology offers a versatile solution allowing for very low-cost local printing of very high quality single crystalline earth abundant solar powders. This powder-based technology [2] is unique in its stability [3], as well as in its low carbon footprint [4] and recyclability.

We will report on the latest progress of this technology based on Kesterite materials. The outline of a completely vacuum-free printing process for the solar cell powder as well as for all contact material will be shown, currently being set up as a prototype in our lab. As has been demonstrated already for most of the process steps, also commercially available printing lines as used in screen printing e.g. for traffic signs can directly be used. So, we now look for commercial partners to collaborate or take over parts of the production process. The main advantage is the possibility to produce already in relatively small scale (MWp/a) for very low costs, so that this technology is especially suitable also for developing countries interested in decentralized power production in remote aries.

This work has received funding from the European Union H2020 Framework Programme under Grant Agreement no. 952982 (Custom-Art) and through the European Regional Development Fund and Archimedes/DoRa project TK141.

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Nanoscale Nucleation Control as a Route Towards Defect-Free Growth of the Earth-Abundant Absorber Zinc Phosphide

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Abstract

Selective area epitaxy (SAE) and vapour-liquid-solid (VLS) growth have recently been explored for defect-free epitaxial growth by limiting the interface area.[1,2] The approach has mainly been developed for III-V semiconductor, but has the potential to impact other material systems as well, including the earth-abundant absorber Zn_3P_2. Zn_3P_2 is an attractive material for earth-abundant photovoltaics due to its direct bandgap (1.50 eV), minority carrier diffusion lengths (~10 μm), and high absorption in the visible range.[2,3] Thus far it has experienced challenges due

to its incompatible lattice parameter and coefficient of thermal expansion, complicating high-quality crystal growth, and lack of controllable doping. Herein, we demonstrate the applicability of nanostructured Zn_3P_2 to address these challenges.[4-6]

Using InP substrates, with nanopatterned SiO_2 masks for SAE and In nanoparticles for VLS, we achieve epitaxial nanostructures of various morphologies.[4-6] Using a circular hole the Zn_3P_2 will grow into nanopyramids.[4,7] We developed a model based on the relative surface energies and geometry to accurate describe the shape evolution for SAE grown structures.[6] If instead a slit was used the resulting shape was horizontal nanowires, which readily grow at arbitrary angles and into networks.[5] In VLS, we show how the interface structure controls the morphology. Furthermore, the SAE nanopyramids would overgrow the mask, and eventually coalesce into high-quality thin films.[4] To investigate their functional properties we used photoluminescence spectroscopy, which shows sub-bandgap emission in addition to a clear bandgap emission at 1.53 eV, indicative of an overall high crystal quality and in the region ideal for photovoltaic applications.[4] Using energy dispersive X-ray spectroscopy we could also observe that the composition can deviate from the ideal stoichiometry as a function of the initial hole size under identical growth conditions.[4,6] This could potentially be used to control the intrinsic doping of the material. Initial conductive atomic force microscopy measurements indicate that the as-grown material was p-type, albeit further investigations are needed to elucidate the exact influence of the off-stoichiometric composition.[4,6]

To summarise, nanostructured Zn_3P_2 is showing great potential for earth-abundant photovoltaic applications. The full impact is still being explored, and the next steps include transferring this approach to earth-abundant substrates (e.g. Si) and the fabrication of prototype photovoltaic devices. The approach also holds promise for other material combinations, and may find use in other earth-abundant photovoltaics.

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Nano-structured electrodes for solar energy harvesting

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Abstract

Drastic man-made environmental changes such as the increase in average temperature, air pollution, and vast amounts of plastic in the oceans significantly lower health, safety, and biodiversity. Following the disturbing effects and growing awareness of society, both social and legislative solutions have been initiated towards minimizing the damages. Among the solutions, increased focus must be placed upon utilizing renewable energy and material sources to achieve the EU goal of a low-carbon economy by 2050. Silicon photovoltaics, hydroelectric, and wind turbines are all mature technologies applied to this grand challenge, but there are limits to their ability to satisfy energy demands. In order to exploit the promise of renewable energy production, we need to learn how to harness and extract energy using new, more clever designs and materials. Nanomaterials provide several unique properties to approach these challenges. The ability to manipulate both photophysics and electronic properties based on geometric and material design will be used to obtain efficient photovoltaic devices.

We show the development of quantum dot (QD) devices where the geometrical properties of the substrates and composition of QDs can be engineered to enhance solar cells. Specifically, how tuning the bandgap, energy level alignments, and optimizing electron transport all lead to high-efficiency devices. We compare various types of metal oxide electron accepting materials (planar TiO_2 and ZnO, spherical nanocrystalline TiO_2 and ZnO assembled via spray drying, and TiO_2 nanotubes made via anodization) all sensitized with a metal sulfide absorber layer.

In Figure panels A and B we show SEM images of TiO_2 nanocrystals sprayed dried and TiO_2 nanotubes made with anodization of a Ti foil, respectively. Coating the TiO_2 with CZTS nanocrystals (XRD pattern shown in panel C) thereby sensitizes the metal oxide leading to the schematic shown in panel D. Other materials: $CuInS_2$ QDs or Sb_2S_3 thin films are also shown to sensitize the TiO_2, all measured by transient absorption spectroscopy. Their respective device performance will be also shown with the planar Sb_2S_3-based device leading to the highest power conversion efficiency of 6%. The various material combinations, their benefits and drawbacks, and a discussion on the limiting factors will all be presented.

On the Impact of Na and Sb doping in Solution Processed Cu2ZnSnS4 Thin-Film: Bulk vs Surface Electronic Properties

Authors

Prof. David Fermin - University of Bristol

Dr. Devendra Tiwari - Northumbria University

Abstract

Thin-film inorganic solar cells based on $Cu_2ZnSn(S_xSe_{1-x})_4$ absorbers remain as one of the most promising PV technologies featuring Earth abundant and low toxic elements, with prototype record cell efficiencies of 12.6% [1] and 13.0% [2] obtained by solution processing and sputtering deposition, respectively. It is widely recognised that cell voltage is the key limiting factor in these devices, which is often linked to compositional disorder. Cu/Zn antisites have been investigated as a source of potential energy fluctuation leading to Urbach tails. Our team have also observed Sn disorder in the bulk [3] and at the surface of these compounds [4], which can also be responsible for deep states highly detrimental to cell performance. However, the precise impact of these defects in the electronic structure and device performance are yet to be elucidated.

Numerous studies have reported improvement in $Cu_2ZnSn(S_xSe_{1-x})_4$ cells performance upon doping and/or alloying with a variety of alkali, group IV and V elements [5]. The introduction of dopants can have multiple effects such as supressing elemental disorder, changes in majority carrier concentration, passivation of recombination sites, changes in grain size and so forth. The material complexity makes rather challenging the establishment of meaningful correlations between composition and device properties.

In this contribution, we uncover the effects of Na and Sb doping in the bulk and interfacial electronic properties of Cu_2ZnSnS_4 (CZTS) thin films prepared by solution process. In a previous study examining over 200 cells, we have shown that Na and Sb doping can lead to an increase in power conversion efficiency from 3.2 to 5.7% [6]. We will show how the surface electronic landscape of CZTS thin films evolves upon doping, employing high-resolution *energy-filtered photoemission of electron microscopy* (EF-PEEM). This technique allows mapping fluctuations in the local effective work function with sub-micron resolution [4,7]. We will uncover correlations between surface electronic properties with key device parameters such as the activation energy for the predominant recombination pathway and Urbach tails. We will also discuss new data correlating variable temperature photoluminescence and admittance spectroscopy, demonstrating the fundamental role of Sb in attenuating Sn disorder [8].

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Optimization of Sb2Se3 thin film deposition on TiO2 by vapour transport method

Authors

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Abstract

Antimony selenide (Sb_2Se_3) is an emerging photovoltaic material spurring major interest in the field of earth abundant and low-toxicity thin film solar cells. Dedicated research on Sb_2Se_3 started almost ten years ago and since then the power conversion efficiency of antimony chalcogenide based solar cells has risen over 10% [1].

In most of the high-efficiency Sb_2Se_3 solar cells, CdS is used as a n-type layer. Although CdS is a nearly perfect candidate to form p-n junction with Sb_2Se_3, it contains heavy toxic metal, Cd, limiting full potential of Sb_2Se_3 as environmentally friendly technology. It has been demonstrated that ZnO and TiO_2 can also serve as compatible partner layers for Sb_2Se_3 [2]. Nevertheless, synthesis of Sb_2Se_3 thin films on TiO_2 is more complicated. Usually, it requires a two-step deposition protocol. Up to now, deposition methods for high quality Sb_2Se_3 thin films on TiO_2 have been demonstrated only by close-space sublimation. Other methods, such as vapour transport deposition which was very successful in fabricating high efficiency devices on CdS [3], have not been reported on TiO_2. Herein, we present optimization of experimental parameters for deposition of Sb_2Se_3 thin films on TiO_2 coated substrates using vapour transport deposition.

Employing three-zone tube furnace we tested two different substrate-source configurations. First, deposition on vertically oriented substrate was tested and termed as low-temperature deposition, because substrate temperature did not exceed 250 °C. Temperature of zones and distance between zone-substrate were varied to produce uniform and homogenous Sb_2Se_3 thin films. Films comprised of compact small grains with a dominant (hkl, l≠0) orientation. Solar cells, produced by this approach had a high short-circuit current density, relatively high fill factor, but low open-circuit voltage. Low temperature deposition is advantageous when temperature sensitive such as organic substrates are used.

In the high-temperature configuration, graphite with horizontally placed substrate is positioned between two sources. Such deposition arrangement increases chemical potential of Sb_2Se_3 vapour. Various combination of source and substrate temperatures were tested to find optimal conditions for synthesis of high quality Sb_2Se_3 thin films. High deposition rate led to films comprised of large grains, but with a higher density of pin-holes. A carefully balanced source, substrate temperatures and ramp were necessary to produce pin-hole free and compact thin films. Solar cells fabricated under optimal conditions demonstrated relatively high open-circuit voltage (> 350 mV), moderate short-circuit density and fill factor.

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Phosphides and phosphochalcogenides: A playground for optoelectronic materials discovery

Authors

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Abstract

Despite the historical success of phosphorus-containing III-V semiconductors, phosphorus-containing materials for photovoltaics – and optoelectronics in general – are still largely unexplored.

I will present results on thin-film synthesis of unusual phosphide semiconductors CaCuP, Cu_3P, CuP_2, and BP. All these materials are found to have potential applications in optoelectronics, ranging from a wide gap PV absorber to a p-type contact, a hole transport layer, and a bipolar transparent conductor. Interestingly, it was possible to deposit all these materials in a reactive sputtering chamber at the National Renewable Energy Laboratory (USA) under a PH_3-containing atmosphere. These encouraging results open a versatile route for high-throughput materials discovery of phosphides.

But there is more than "just" phosphides. Phosphorus is one of the most versatile elements in the periodic table, as it can take a range of positive and negative oxidation states giving nearly infinite possibilities for materials discovery. An intriguing possibility is to add complexity on the anion side rather than on the cation side. In particular, very interesting materials can be obtained using chalcogens (S, Se, Te). Many of the (known) phosphosulfides are semiconductors with band gaps in the visible. Yet, there are less than 5 five reports of phosphosulfides in thin-film form. Phosphosulfides with phosphorus in the -3 oxidation state are completely unexplored by experiment, although recent calculations show direct band gaps, disperse bands, and a high degree of versatility. With some preliminary data at hand, I will argue that phosphosulfides represent a great opportunity for materials discovery for optoelectronics and beyond.

Experimental work on phosphides was hosted by the groups of Dr. Andriy Zakutayev (National Renewable Energy Laboratory, USA) and Dr. Thomas Unold (Helmholtz Zentrum Berlin, Germany), who are gratefully acknowledged.

Photogenerated carrier transport in flexible Cu2ZnSn(S,Se)4 thin film solar cells with various insertion of NaF layer

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Abstract

Incorporation of sodium in earth-abundant kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin film solar cells is well known methods to maximize its performance. One effective method to incorporate sodium in CZTSSe deposited on flexible metal substrate which does not containing sodium is applying NaF layer.[1] With incorporation of Na, Na-related defects can suppress the formation of intrinsic defects.[2] Therefore, optimizing the insertion of NaF layer in metal precursor stacking synthesis is essential to understand the characteristics of defect formation. In this study, we have studied the defect passivation effect of various insertion position of NaF in CZTSSe fabricated by stacking the metal precursors. Five CZTSSe thin film solar cell samples with different stacking order of 10 nm-thickness NaF layer within Zn, Cu, Sn metal precursors and sample without NaF layer were prepared.[3] Photogenerated electrical properties of Na-doped CZTSSe were investigated by photo-assisted Kelvin probe force microscopy. Work function distributions of CZTSSe absorbers were obtained from the contact potential difference between the sample and the tip. With photon energy greater than the bandgap energy, 532 nm wavelength illuminated condition here, spectral work function shift was occurred at the surface of CZTSSe absorber indicating the formation in surface photovoltage (SPV). Generation of SPV was limited if the photogenerated charge carriers were trapped by defect states therefore, the larger SPV was formed in Na passivated CZTSSe samples. Defect passivation effect of Na was maximized in samples with applying NaF layer between the Zn and back contact and with applying NaF layer between Zn and Cu precursors.

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Polymeric carrier selective contacts for crystalline silicon solar cells

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Abstract

Crystalline silicon solar cells have reported close to Shockley Queisser limit efficiencies up to 26.7 %, while simultaneously being a cost-effective technology that occupies 90% of the world PV market [1].

The most common feature that limits the efficiency of the aluminum back surface field (Al-BSF) and the passivated emitter and rear cell (PERC) is the high-temperature diffusion process. The development of silicon heterojunction solar (SHJ) cells avoids this high-temperature diffusion but this involves the complex plasma-enhanced chemical vapor deposition systems using hazardous gas precursors to grow the doped layers. The main disadvantage behind these doped layers is parasitic absorption and recombination loss due to the defects in films.

Recently, the concept of charge carrier selective contacts has emerged in the field of silicon solar cells. Layers of appropriate materials can easily transport one charge-carrier type while simultaneously blocking the other one[2]. They have attracted researchers due to their ease of fabrication and high efficiency. The fabrication process involves simpler techniques such as thermal evaporation, sputtering, spin coating, Atomic Layer Deposition, etc. They are based on metal oxides, nitrides, alkali/alkaline earth metal salts, and organic polymers are capable of silicon surface passivation, and allow the elimination of unpleasant effects such as Schottky barriers and Fermi level pinning at the metal-semiconductor interface.

Carrier selective contacts based on organic molecules have attracted the research due to their highly adjustable electronic and chemical properties, and cheaper fabrication processes. Interfacial layers based on organic molecules have shown to modify the apparent work function of the metallic electrodes. In this sense, the electric dipole moment of these interlayers has proven to play an essential role in shifting the electronic band alignment across the interface and therefore the properties of the M/S junction. Various organic molecules investigated for ETL layers such as conjugated polyelectrolyte poly [(9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene) (PFN), amino acids such as Glycine, Histidine,

phenylalanine and HTLs such as poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), fluorescent polymers PFO and Green B have reported good efficiencies beyond 14 % [3] .

In this work, we explore the use of different conjugated polymers as hole and electron selective contact, and prospect for a deeper explanation of its working principle involving the conduction mechanisms related to dipole layers (e.g. conjugated polyelectrolytes) as well as their specific effect in Metal/Insulator/Semiconductor junctions (i.e. M/CP/S). Finally, polymers are integrated as the ETL and HTL layers in a dopant-free crystalline silicon solar cell state-of-the-art test structure with efficiencies beyond 16%.

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Role of cation disorder in the low efficiency of Cu2ZnSnS4 kesterite solar cells

Authors

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Abstract

Cation disorder has been often blamed for the poor power conversion efficiency of kesterite solar cells, which remains at a low level compared to other thin-film technologies despite years of optimizations. Recent experiments show that a higher degree of ordering does not necessarily improve the open-circuit voltage, questioning the role of cation disorder in the low efficiency of kesterite solar cells. Through a statistical treatment of disorder in the Cu_2ZnSnS_4 (CZTS) absorber, we show that extensive Cu-Zn disorder alone cannot be responsible for the large Urbach tails observed in many CZTS solar cells. While cation disorder reduces the band gap as a result of the Gaussian tails formed near the valence-band edge due to Cu clustering, band-gap fluctuations contribute only marginally to the open-circuit voltage deficit, excluding Cu-Zn disorder as the primary source of the low efficiency of CZTS devices. On the other hand, the extensive disorder stabilizes the formation of Sn on Zn antisite and its defect complexes, which as nonradiative recombination centers account for the large open-circuit voltage loss in CZTS. Taking into account the nonradiative recombinations, our analysis predicts a maximum power conversion efficiency at 14% for cation-disordered CZTS. In view of the restricted growth conditions and the remnant degree of cation disorder due to the slow ordering kinetics, we expect the Sn on Zn antisite and its defect complexes remain the fundamental limiting factors towards CZTS devices with higher efficiency.

Sb2Se3 solar cells and surface oxidation: A combined XPS and device study

Authors

Ms. Nicole Fleck - University of Liverpool

Dr. Oliver Hutter - Northumbria University

Dr. Laurie Phillips - University of Liverpool

Dr. Jon Major - University of Liverpool

Abstract

Sb_2Se_3 has recently attracted great interest as an absorber layer for photovoltaic devices. It has a suitable band gap, high absorption coefficient and good stability. Efficiencies using Sb_2Se_3 in PV devices have increased rapidly, now reaching 10%. As with most solar cell fabrication procedures, the cells are exposed to air at intervals during fabrication. While Sb_2Se_3 solar cell and material papers often comment on oxides present in the sample, little work has been undertaken on the analysis of the effects of this oxide. Here we show that oxidation of the surface plays a significant role in device performance and back interface passivation in superstrate cells.

We discuss the effect of the formation of a surface oxide on solar cell performance which, contrary to expectation, we have observed to improve over time. Oxidation takes place within the first 48hrs after deposition of Sb_2Se_3, a timeframe which is not generally studied in relatively stable solar absorber materials. A combined device characterisation and surface science (x-ray photoelectron spectroscopy) study is presented over a timescale of several days/weeks demonstrating that exposure to oxygen forms a thin, passivating and recombination-reducing layer on the order of nanometers. In particular, oxidation of the Sb in the Sb_2Se_3 film leaves a more Se-rich back surface which is also shown to improve device performance by ~10%. Replicating these changes via coating the back-surface with thin films of Se, Sb_2O_3, or both produces a similar reduction in recombination at the Sb_2Se_3-Au interface achieving peak solar cell efficiencies of over 5.8%. We conclude that that inclusion of an intentional oxide layer at the back contact, either by deposition of an oxide or controlled oxidation represents a method to increase the power conversion efficiency of Sb_2Se_3 solar cells and may also be relevant to device production of other chalcogenide-based photovoltaics.

Solution-Processed Thin Films of Earth-Abundant Chalcogenides for Solar Cells

Authors

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Abstract

Solution-based deposition of semiconductor materials is a promising method for rapid, low energy, and materials efficient manufacturing of photovoltaics. As a model system, chalcopyrite $Cu(In,Ga)(S,Se)_2$ has emerged as a leading absorber material for single-junction solar cells. Solution-based approaches have been used to fabricate $Cu(In,Ga)(S,Se)_2$ solar cells with efficiencies above 18%. However, $Cu(In,Ga)(S,Se)_2$ has several limitations that may restrict its use in the future. This has prompted us to investigate the synthesis and characterization of alternative, emerging chalcogenide absorber materials.

In this presentation we will first discuss our research on $AgIn(S,Se)_2$ as a promising alternative to $Cu(In,Ga)(S,Se)_2$ that retains the same chalcopyrite crystal structure but has dramatically different defect properties. While limited literature exists on this material, it has been shown that substituting silver into the chalcopyrite structure converts it from a p-type material to a weakly n-type material. With this change in carrier concentration and type, alternative device architectures may be enabled by utilizing $AgInSe_2$ as an n-type or intrinsic absorber. Additionally, while production of large-scale $Cu(In,Ga)(S,Se)_2$ devices may be limited by the challenges of maintaining various compositional gradients over large areas, the simplified composition of $AgInSe_2$ may ease large-area scale up. Our group has developed a facile method to directly solution-deposit $AgInS_2$ films and convert the films to a coarse-grain $AgInSe_2$ absorbers by heating the film in a selenium-containing atmosphere. $AgInSe_2$ shows excellent Hall mobilities above 12 $cm^2/V\text{-}s$ along with strong, narrow band-to-band photoluminescence signals at high quantum yields, and good minority carrier lifetimes.

In the second part of this presentation, we will discuss our work on chalcogenide perovskites. This promising class of materials may combine the stability of chalcogenide materials like $Cu(In,Ga)(S,Se)_2$ with the defect tolerance and excellent optoelectronic properties of the halide perovskites. In particular, $BaZrS_3$ has emerged as a promising target for photovoltaic applications with a bandgap of 1.7-1.8 eV, high absorption coefficient on the order of 10^5 cm^{-1}, and experimentally verified air-stability. Additionally, while $Cu(In,Ga)(S,Se)_2$ production could be stressed by competition over limited indium and selenium availability, $BaZrS_3$ is composed entirely of earth abundant elements. Yet despite all these benefits, the synthesis of $BaZrS_3$ has proven to be a significant challenge. To date, synthesis has been limited to solid state reactions, vacuum-based deposition, or the sulfurization of oxide films. Each of these methods generally

requires temperatures exceeding 800°C, significantly beyond the typical temperature range that is compatible with the manufacturing of thin-film solar cells. In our work we have successfully developed solution-deposition routes for the synthesis of $BaZrS_3$ by using reactive and oxygen-free precursors. Upon sulfurization at temperatures below 600°C the precursors are converted to the desired chalcogenide perovskite phases, as confirmed by X-ray diffraction and Raman spectroscopy.

Structural systematisation of wurtzite-derived nitrides – a group-subgroup analysis

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Abstract

Nitrides offer the promise to combine potent semiconductor materials suitable for photovoltaic applications with enhanced sustainability considerations. This latter implies that only earth-abundant and low-toxic elements are being used in such compounds while preserving all relevant properties for a photovoltaic material.

The traditional III-V nitride semiconductors (In,Ga)N do not fulfil this criterion, since In is a very scarce element. As a potential alternative, II-IV-N_2 semiconductors (e.g. with II = Zn, IV = Si, Ge, Sn) have moved into focus. Chemically, they can be thought of as derivative compounds, where the trivalent cations are replaced by equimolar amounts of divalent and tetravalent cations. Many of these compounds are not only chemically, but also structurally related to the wurtzite-type III-V materials, in that they either crystallise in the wutzite aristotype (s.g. $P6_3mc$) or one of its hettotypes.[1]

Together with further ternary and multinary nitrides and oxide nitrides, II-IV-N_2 nitrides form the class of wurtzite-derived nitride materials. We will discuss the different cation ordering motifs and structural distortions in this class of materials, which open a rich variety of different crystal structures in subgroups of the wurtzite-type. We further establish a structural systematisation of this class of materials, which culminates in the establishment of a Bärnighausen tree.[2]

Finally, a third potential structure in the wurtzite subgroup $Pmc2_1$ and with a nominally higher symmetry than the ß-$NaFeO_2$-type in space group $Pna2_1$ has been the matter of numerous theoretical considerations.[3] We demonstrate why this alternative in space group $Pmc2_1$ is unlikely to form from a crystal structural point-of-view, due to the symmetry arrangement in this space group.[4]

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Synthesis of a new ternary nitride semiconductor - Zn2VN3: A combinatorial exploration of the Zn-V-N phase space

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Abstract

Nitrides are promising functional materials for a variety of applications. Despite their technological im-portance, many promising theoretically predicted metal nitrides are yet to be discovered. This is partly rooted in their challenging synthesis as compared to oxides. Non-equilibrium PVD in UHV conditions, such as reactive RF-magnetron sputtering, provides ideal prerequisites for the formation of novel metastable nitride thin films. In this work, a computationally guided combinatorial PVD screening of the entire Zn-V-N phase space is performed, resulting in the synthesis of the previously unreported ternary nitride Zn2VN3. [1]

Reactive RF co-sputtering of Zn and V targets is performed in Ar/N2 atmosphere with N2 is supplied directly to the sputter plasma to increase the N2 dissociation rate. The combinatorial libraries are grown with com-position and deposition temperature gradients to quickly cover large areas of the synthesis phase space. A comprehensive automated mapping characterization of the sample is performed to investigate the struc-ture, composition, chemical-state as well as optoelectronic properties. XRD mapping and analysis of Zn Auger parameter evolution reveal presence of a wurtzite Zn1-xVxN phase over a large compositional range with a narrow process window for single-phase Zn2VN3.[1,2] Following the combinatorial screening, we demonstrate that cation-disordered, but phase-pure (002)-textured wurtzite Zn2VN3 thin films can be grown

using epitaxial stabilization on α-Al2O3 (0001) substrates at remarkably low growth temperatures well below 200 °C as evidenced by (S)TEM analysis. RBS/ERDA and XPS/HAXPES reveal a stoichiometric material with no oxygen contamination, besides a thin surface oxide. We find that Zn2VN3 is a p-type sem-iconductor with a charge carrier concentration of ~ 1017 cm-3 and Hall mobility of ~80 V·s/cm2. In addition, the electronic properties can be tuned over a wide range via isostructural alloying on the cation site, making this a promising material for optoelectronic applications. Zn2VN3 thin films demonstrate broadband room-temperature PL spanning the range between 2 eV and 3 eV, consistent with the bandgap of similar mag-nitude predicted by DFT calculations. In conclusion, the novel Zn2VN3 wide band gap semiconductor may be an interesting candidate for the formation of hole selective contacts owing to its promising properties.

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Synthesis of BaZrS3 Perovskite Thin Films at Moderate Temperature on Conductive Substrates

Authors

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Abstract

The $BaZrS_3$ perovskite is only composed of earth-abundant elements and expected to be an excellent absorber material[1]. In our previous work, amorphous Ba-Zr-S precursors were deposited by reactive cosputtering and later crystallized in a rapid thermal furnace at around 900 °C in an inert atmosphere[2]. The resulting $BaZrS_3$ thin films were rather inhomogeneous and the high formation temperature may prohibit the integration of this absorber material into a tandem cell. On the other hand, Wang *et al*. discovered that an appropriate S pressure plays a key role in the formation of $BaZrS_3$ perovskite powders: It can accelerate the crystallization process, which can already occur at 500-600 °C[3].

In the present work we follow a new sputtering route. First, Ba and Zr are cosputtered from metallic targets to form an intermixed layer on a Mo-coated Si wafer. Then a thin SnS capping layer is sputtered *in-situ* on top to prevent Ba oxidizing in ambient air. In this way the precursor can be transferred from the sputter system to the sulfurization furnace without excessive oxidation. Sulfurization takes place at around 600 °C for 20 minutes. In these conditions, SnS evaporates and the underlying intermixed Ba-Zr film reacts with S to form $BaZrS_3$. The S source that is introduced at this stage is in the form of powder and its temperature is varied from run to run. By measuring the weight of the S source before and after sulfurization, the S pressure can be roughly estimated and its effect on crystallization investigated.

X-ray diffraction (XRD) confirms that $BaZrS_3$ is the main formed phase. The new processing route with metal precursors annealed in presence of S results in a much greater homogeneity than that achieved in our original work, while keeping a similar crystalline quality at a process temperature 300-400°C lower. We have studied both the crystalline quality and the formation of secondary phases as a function of S pressure. As the Mo-coated Si substrate is not rotated during sputtering, XRD measured on different areas of the sulfurized sample can reveal how deviations from stoichiometry can also affect crystallinity and the formation of secondary phases. Elemental x-ray Diffraction Spectroscopy (EDS) and Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) also provide insights into the O content and its distribution in the $BaZrS_3$ film as a function of depth.

The direct deposition onto a Mo-coated Si substrate could enable the fabrication of initial $BaZrS_3$ solar cells to study not only optical properties, but also electrical ones. Moreover, the current low fabrication temperature is now compatible with future integration of $BaZrS_3$ thin films as top absorber in a tandem device, where Si can be the bottom cell.

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Synthesis, Properties, and Prospects for Photovoltaics of Chalcogenide Perovskite Thin Films

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Abstract

Sulfides and selenides in the perovskite and related crystal structures - chalcogenide perovskites - are an exciting family of semiconductors for optoelectronics and energy conversion applications.[1] Here, we explore the processing and properties of materials in the Ba-Zr-S system to determine their potential for thin-film photovoltaics (PV).

We demonstrate making $BaZrS_3$ thin films by gas-source molecular beam epitaxy (MBE).[2] $BaZrS_3$ forms in the orthorhombic distorted-perovskite structure with corner-sharing ZrS_6 octahedra (space group Pnma, no. 62), and has a direct band gap of $E_g = 1.85$ eV. We present a wealth of data reporting film processing and properties, including reflection high-energy electron diffraction (RHEED), atomic-force microscopy (AFM), X-ray reflectivity and diffraction (XRR and XRD), scanning transmission electron microscopy (STEM), spectroscopic ellipsometry, Hall transport, and photoconductivity. Our single-step MBE growth process produces films that are atomically smooth, single phase, chemically homogeneous, and oxygen free. The films are brightly colored even at 20 nm thick, due to the strong optical absorption typical of chalcogenide perovskites. Films grow via two, competing epitaxial growth modes: (1) buffered epitaxy, with a self-assembled interface layer that relieves the epitaxial strain, and (2) direct epitaxy, with rotated-cube-on-cube growth that accommodates the large lattice constant mismatch between the oxide and the sulfide. The propensity for these two modes can be tuned by adjusting the H_2S gas delivery rate. We further show results making thin films of $BaZr(S,Se)_3$ alloys (achieved by co-flowing H_2S and H_2Se), which provide a path towards tuning the direct band gap in the range 1.3 – 1.9 eV.

We also report on time-resolved photoluminescence (TRPL) and photoconductivity (TRPC) studies of excited-state transport in $BaZrS_3$ and the related, Ruddlesden-Popper phase $Ba_3Zr_2S_7$ (= 1.25 eV). We measure thin films and single crystals. We model the data using semiconductor physics simulations, to enable more direct determination of parameters key for photovoltaic performance (*e.g*. surface recombination velocity, Shockley-Read-Hall lifetime, diffusivity) than is possible with empirical data modeling. We find that chalcogenide perovskites have SRH lifetime (τ) exceeding 50 ns and ambipolar diffusion length on the order of 5 micron. If time allows, we will present further results of advanced characterization including impedance spectroscopy and X-ray absorption spectroscopy.

Our high-quality thin-film synthesis and excited-state transport measurements suggest a bright future for chalcogenide perovskites thin-film PV. We will end by briefly summarizing the state of the field, and highlighting key challenges on the road to device demonstrations and commercialization.

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Ultra-Thin Si Solar Cells With Hyperuniform Disordered Light Trapping

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Abstract

Mono- and multicrystalline silicon as absorbing materials in solar cells comprise about 90% of the global photovoltaics market and a total worldwide installed PV capacity of close to 3TW was reached in 2020[1]. The benchmark efficiency of 19% for industrial modules reached in 2018 was enabled by the widespread adoption of Passivated Emitter and Rear Cell (PERC) device architecture. Typically, these cells feature 160µm-thick absorbing layers produced via the Czoralski method, which expunges up to 40% high-quality silicon as kerf loss. It has been inferred that the PERC baseline is not able to achieve the cumulative installed PV capacity target set by the IPCC of 7-10TW by 2030[2] and further reduction of capital expenditure (capex) is needed. Reducing the thickness of Si-wafers for solar cells to 50µm could potentially reduce the manufacturing capex by 48%, module cost by 28%, and LCOE by 24%[3]. Thin c-silicon suffers from poor light absorption already at 100µm thickness necessitating light trapping to reach competitive efficiencies. High-performance light-trapping structures with sub-micron features, however, usually involve slow and complex manufacturing processes hindering their adoption by industry.

We present hyperuniform disordered (HUD) light-trapping structures applied to ultra-thin solar cells via substrate-conformal imprint lithography[4]. This approach enables rapid patterning of large areas (m^2) at the nanoscale and can be performed on virtually any substrate and for any type of functional layer, such as the absorber, back-reflector, anti-reflection coating or carrier transporting layers. Correlated-disorder structures were shown to outperform periodic light trapping architectures[5] and the hyperuniform platform offers in-plane diffraction tailoring to couple light efficiently to guided modes of ultra-thin absorbing layers[6]. We show experimentally absorption in ultra-thin, free-standing, hyperuniform-patterned silicon slabs of thicknesses ranging from 1-30µm and compare with FDTD simulations. We further developed a coupled-mode theory approach for estimating absorption with HUD patterns of specified k-space profiles, which allows pattern optimization at low computational effort [7]. Finally, we show the performance of thinned-down inter-digitated back-contact solar cells before and after the application of HUD light trapping structures.

In conclusion, our work aims to further expand the success of earth-abundant silicon to ultra-thin, flexible and semi-transparent PV devices, which can be produced with kerfless bottom-up technologies at significantly reduced capex and accompanying CO_2 emissions while maintaining high power conversion efficiencies.

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Understanding field-driven charge transport in mixed-metal halide perovskite semiconductors

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Abstract

Mixed metal (Pb-Sn) halide perovskite compositions have recently gained traction for their applications in all-perovskite tandem solar cells and near-infrared light emitting diodes. In this work, we demonstrate, for the first time, a comprehensive study on the field-driven charge transport physics of mixed Pb-Sn perovskites using thin film field-effect transistors (FETs) as a platform.

As shown in **Figure 1a-b**, the incorporation of even a small amount of Sn (as low as 25%) in $Cs_{0.15}FA_{0.85}PbI_3$ transforms the channel from n-type to p-type, with the optimal composition of $Cs_{0.15}FA_{0.85}Pb_{0.5}Sn_{0.5}I_3$ demonstrating a very high hole mobility of 5.4 cm^2/Vs (average ~ 3.1 cm^2/Vs) at room temperature (**Figure 1c**), along with impressive ON/OFF ratio approaching 10^6 and normalized channel conductance of 3 S/m, which are among the best reported metrics for 3D perovskite thin film FETs.

To understand the transport trends upon B-site compositional variation, we performed ab initio electronic structure calculations (**Figure 1d-e**), which suggests that addition of Sn at the B-site results in enhanced density of states predominantly at the valence band maximum (VBM), while having minimal contribution at the conduction band minimum (CBM). Moreover, Upon Pb-Sn alloying, the reduced carrier effective mass exhibits a monotonic decrease (**Figure 1f**) with an increase in Sn contents, thereby supporting our observation of high mobility in mixed Pb-Sn compositions. Moreover, morphological grain sizes seen from scanning electron microscopy (SEM) also show a consistent increase with Sn contents, which is along the expected lines.

To further understand the transport mechanisms, we performed temperature dependent transport measurements (**Figure 1g-h**) which reveal an interesting reversal from a negative coefficient of mobility for pure-Pb perovskite to a positive temperature coefficient for mixed Pb-Sn perovskites based on FA-Cs compositions. Such temperature-activated behaviour of mobility is characteristic of shallow defects present in these solution processed semiconductors, which has to date not been possible to observe in 3D hybrid perovskite FETs due to competing ionic screening (from mobile species) and dipolar disorder (from the presence of MA^+ in the composition) effects that we have successfully mitigated here. Interestingly, the presence of MA at the A-site causes a transition from positive to negative temperature coefficient of mobility for mixed Pb/Sn compositions (**Figure 1i**), thereby supporting the need for employing MA-free compositions for future perovskite optoelectronic devices. To probe this further, we performed photoluminescence mapping measurements on lateral devices of the same compositions (**Figure 1j-l**), which clearly shows suppressed evolution of PL (indicative of ionic migration

effects) in the channel region upon biasing for pure-Sn and mixed Pb-Sn perovskites when compared to pure-Pb perovskites. However, the brightening of negative electrode is seen upon biasing for Sn-containing perovskites, which gradually reverses upon removing the bias (not shown here), thereby indicating reversible electrochemical reduction of Sn^{4+} to Sn^{2+} happening under device operation. Using spectroscopic measurements, we have established Sn^{4+} as a major source of defect in these Sn-containing perovskites and therefore such precise control of defect dynamics upon biasing brings out the transformative nature of these materials for designing high performance photovoltaic and other optoelectronic devices.

What do we know about Binary/ternary phases in kesterite thin-film solar cells?

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Abstract

Kesterite semiconductors are promising materials and potential candidates for future thin-film photovoltaic application. However, the efficiency of the solar cells based on these compounds is still below the record efficiency obtained with chalcopyrite based materials such as Cu(In,Ga)Se2. There are several factors behind the efficiency limitations in kesterite thin-film solar cells but the most detrimental factor is the presence of unfavorable binary and ternary phases in the absorber. The most commonly reported secondary phases in kesterite compounds are Zn(S)Se, Cu2(S)Se, Sn(S)Se2 and Cu2Sn(S)Se3, some were present even in devices with high efficiency and their effect on the device performance depends on their position in the absorber.

In this work, secondary phases in kesterite absorrbers Cu2ZnSnSe4, Cu2ZnGe(S)Se4 and Cu2ZnGeSe4 [1-2] prepared using different fabrication processes are investigated and analyzed using several characterization techniques, among others Fourier-transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). We found that the formation of the different secondary phases observed in these studied compounds strongly depends on

the film growth conditions and device preparation. The impact of the different phases on the device performance, especially on the open-circuit voltage and efficiency, is discussed together with some suggested solutions to remove or reduce their formation at different parts of the absorber. In addition, the cell performance is analyzed using numerical modelling and the results obtained for pure germanium substitution compound Cu2ZnGeSe4 with a record efficiency of 8.5% [3], show that device efficiency up to 14% could be achieved if no binary/ternary phases were present in the absorber.

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Posters

…to grind or not to grind? Cu/Zn disorder in Cu2ZnSn(SxSe1-x)4 monograins

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Abstract

Kesterite-type based thin film solar cell technologies are mainly based on polycrystalline absorber layers, which makes it quite hard to correlate the crystallographic structure (determined via neutron diffraction) to the photovoltaic performance of these materials. A promising low cost alternative PV technology uses $Cu_2ZnSn(S,Se)_4$ (CZTSSe) monograins (single crystals of 50-100 µm size) which are fixed in a polymer matrix to form a flexible solar cell [1]. The experimental determination of the order parameter Q which is a quantitative measure of the degree of Cu/Zn disorder [2] requires a differentiation between the isoelectronic cations Cu^+ and Zn^{2+}. An in-depth analysis of neutron diffraction data provides information on the cation distribution in the crystal structure allowing the determination of type and concentration of intrinsic point defects including a distinction between Cu and Zn [3]. On the other hand neutron diffraction requires large sample volumes, thus kesterite monograins offer the unique possibility to correlate structural disorder in kesterite-type absorbers with device performance parameters.

In our previous study [4] we confirmed a correlation between the order parameter Q determined by neutron diffraction and a thermal treatment of the monograins (quenching or slow annealing procedures, so-called order-disorder procedure) as well as the influence of very small changes in the chemical composition. In this and all the previous studies the monograins were ground before the diffraction measurement. In this study we tackle the influence of the grinding on the stoichiometry deviation, the Cu/Zn disorder as well as the intrinsic point defects and optoelectronical properties of CZTSSe monograins. In order to achieve this goal, one homogenious CZTSSe monograin sample (15 gram) was first divided in two parts. One of them was kept “as grown”, and the second half was ground. In the following each of the 7.5 gram powder was divided in three parts and processed the same way as described in [3,4]. In this way 2 groups of as grown, quenched and slowly annealed monograin samples were formed. The grinding was not repeated at any stage of the experiment.

We will present detailed structural investigations of the obtained CZTSSe monograins based on neutron powder diffraction experiments. The obtained results show the influence of grinding on

the Cu/Zn disorder and the off-stoichiometry type related point defects. A further investigation of the effect of the disordering procedure (quenching) and ordering procedure (long annealing at a temperature below the order-disorder transition) on the Cu/Zn disorder and optical properties of the CZTSSe monograins will be presented as well.

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12.5% efficient kesterite solar cell with open circuit voltage deficit of 0.297V: Ag+ incorporation with controlled grain growth

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Abstract

Kesterite (CZTS, CZTSe and CZTSSe) semiconductors, composed of non-toxic and earth-abundant elements, have great potential as low cost photovoltaic absorber materials. However, the efficiency of CZTSSe solar cell (12.6%) is much lower than similar structured $Cu(In,Ga)Se_2$ (CIGS) solar cell (23.35%). The bottleneck that limits CZTSSe solar cell efficiency is the large open-circuit voltage deficit ($V_{oc,def}$, which can be evaluated by V_{oc}/V_{oc}^{SQ}, V_{oc}^{SQ} is the maximum achievable V_{oc} based on Shockley-Queisser limit). The high concentration of Cu-Zn antisite defects and its related defect clusters were believed to account for the band tailing that limit V_{oc}. Substitution of Cu^+ by large ionic Ag^+ was one strategy to mitigate the defects. However, the efficiency (11.2%) of the best performing Ag^+ substitution kesterite solar cells is still much lower than current world record (12.6%), revealing that some intrinsic defect property cannot be mitigated by current approach. Therefore, implementing Ag^+ substitution in kesterite semiconductors with lower intrinsic defects and understanding the synthetic routs of Ag^+ substitution kesterite can more clearly evaluate the benefits of Ag substitution strategy on defect properties. Here we report a novel strategy of incorporation of Ag^+ into kesterite that Ag^+ was incorporated into the lattice of kesterite(ACZTS) in precursor film by a Ag^+ and Sn^{4+} based DMSO precursor solution and high quality Ag incorporated kesterite (ACZTSSe) are fabricated at the whole substituted concentration through a unique direct phase transformation grain growth mechanism. Further, it was found that this approach can sufficient suppress the formation of Cu_{Zn} defect, defect cluster $[2Cu_{Zn}+Sn_{Zn}]$ and deep level defect Cu_{Sn}. Finally, a champion ACZTSSe solar cell with an efficiency of 12.5% (active area efficiency 13.5%, no antireflection coating), a FF of 72.0%, and a V_{oc} of 0.540 V was achieved with 5% Ag substitution. The V_{oc} deficit of 0.297 V of this device is the lowest among all kesterite solar cells reported so far with V_{oc}/V_{oc}^{SQ} as high as 64.2%. Our results demonstrate direct transformation grain growth mechanism is an effective strategy to engineer the defect property of kesterite, which can be applied to other strategies beyond Ag alloying and further improve kesterite solar cell efficiency.

A Numerical Study of Sb2Se3: Interfacial Defect passivation

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Abstract

Sb_2Se_3 is an emerging earth-abundant material praised for its promising optoelectronic properties. However, Sb_2Se_3-based solar cells are still limited by a high V_{oc} deficit compared to other thin-film PV technologies. One of the reasons for such a low V_{oc} lays in the presence of deep interfacial defects at the vicinity of the p-n junction. Using a device modelling approach and a realistic set of material parameters, we unravel pathways to mitigate the impact of interfacial defects on the optoelectronic performance of a baseline device in substrate configuration: Mo/$MoSe_2$/Sb_2Se_3/CdS/i:ZnO/ITO.

We created a baseline solar cell in SCAPS-1D according to literature and in-house processes. Several investigations have been reported regarding defects characterization on Sb_2Se_3/CdS-based solar cells. Among those articles, defects attributions were done based on numerical modelling or first principle calculations. We implemented to our baseline model a set of defects characterized by Chen et al[1]. We ran simulations with different combinations of the defects[1] ascribed D1, D2 and D3 to assess their impact on cell performance. Thanks to those simulations, we proved that the limiting factor in our baseline is the interfacial defect D3 located at the interface between Sb_2Se_3 and CdS (Figure 1a). Two straightforward and easy to implement strategies are devised and tested against the baseline.

Firstly, a thin surface sulfurization allowing a local lowering of the valence band and thus creating a “front surface field”, resulting in an increased carrier selectivity and limiting the density of holes available for interface recombination. A significant improvement of the conversion efficiency appears possible for optimized conditions (Figure 1b). In comparison with our baseline performance, the surface sulfurization enables in optimum conditions ($40\% < \%Sb_2S_3 < 60\%$) an overall improvement of 20% for each figure of merit.

Secondly, the use of an ultrathin insulating TiO_2 layer is considered, which helps in preventing chemical interdiffusion at the junction[2]. This strategy, currently investigated in a broad range of chalcogenide-based solar cells, provides a direct interface passivation, though the interlayer thickness needs a fine tuning to balance the benefits of reduced interface recombination and a detrimental low-conductivity (Figure 1c); since as TiO_2 thickness increases every figure of merit decreases (Figure 1c). However even with a thickness of 10 nm for TiO_2, the performance is well above our baseline ones.

To summarize, in this investigation we demonstrate that the limiting factors to our baseline performance are interfacial defects. Additionally, we propose two alternatives to passivate those defects either the implementation of an ultrathin TiO_2 insulating layer or a thin surface sulfurization. Alternatives to mitigate interfacial defects impact on the device performance are one of the critical points to achieve high efficiency for Sb_2Se_3-based solar cells.

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A study of the efficiency limiting defects in Cu2BaxZn1-xSnSe4 thin film based solar cell

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Abstract

$Cu_2Ba_xZn_{1-x}SnSe_4$ (CBZTSe) is a peculiar material with a suitable bandgap, high absorption coefficient and comprise of earth-abundant elements which make it an ideal choice as a solar cell absorber. However, to obtain high power conversion efficiency (*PCE*) from CBZTSe solar cells, understanding the role of defects in bulk and at the interface of CBZTSe is critical. A theoretical study on the CBZTSe solar cell using a one-dimensional solar cell capacitance simulator (SCAPS-1D) has been performed. The solar cell structure studied here is a standard structure [Glass/Mo/CBZTSe/CdS/i-ZnO/AZO/Al] which comprises Molybdenum (Mo) as a back contact, molybdenum selenide ($MoSe_2$), which is usually formed at the interface of Mo and CBZTSe, cadmium sulfide (CdS) followed by intrinsic-zinc oxide (i-ZnO), aluminum-doped zinc oxide (AZO) and Aluminium (Al) as a front contact.

Effects of different composition ratio [$x = Ba/(Ba + Zn)$] on solar cell performance has been studied. The best PCE of 21.76 % has been obtained with $x = 0.50$ when the conduction band offset at CBZTSe/$MoSe_2$ and CBTSe/CdS interface are 40 and 20 meV, respectively. The effect of the presence of different defects in various densities for different compositions of CBZTSe, namely, Cu-poor and Se-moderate, Cu-poor and Se-rich and Cu-rich and Se-poor has been studied. For the Cu-poor and Se-moderate composition, the tin at copper site (Sn_{Cu}) defect is a PCE limiting defect with PCE of solar cell reduced from 21.71 to 7.83 % for the Sn_{Cu} defect density of 10^{13} to 10^{16} cm^{-3}, respectively. For Cu-poor and Se-rich composition, selenium at intrinsic voids (Se_i), vacancy at copper site (V_{Cu}), and selenium at copper site (Se_{Cu}) moderately affect the PCE. For Cu-rich and Se-poor composition, copper at intrinsic voids (Cu_i), tin at barium site (Sn_{Ba}), $Sn_{Cu,}$ and Sn_i are dominating *PCE* limiting defects. Cu_{Ba} defect at the CBZTSe/CdS interface is found to be critical and limits the solar cell efficiency.

Antimony selenide semiconductors and nanorod array solar cells

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Abstract

The antimony selenide (Sb_2Se_3) semiconductors have attracted enormous research interests because of its low toxicity and superior stability, high light absorption coefficient, suitable band gap, and excellent photoelectric properties, which are applied as the light harvesters in solar cells. Since 2014, the Tang group has explored the rapid thermal evaporation (RTE) and vapor transport deposition (VTD) to fabricate the planar Sb_2Se_3 solar cells, leading to a rapid increase of PCE to 7.6%. Recently, our group reported the core-shell structured Sb_2Se_3 nanorod array solar cells with the PCE of 9.2%, which was the highest efficiency for Sb_2Se_3 solar cells so far. The Sb_2Se_3 nanorod array with the (001) orientation can enable more efficient and long-range carrier transport in vertical direction, resulting in a superior performance of the nanorod solar cells. Secondly, we constructed an In_2S_3 nanosheet-CdS composite as the buffer layer, compactly coating on the Sb_2Se_3 nanorod surface. The Sb_2Se_3 nanorod array solar cell based on In_2S_3-CdS composite buffers achieves a PCE of 9.19 %. Thirdly, we fabricated the Sb_2Se_3 nanorod array with highly (hk1) orientation on CdS substrate, and constructed the superstrate solar cells innovatively. Compared to the planar Sb_2Se_3 solar cells, the Sb_2Se_3 nanorod solar cells exhibit higher efficiency and more efficient charge transport. Furthermore, $CuInSe_2$ QDs is employed to fill the gaps between nanorods, which can not only suppress the interface recombination, but also serve as the light harvester to contribute photocurrent. Consequently, the vertical heterojunction Sb_2Se_3/$CuInSe_2$ solar cells display a PCE of 7.54%, which is the highest efficiency for superstrate solar cells based on Sb_2Se_3 nanorod array.

Band gap grading strategies for high efficiency kesterite based thin film solar cells

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Abstract

Renewable energy supplies based on thin film solar cells and focused on sustainable materials such as kesterite (CZTS) could perform very successfully in a wide variety of energy application scenarios. This is due to its potential to be deposited on flexible substrates, its aesthetics and selective transparency for integrations in construction and automotive industrial sectors. As well as its use in new energy concepts such as agrovoltaics or energetic portability concepts like the Internet of Things (IoT). The current kesterite devices hinder the potential energy conversion efficiencies of a single absorber layer PN junction. Therefore, the next generation of kesterite and chalcopyrite solar cells power energy efficiency improvements may be enhanced after developing novel and more strategic methodologies for collecting photon energy. Thus, the graded bandgap profiling in kesterite is proposed as a sustainable strategy to improve the Solar spectrum utilization, through the generation of internal quasi-electric fields situated along the thin films, increasing the drift and diffusion length of the minority charge carriers and finally improving the power conversion efficiency of the photovoltaic device. Hence, this work develops advanced material synthesis techniques and surface characterization, which, when integrated with the structural complexity of double graded bandgap profiles in kesterite (CZTGSSe) thin films, allow Nature to reveal several disruptive and novel properties of matter, deliberately manipulable when working in conditions out-of-thermodynamic equilibrium.

Co-doping of solution-processed CZTSe absorbers using Li and Na

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Abstract

$Cu_2ZnSn(S,Se)_4$ compounds, widely known as CZT(S,Se) and kesterite referring to their crystal structure, are considered important as light absorbers for low-cost thin film solar cells as they are composed of non-toxic and earth-abundant elements. However, solar cells based on such absorbers suffer from high V_{oc}-deficit due to inherently high defect density. Alkali doping – mainly with lithium and sodium – has been reported to be a promising way to suppress and passivate defects, effectively improving photovoltaic performance of devices.

Lithium has very similar ionic radius as copper and can be easily incorporated into the CZT(S,Se) lattice resulting in crystallinity and conductivity improvement, a reduction in grain boundary recombination and a tunability of the band gap. Sodium, on the other hand, improves absorber morphology via larger grain sizes, and additionally passivates defects at grain boundaries. So far, these two alkali dopants have been thoroughly investigated individually but not together.

In this work, we modify our 2-step solution-processed precursor – annealing approach by simultaneously adding Li and Na into the precursor layer. Our goal is to get a better understanding of the effect of Li-Na co-doping on the synthesis and electronic properties of solution-processed kesterite, aiming at overcoming the current limitations of kesterite absorbers in terms of V_{oc} – deficit. We will present the impact of the co-doping processes on the absorber morphologies and especially improved layer crystallization. Influence and benefits of combined sodium and lithium doping on the electrical and electronic properties on the basis of J-V, capacitance and optical characterization will be presented. Our results highlight the importance of alkali element management during the synthesis of kesterite absorbers, and point towards an improved electronic quality of the solution-processed kesterite absorbers with the co-doping approach.

Cu2MnSnS4 (CMTS) thin films by sputtering technique for photovoltaic

Authors

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Abstract

Many efforts have been made word-wide to obtain earth-abundant variants of $CuIn_xGa_{(1-x)}Se_2$ (CIGS) for photovoltaic application: together with the most famous Cu_2ZnSnS_4 (CZTS), a lot of metals and semimetals have been tested to substitute zinc. An interesting alternative to CZTS is copper manganese tin sulfide (CMTS), a p-type semiconductor consisting of Earth-abundant and low-cost elements. CMTS, which crystallizes into a stannite structure (space group: I-42m), shows high absorption coefficient (@10^4 cm^{-1}) and direct band gap suitable for PV applications. Manganese is cheaper (2$/kg vs. 2,7$/kg) and has higher occurrence in the Earth crust than zinc (440ppm mean vs. 65ppm mean) leading to a more economical and environmental sustainability of CMTS in respect of CZTS.

In this work Cu_2MnSnS_4 (CMTS) thin films were grown by an high-throughput two-steps deposition process: metallic precursors were deposited by sputtering technique, subsequently treated at high-temperature in sulphur vapours.

CMTS thin films have been deposited both on Molybdenum-coated soda-lime glass (Mo-SLG) to finalize preliminary solar device and on bare glass substrates to measure Eg via UV-Vis absorption spectra; on the Mo-SLG samples different thin films have been deposited to finalize the solar cells i) Cadmium Sulphide (CdS) with chemical bath deposition as buffer layer for p-n junction, ii) intrinsic- ZnO insulating layer via sputtering to avoid short-circuits phenomena, and Aluminum-doped ZnO (AZO) window layer and iv) evaporated collecting grid. During the CMTS solar device optimization have been tested different post-deposition treatment (PDT) mutuated from CZTS licterature to carried out a comparative study. A heat treatment in air atmosphere on the entire device has been validate as effective way to improve CMTS photovoltaic performances.

μ-Raman spectroscopy and X-ray diffraction (XRD) measurements carried on pristine samples and on PDT- solar cells have confirmed that CMTS is the main phase in our thin films, with just a small contribution of manganese sulphide (MnS) as secondary phase. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis have been used to check the morpholody and chemical composition. For the present optimization of the deposition process parameters, CMTS thin films are compact and uniform films with a thickness of about 900 nm, and a chemical composition close to perfect stoichiometry ($[Cu]/[Mn]+[Sn] \approx 1$, $[Mn]/[Sn] \approx 1$, $[S]/[met] \approx 1$).

On the preliminary CMTS-based solar devices, J-V and External quantum efficiency (EQE) measurements hve been carried out. Optimized materials lead to a final device with a 0.5% efficiency, composed of a promising Voc of 430mV, a low Jsc of 6.14mA/cm^2 and a fill factor of 33.69%. EQE measurements suggest low recombination in the bulk of the material.

Cu2ZnXS4 (X=Sn,Ge,Si) kesterite solar cell efficiency modelling based on ab initio computed materials properties.

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Abstract

Extensively studied over the past decades, Earth-abundant and non-toxic $Cu_2ZnSn(S,Se)_4$ kesterite material appears as a promising candidate for photovoltaic applications. Showing first a constant increase of the reported efficiencies, further improvements were prevented within the last years. As possible culprits, recombination centers are believed to be the actual limitation sources. As a result, high kesterite-based cell efficiencies are still awaited. One of the pathways considered to improve the device performance consists in alloying the absorber layer by substituting Sn with Ge. Yet, this approach brings up a question concerning the efficiency upper limits of the cells fabricated with these novel absorber layers. In this work, we model the solar cells characteristics with an improved version of the Shockley-Queisser model. As input data for the simulation, we used the kesterites Cu_2ZnXS_4 (X = Sn, Ge, Si) optical properties obtained via *ab initio* calculations. We report high absorption coefficients (10^4 cm^{-1}) with band gap values of 1.32, 1.89 and 3.06 eV, respectively for the Sn-, Ge- and Si-compound. Following the report of the good kesterites absorption properties, we then focus on the second key ingredient for efficient solar cell which is the charge carriers extraction. We modelled the cell efficiency by introducing an external parameter which allows us to tune the non-radiative recombination rate. Ultimately, we demonstrate that for optimal absorber layer thicknesses between 1.15 and 2.68 μm, kesterite-based cell efficiencies of 25.71, 19.85 and 3.10 % could be obtained for the three Cu_2ZnXS_4 (X = Sn, Ge, Si) materials under study in the case of vanishing non-radiative recombination rate. Our study thus highlights the applicability of Cu_2ZnSnS_4 for single-junction solar cell demonstrating a possible efficiency improvement of 9.83% while promoting the use of Cu_2ZnGeS_4 as top cell for tandem approach.

Development of band gap tuned Cu2Zn(Sn1 − xGex)S4 monograin powders

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Abstract

Cu_2ZnSnS_4 (CZTS) has received considerable interest as a promising solar cell material owning to its earth abundance and non-toxicity. The primary limitation of these types of solar cells is their low open-circuit voltage due to bulk and interface recombination [1,2]. The electronic properties of the CZTS absorber can be tuned by cationic substitution of isovalent Ge onto multivalent Sn sites to reduce Sn-related deep defects. $Cu_2Zn(Sn_{1-x}Ge_x)S_4$ (CZTGeS) absorbers show a high absorption coefficient of 10^{-4} cm^{-1} with a tunable bandgap between 1.5 – 2.1 eV, making them a possible candidate for multi-junction solar cells and bandgap-graded devices [3].

In this study, Ge alloyed $Cu_2Zn(Sn_{1-x}Ge_x)S_4$ (CZTGeS) monograin powders were synthesized over the entire composition range (x = 0; 0.2; 0.4; 0.6; 0.8; 1) and their materials and solar cell properties were examined. The CZTGeS monograin powders were synthesized by the molten salt method in closed quartz ampoules using high purity binaries as precursors and KI as flux material. The synthesis was followed by chemical etching and thermal annealing processes to modify the as-grown surface of the crystals. The surface composition and morphology of the monograins were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM) and Raman spectroscopy. Raman spectra in Figure 1 showed two main vibrational A modes for CZTS at 288 and 338 cm^{-1} and for Cu_2ZnGeS_4 (CZGeS) at 297 and 361 cm^{-1}. A blueshift was observed with increasing the Ge content for both A_1 and A_2 symmetry modes. The samples with x = 0.2, 0.4, 0.6 and 0.8 showed the A_1 modes of both CZTS and CZGeS modes due to the coexistence of Ge-S and Sn-S bonds [4]. For two samples with the highest Ge content, the peak around 400 cm^{-1} denoted the signal enhancement due to the resonant effect [3]. Energy-dispersive X-ray (EDX) spectroscopy confirmed the coincidence of the intended compositional ratio of Ge/(Ge+Sn) and Cu-poor Zn-rich composition in the bulk of the crystals. The main secondary phase has been found as ZnS for all samples. The change in the defect structure of $Cu_2Zn(Sn_{1-x}Ge_x)S_4$ monograins was studied by low-temperature photoluminescence (PL). Ultimately, all synthesized absorber materials were implemented in the monograin layer solar cells and the

performance of the devices was evaluated by current-voltage measurements and external quantum efficiency measurements. More detailed results will be presented at the Conference.

Development of Bi2S3 thin film solar cells by close-spaced sublimation

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Abstract

Development of new photovoltaic (PV) technologies based on novel green materials with higher efficiency and lower cost options could create a new industry with independent supply chains, foster PV market diversification, and attenuate market volatility. Bi_2S_3 has emerged as promising inorganic absorber material for PV and other optoelectronic applications owing to its optimum direct band gap of 1.3 eV, high absorption coefficient (10^5 cm^{-1}, and absorption onset in the infrared), exhibits both n-type and p-type conductivity, nontoxic and earth abundant elements. Related to its non-toxic nature, so far it has been very popular to deposit the material by chemical solution routes. Research investigations on development of the Bi_2S_3 as well as the solar cell structures by physical vapor deposition methods are almost absent to date. Thus, the focus of the current study was to develop for the first time, Bi_2S_3 thin film and solar cells using robust, rapid and high yield close spaced sublimation (CSS) technique.

Four sets of samples were fabricated: glass/Bi_2S_3, glass/FTO/CdS/Bi_2S_3/Au, glass/FTO/TiO_2/Bi_2S_3/Au and glass/FTO/NiO/Bi_2S_3/Au. To find the optimal processing condition for the absorber, the CSS substrate deposition temperature was varied from 250 to 450 ^oC. The absorber films deposited at 250 and 300 °C exhibit highly dispersed and porous ribbon-like structures, whereas deposition at 350-450 °C leads to denser absorber with larger grain size. The diffractograms showed the peaks for (221), (141), and (431) planes, which correspond to the orthorhombic Bi_2S_3 crystal structure with space group Pbnm (62) (PDF 00-017-0320). Band gap, resistivity, conductivity type and carrier concentration of Bi_2S_3 films on glass substrates were revealed by UV-Vis, hot probe and Hall effect measurements. The layers exhibited E_g ~1.25 eV, n-type conductivity and carrier concertation of ~10^{17} cm^{-3}. Photoluminescence study of the absorber showed two emission bands with peaks at 1.15 eV and 0.84 eV. The presence of these bands indicates that there at least two different recombination centres in CSS Bi_2S_3 which tentatively are related to sulfur and bismuth vacancies defects. When combined with CdS and TiO_2 buffer layers, the performances of devices have been modest ($\eta < 1\%$). The n-type conductivity of the absorber and respective buffer layers indicate to the formation of isotype heterojunction. Hence, the efficiency is mainly limited by the unbalanced carrier concentration and improper band alignment. For NiO/Bi_2S_3 configuration efficiency of ~0.5% was obtained and p-n isotype heterojunction behaviour

demonstrated. These results demonstrate the potential of NiO/Bi_2S_3 cell architecture and encourages further research efforts towards identification of suitable dopants and partner layers for sublimated Bi_2S_3 absorber.

Development of sputtered oxide window layers for Sb2Se3 solar cells

Authors

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Abstract

It is well established that CdS is an imperfect window layer for solar cells due to it's comparatively small 2.4eV bandgap leading to optimal losses. For Sb_2Se_3 solar cells solution processed TiO2 has previously been demonstrated as a suitable alternative but the reliance on solution process can lead to issues of reproducibility, film uniformity and scalability. This paper studies the development of a sputtered TiO_2 layer, examining the comparative benefits with solution processed material and barriers limiting device performance. The role of surface roughness on Sb_2Se_3 morphology, film growth and ribbon orientation will be examined as well as secondary factors such as the influence of TiO_2 phase and doping density on the window/absorber interfacial conduction band offset and resulting interfacial barrier. Initial results demonstrate the promise of sputtered TiO_2 window layer Sb_2Se_3 devices with Jsc outperforming solution processed TiO_2, however performance is limited by a lower FF, likely a result of sub-optimal band alignment.

Electronic and optical properties of quaternary chalcogenide solid solutions

Authors

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Abstract

Quaternary chalcogenides, A_2ZnCX_4 with A=Cu,Ag, C=Si,Ge, and X=S,Se, are potential building blocks for the third generation of thin film solar cells. While the prime examples like Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ crystallise in the kesterite structure, for the other quaternary chalcogenides different crystal structures can be found, e.g. stannite, wurtz-kesterite, and wurtz-stannite. Moreover, in order to tune material properties to be more suitable for possible device applications, solid solutions on the A, C, and X sites have been proposed, leading to a complicated interplay of structural properties of the quaternary end members involved.

Here we present our results on electronic and optical properties of quaternary chalcogenide solid solutions based on density functional theory calculations, employing different levels of sophistication for the exchange and correlation functional [1]. All our structure models are geometry optimised using the recently developed SCAN exchange and correlation functional. In order to obtain more reliable electronic and optical properties, selected optimised structures are subjected to one-shot calculations employing the more accurate hybrid functional HSE06 and subsequent quasiparticle calculations based on the GW method. In order to simulate the different concentrations within the solid solutions, we're employing a supercell approach and different theoretical methods. All the presented results on the structural, electronic, and optical properties will be critically discussed alongside experimental findings.

This work made use of computational resources provided by the North-German Supercomputing Alliance (HLRN), and the Curta and Dirac HPC facilities of the FU Berlin and the Helmholtz-Zentrum Berlin, respectively.

[1] D. Fritsch and S. Schorr, J. Phys. Energy **3**, 015002 (2021).

Encapsulation of silver nanowires via metal oxynitride reactive sputtering for highly stable transparent electrodes

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Abstract

Silver nanowire networks (AgNWs) are a promising candidate for transparent electrodes due to their high transparency, low sheet resistance, flexibility, and potential for low-cost implementation, owing to their high DC-to-optical conductivity ratio and low metal loading. These properties make it suitable for applications such as transparent heaters and solar cell electrodes. However, these electrodes are susceptible to electrothermal and chemical degradation, which have largely stifled their large-scale implementation – which implies that effective encapsulation strategies are needed. To ensure the encapsulation approaches are scalable, industrial scale, high throughput deposition methods should be targeted. Moreover, encapsulation methods should use low cost, high-abundance elements with low-temperature processing. A variety of encapsulation approaches have been considered in the past, but physical vapor deposition approaches are the most promising for these criteria.

In this work, reactive pulsed DC and RF magnetron sputtering at room temperature are demonstrated as a promising approach to encapsulate AgNWs. Since using O_2 as a reactive gas can significantly oxidize and damage the AgNWs and active layer surfaces, N_2 is used as a reactive gas under moderate base chamber pressures (0.5e-4 Torr). Low-cost metal sputtering targets (Al, Ti) are then used to deposit as little as 20 nm of Al and Ti oxynitrides using mixed Ar and N_2 gas flows. Oxynitride-encapsulated AgNW films show exceptional electrothermal stability, surviving at temperatures of 100°C more than unencapsulated AgNWs (>250°C). They also show exceptional chemical stability, where the electrical properties of Al oxynitride encapsulated wires stay nearly unchanged after >7 days under modified Damp Heat testing conditions (80°C, 80%RH). This work demonstrates a versatile approach to encapsulating AgNWs with sputtering, which can be extended to encapsulate lithographically patterned electrodes and other solar cell device architectures.

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Engineered photoanode based on Indium-doped Zinc Oxide Nanoparticles for Dye-Sensitized Solar Cell

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Abstract

Indium-doped zinc oxide nanoparticles were synthesized using the sol-gel technique. The strategy of incorporation of In^{3+} ion into ZnO lattice (1.0, 3.0, and 5.0 mole % doping levels, ZnO: In) was based on controlled reaction parameters of the sol-gel method. The dissimilarity in the ionic radii of Zn^{2+} (0.74Å) and In^{3+} (0.81Å) can induce strain/distortions in the ZnO lattice. We recorded diffractograms to establish the incorporation of In^{3+} ion into ZnO lattice in the pure wurtzite phase of ZnO. No evidence of the In_2O_3 phase was found even for a higher doping concentration of indium. Spectroscopic studies were made to decipher the chemical environment interaction in the doped samples, and we noted that In^{3+}doping into ZnO lattice affected the microstructure. To demonstrate the applicability of the engineered materials, we employed them as photoanode in dye-sensitized solar cells. ZnO: In1 based devices gave improved short circuit current density. The charge storage capacity as well as the number of free charge carriers enhanced with the addition of minimal In^{3+} ion into ZnO lattice.

Keywords: ZnO; photoanodes; Dye-sensitized solar cell, electrochemical impedance spectroscopy. Solar energy, nanoparticles

Enhancement of solution-processed Cu2ZnSnS4 film properties via a facile approach of sodium incorporation

Authors

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Abstract

Properties of solution-processed thin-films of Cu_2ZnSnS_4 (CZTS), a promising photo-absorber material for the photovoltaic application, were investigated as a function of sodium (*Na*) incorporation. This is achieved via a facile approach in which the *Na* source was introduced at the bottom of the CZTS precursor as well as at the top. A significant increase in the grain size, from 319 to 1125 nm, and a large drop in the resistivity from 7.9×10^3 to 5.0×10^1 Ω·cm have been observed. Large grains are desirable for reducing the recombination loss of the carriers at the defect sites at grain boundaries. Additionally, the approach incorporated in this work was also found beneficial for the suppression of tin loss. The effect of *Na* incorporation was also measured on the optical band gap, and the results indicate that Na_i is the dominant defect present in these CZTS films.

External pressure to manipulate phase-segregation in mixed-halide perovskites

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Abstract

Halide perovskite semiconductors have recently gathered significant attention due to their intriguing optoelectronic properties combined with low-cost and simple fabrication method. In addition, the easy bandgap tunability of this material by changing the ratio of halides in the chemical composition, makes them promising candidate for LEDs and tandem solar cells in combination with silicon. However, illuminating mixed-halide perovskites results in the formation of segregated phases enriched in a single halide. Phase segregation affects the homogeneity of the bandgap compromising the purity and the quality of the absorption/emission and therefore its applications. This segregation occurs through ion migration, which is also observed in pure-halide compositions, and whose control is essential to enhance lifetime and stability.

In this work, we investigate how pressure-induced compression affects the kinetics aspects of phase segregation in mixed halide perovskite MAPbBrxI1-x (xbr-= 0.25, 0.5 and 0.7). Using pressure-dependent transient absorption spectroscopy, we find that the formation rates of both iodide- and bromide-rich phases in MAPb(BrxI1-x)3 reduce by ~2 orders of magnitude upon increasing pressure to 0.3 GPa (Figure a). We interpret this change as a compression-induced difference in the activation energy for ion migration, which is supported by first-principle calculations. A similar mechanism occurs when the unit cell volume is reduced by incorporating a smaller cation. Furthemore, we find that high external pressure increases the range of stable halide mixing ratios by alteration of the Gibbs free energy via the largely overlooked PΔV term (Figure b).

These findings reveal that stability with respect to halide segregation can be achieved either physically through compressive stress or chemically through compositional engineering and

that in principle any iodide-bromide ratio can be thermodynamically stabilized by tuning the unit cell volume. Understanding how manipulate phase-segregation is crucial for highly efficient devices that require bandgap tunability.

Fabrication of Cd-free In2S3/Cu3SnS4 Heterojunction Thin Film Solar Cells

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Abstract

In recent years, I-IV-VI ternary semiconductor compound Cu_2SnS_3 (CTS), which is composed of earth-abundant and nontoxic elements, has been intensively studied by the researchers as a promising absorber material owing to its suitable optoelectronic properties such as direct band gap ranging from 0.8 eV to 1.7 eV, high optical absorption coefficient in the order of 10^4 cm^{-1} and p-type conductivity [1]. The record efficiency value reported for CTS-based solar cells that have CdS buffer layer and pure CTS absorber is ~4.3% up to now [2]. This value is still so far from Schockley-Queisser efficiency limit of ~30% estimated for a single junction solar cell based on CTS [3]. Here, we present the studies on the growth of Cu_3SnS_4 thin film absorbers by a two-step approach including the deposition of precursor stacks and subsequently their sulfurization, and the development of thin film solar cells with In_2S_3 buffer layer. At first, we show the effect of sulfurization time on the structural and morphological properties of the films by using X-ray diffraction, Raman spectroscopy, energy-dispersive X-ray spectroscopy, scanning electron microscopy and secondary ion mass spectroscopy (SIMS) techniques in detail. We discuss on the co-existence of different structural polymorphs of CTS and the phase transformation from CTS to Cu_3SnS_4 depending on sulfurization time by considering both the findings in previously reported studies and our study and the discrepancies in the literature. Then, we report an efficiency value of ~3% obtained from a solar cell device that have Cu_3SnS_4 absorber and In_2S_3 buffer layers and indicate a slight increase in the efficiency over a thermal annealing process of the device. To the best of our knowledge, only one study was reported on the photovoltaic behaviour of Cu-rich films among the members of Cu-Sn-S family up to now [4]. In that study, an efficiency value of 2.34% was obtained from a solar cell structure of

$Mo/Cu_4SnS_4/In_2S_3/TiO_2$/FTO glass. In this context, we report photovoltaic property of Cu_3SnS_4 absorber in a In_2S_3/Cu_3SnS_4 heterojunction structure for the first-time. Furthermore, we show that diffusion of In element from the In_2S_3 buffer layer into the absorber occurs up to a certain depth independent of the thermal annealing process of the solar cells by SIMS analysis. We think that this might be leaded to the partial substitution of In atoms by Sn atoms in the crystal structure. However, more detailed studies are needed to fully understand it.

Fig. 1. (a) The surface, (b) cross-sectional SEM images of the films sulfurized for 40 min and (c) J-V characteristics of In_2S_3/Cu_3SnS_4 heterojunction thin film solar cell.

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Fe2O3-based pn junction solar cells with a Mg(OH)2 interface layer

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Abstract

Iron is the most abundant metal element in the earth crust, and iron oxides are quite ubiquitous. Fe_2O_3 is an n-type semiconductor having bandgap of about 2.0 eV, and it has been shown that the conduction type can be converted to p-type by acceptor doping. We have reported that p-type Cu-doped Fe-O can be deposited by electrochemical deposition (ECD), which is a low-cost technique and advantageous for solar cell production [1]. Since both n- and p-type materials can be obtained, one can construct pn junctions based on Fe_2O_3. In a previous work, we fabricated pn junction solar cells consisting of non-doped and Cu-doped iron oxides by ECD [2]. However, the performance was very poor, with the output voltage of the order of mV. This would be due to a disordered interface. Thus, to improve the diode characteristics, in this work we insert a $Mg(OH)_2$ interface layer using drop-dry deposition (DDD) [3]. $Mg(OH)_2$ has a large bandgap but is semiconducting, and thus it will be able to suppress carrier recombination at the interface.

For non-doped, the deposition solution contained 100 mM Na_2SO_4 as a supporting electrolyte and 50 mM $FeSO_4$ [4]. The solution was saturated with oxygen by blowing oxygen gas for 10 min. The solution temperature was 15°C, the deposition current -0.192 mA/cm^2, and the deposition time 10 min. For p-type layers, 5 mM of $CuSO_4$ was added. The two-step pulse bias was adopted (-0.86 V, 10 s; 0 V, 10 s), and the cycles were repeated 30 times [2]. First, the p-type layer was deposited on an ITO substrate, and next $Mg(OH)_2$ was deposited by DDD [3]. The solution contained 25 mM $Mg(NO_3)_2$ and 50 mM NaOH. A small amount of the solution was dropped on the sample, and it was dried at 60ºC; this cycle was repeated 5 times. Then the n-type layer was deposited, and the sample was annealed in air at 400ºC for 60 min.

Without the $Mg(OH)_2$ interface layer, the sample showed weak rectification properties, and very weak photovoltaic effects, with V_{oc} = 3.2 mM, J_{sc} = 0.23 μA/cm^2. With $Mg(OH)_2$ inserted, the leakage current was decreased, and the output voltage was increased (V_{oc} = 14 mM, J_{sc} = 0.25 μA/cm^2). Thus, the $Mg(OH)_2$ interface layer seems to suppress recombination of majority carriers at the interface, decrease the dark current, and enhance the solar cell output. However, the output was still very low. For further improvement, we will attempt to insert an interface layer of different materials.

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Flexible Sb2Se3 solar cells and mini-modules

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Abstract

Antimony selenide (Sb_2Se_3) has attracted wide attention as a photovoltaic material. The Sb and Se are both Earth-abundant and non-toxic, the high absorption co-efficiency ($>10^5$ cm^{-1}) and suitable bandgap (direct ~1.17 eV, indirect ~1.04 eV) enable Sb_2Se_3 a Shockley–Queisser efficiency of > 30%. In recent years, the Sb_2Se_3 solar cells have achieved power conversion efficiency (PCE) of near 10% because of their superior optoelectrical properties.[1-4] Theoretical studies have shown that Sb_2Se_3 has a special one-dimensional crystal structure and demonstrates tolerance to deformation. Sb_2Se_3 has natural advantages for the preparation of flexible solar cells.

Herein, we constructed flexible Sb_2Se_3 thin-film solar cells on polyimide (PI) substrates with PCE of >6.0% and power-per-weight >2.0 W g^{-1}, respectively. Moreover, the flexible devices demonstrated superb bending stability, maintaining 95% of their original efficiency after 1000 bending cycles folding with a diameter of 1 mm. Further, the Sb_2Se_3 solar mini-module (25 cm^2 area) was constructed and its application in powering the Internet of Things sensors was demonstrated.

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Formation path of Cu2Zn(Sn,Ge)Se4 using vapor phase incorporation of Germanium

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Abstract

Germanium incorporation into kesterite ($Cu_2ZnSnSe_4$) is studied using the strategy of incorporating GexSey vapor from an externally supplied Germanium source during the annealing of alloyed Zn/Cu-Sn/Zn precursors. Our reference selenization process (i.e. without Germanium) includes an in-process composition shift due to availability of $SnSe_2$ vapour in the annealing volume during the high temperature stage (i.e. at $T > 530°C$). The incorporation of additional Sn during the annealing process results in an overall film composition shift (from Cu-rich to Cu-poor). This mechanism was successfully adapted to incorporate Germanium in the kesterite absorber. We performed an interruption series, stopping the annealing process at various points, to track the elemental and phase composition in the layer during the formation of $Cu_2Zn(Sn,Ge)Se_4$.

The results show an initial formation of a Cu-rich CZTSe film and the subsequent composition shift towards a Cu-poor layer by an in-process Tin / Germanium incorporation, resulting in a Cu-poor $Cu_2Zn(Sn,Ge)Se_4$ absorber, suitable for high efficiency kesterite solar cell. At $T < 400$ °C the initial formation of CZTSe is observed in presence of Cu_xSe_y and ZnSe secondary phases. Above 400 °C, GeSe and $GeSe_2$ are formed in the susceptor volume. Below 480°C no noticeable amount of Ge was observed in the layer. The Ge/(Ge+Sn) ratio in the absorber significantly increases from 0.07 (at 480 °C) to 0.25 upon reaching 530 °C annealing temperature. The composition at this point, say at the beginning of the dwelling stage, shows a very Ge-rich $Cu_2Zn(Sn,Ge)Se_4$ layer near the surface of the absorber (see Raman shift in Figure 1). During the dwelling stage of the annealing further Germanium is incorporated and distributed in the layer which ultimately leads to a homogeneous composition of $Ge/(Ge+Sn) \approx 0.3$ in the final absorber, with no detectable gradient left. The Sn content during the interrupted annealing study stayed constant. Raman spectra measured on the various stages of the annealing study are shown in Figure 1.

Detailed investigation on the absorber composition shift from a Cu-rich-Sn-poor to Cu-poor-(Sn+Ge)-rich is under progress. First results showing efficiencies up to 10.4 % (FF: 54 %, J_{SC}:36

mA/cm2, V_{OC} = 540 mV, V_{OC} deficit = 417 mV) demonstrates the potential for Germanium containing kesterite solar cells with a tuneable band gap.

Figure 1: Raman spectra of (partially) annealed samples at given temperatures.

Germanium Chalcogens for Photovoltaic Applications

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Abstract

One of the key reasons for methylammonium lead iodide's (MAPI) successful rise in efficiencies is related to the Pb 6s lone pairs. The lone pairs in the valence band lead to shallow rather than deep states and hence the formation of benign grain boundaries and a stronger defect tolerance. Furthermore, the Pb 6s orbital will lead to band edges with greater dispersion which causes smaller carrier effective masses and enhanced carrier mobility.

Another series of lone pair materials attracting growing interest are the antimony chalcogenides which have Sb 5s lone pairs. Antimony selenide and antimony sulfide have

achieved PCEs of 9.2% and 7.5% respectively whilst the mixed solutions ($Sb_2(S,Se)_3$) has achieved a PCE of 10.0%. As well as the desirable Sb 5s lone pair and suitable band gaps, the antimony chalcogenide structure has additional potential benefits. They form in an orthorhombic Pnma crystal structure, which comprises of 1D ribbons of covalent bonds in the [010] direction and van der Waal interactions between the ribbons in the other directions. Theoretical studies, supported with experimental evidence, suggest strong conductivity parallel to the ribbons but weak conductivity when the electrons must hop between the ribbons, suggesting highly conductive solar cells if in the correct orientation.

Germanium chalcogens share the same Pnma structure of the antimony chalcogenide but they have covalent bonding in two directions, thus creating nanosheets rather than nanoribbons, which could make for easier solar cell design than the antimony chalcogenide solar cells. Germanium selenide (GeSe) has had fewer than ten publications using the material as an absorber layer in a solar cell and already has achieved a PCE of 5.2%.

In this work, we present work showing the corrected value for the GeSe band gap determined by measuring the optical properties of a thin film at different temperatures to determine the band gap at 0K and compared to band gaps predicted by DFT. We successfully show that the 0K experimental value of 1.33eV agrees with the theoretical value as one moves to the higher level of theory, and the corresponding computational cost increases. Furthermore, we successfully show why previous studies underestimated the band gap at 1.1eV using a GeSe crystal which leads to Urbach tailing and other defect-related effects.

Furthermore, we present further work on the lone pairs of GeSe and germanium sulfide (GeS). We use x-ray photoemission spectroscopy (XPS) and hard x-ray photoemission spectroscopy (HAXPES) in combination with DFT calculated to give experimental evidence for the active lone pairs in both materials, like MAPI and the antimony chalcogenides. XPS was also used to find band alignments between GeSe and GeS with related materials including potential heterojunction partner layers. Finally, we present our results for the mixed solution (Ge(S,Se)) which includes compositional dependence on the structure, bandgap and Raman and infrared modes.

Growth and characterization of spin coated bismuth sulfide thin films

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Abstract

Non-toxic, stable and earth abundant bismuth is an ideal alternative to poisonous lead in environmentally friendly perovskite solar cell devices. Bi_2S_3 thin film is metal chalcogenide which presents substantial promise because of its optical and electronic properties. In contrast to expensive methods, there are very few studies in the literature on n-Bi_2S_3 thin films prepared by low-cost sol-gel method. Whereas, thin films with large surfaces can be easily prepared using the sol-gel spin coating method. Therefore, in this study, Bi_2S_3 thin films were spin coated on a glass substrate and the effect of thickness and annealing temperature on the film properties were elaborated by means of crystallinity, morphological and optoelectronic characterizations. The films prepared at 650 nm thickness exhibited an orthorhombic phase polycrystalline structure and an n-type semiconductor property. The forbidden band gap and crystallite size of the champion film, which has optimum crystallinity annealed at 350 °C, is 1.9 eV and 28.6 nm, respectively. The forbidden band gap and crystallite size of the film, which has optimum optoelectronic properties annealed at 400 °C, is 1.5 eV and 18.4 nm, respectively.

Impact of lithium and potassium co-doping on the CZTS monograin powder optoelectronic properties

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Abstract

Several studies have shown lithium doping as promising method to boost the efficiency of $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells. The ionic radius of Li^+ (0.59 Å) and Cu^+ (0.6 Å) are very similar to each other, thus Li has a high probability to be incorporated into the lattice of kesterite phase and significantly inhibit the formation of Cu_{Zn} antisite defects. This in turn decreases the disordering of materials resulting in lower V_{OC} deficit. Also, potassium could be incorporated into CZTS lattice, although studies revealed that K is usually segregating on the grain boundaries of CZTS. Potassium doping have been found to increase the carrier concentration and to reduce the series resistance of solar cell devices. There have not been any studies yet about co-doping of Li and K.

In this work, we have investigated the effect of lithium and potassium on the properties of kesterite Cu_2ZnSnS_4 (CZTS) monograin powders. CZTS powders were synthesized in the liquid phase of flux materials with different LiI-KI ratios. The Li amount in the flux mixtures was changed from 0.08 to 14.47 mol%. All the powders were synthesized by molten salt method at high temperature using high purity precursors and subsequently used as absorber materials in monograin layer (MGL) solar cells.

Atomic absorption spectroscopy confirmed the potassium and lithium incorporation into the host material. All powders synthesized in flux containing KI, had potassium concentration in the synthesized material around 10^{18} cm^{-3}. When pure LiI flux was used, the concentration of Li in the powders was 10^{21} cm^{-3} which corresponds to around 2.4 at % from CZTS, indicating that a solid solution of $Cu_{2-x}Li_xZnSnS_4$ had formed. According to SEM images, the CZTS powder crystals synthesized in KI had sharp edges and well-defined planes, but crystals grown in LiI flux were more rounded (Figure 1).

Structural analysis by XRD confirmed the incorporation of Li in the CZTS lattice, as the main diffraction peak (112) showed slight shift from 28.48 to 28.39 degree (Figure 1). Also, the lattice parameters *a* and *b* enlarged from 5.430 Å to 5.443 Å and parameter *c* increased from 10.831 Å to 10.862 Å, with Li addition. According to EQE measurements, the E_g* of the material synthesized in KI flux was 1.56 eV. The inclusion of Li increased the bandgap up to 1.65 eV. Raman spectra revealed that the main intensive peak at around 338 cm^{-1} shifted to higher position with increasing Li amount.

It was found that Li inclusion increased the V_{OC} from 721 mV to 784 mV. The best performing cell with KI-LiI mixture was achieved with Li concentration of 5.1×10^{18} and KI concentration of 4.06×10^{18} cm^{-3} in CZTS, resulting in PCE of 9.4%.

In addition, detailed analysis about the changes in the defect structure by photoluminescence spectroscopy and in solar cell parameters will be discussed.

Influence of alkali metals on Cu2ZnSnS4 monograin powder properties and performance of solar cells

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Abstract

The growth mechanism and properties of CZTSSe materials have been investigated in great detail, however recorded maximum efficiency of devices based on CZTSSe is still ~13 %. The phase purity, electronic and optical properties of the absorber layer are critical and in dependence of the preparation technology as they directly affect the efficiency of CZTSSe solar cells. Molten salt synthesis-growth method is one possibility to produce very high-quality absorber materials for solar cells. As addition of various alkali metals to the kesterite have shown a positive effect on thin film solar cell parameters, the aim of this research was to investigate the influence of different alkali salts on the powder growth and impact on the performance of CZTS monograin layer (MGL) solar cells.

$Cu_{1.85}Zn_{1.1}SnS_4$ powder materials were synthesized from binary compounds CuS (5N), ZnS (5N), SnS (5N) and elemental sulfur (5N) by isothermal molten salt synthesis-growth method in the presence of molten LiI, NaI, KI, RbI and CsI salts as flux materials. The syntheses were performed in sealed vacuum quartz ampoules by heating at 740 ^{o}C for 136 hours.

Morphology studies by SEM showed that the shape of the formed crystals can be controlled by the nature of the flux materials. Determined bulk composition by EDX analysis showed that Cu-poor and Zn-rich composition of CZTS was obtained by using RbI, LiI, NaI or KI as flux material, whereas in the case of CsI the produced monograin powder showed nearly stoichiometric chemical composition. Structural studies by XRD showed a shift of all diffraction peaks to lower angles for CZTS crystals grown in LiI and a larger lattice parameter values in comparison with powder crystals formed in CsI, RbI, NaI and KI. Also CZTS monograin powders grown in LiI showed the widest main Raman peak (hwhm= 3.55 cm^{-1}). In case of CsI and RbI Raman peaks were sharp and narrow with hwhm of 2.25 and 2.81 cm^{-1}, respectively, showing a higher level of

crystallinity compared to other produced powders. The estimated effective bandgap values (E_g*) from EQE measurements for CZTS monograin powders grown in RbI, NaI and KI were 1.569 eV, 1.571 eV and 1.568 eV, respectively. The CZTS powder grown in LiI showed the highest E_g* value (1.661 eV). All these results confirmed that Li^+ from the molten flux (LiI) incorporated into the Cu_2ZnSnS_4 crystals structure and most probably replaced part of Cu^+ sites in the lattice and formed new $(Cu_{1-x}Li_x)_2ZnSnS_4$ solid solution. In addition, detailed analysis about the changes in the defect structure by photoluminescence spectroscopy and in solar cell parameters will be discussed.

Investigation of band gap and band tailing in (Cu1-xAgx)2ZnSnSe4 thin films alloys.

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Abstract

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) absorbers have attracted a considerable attention in the past few years due to their favorable opto-electronic properties for thin film photovoltaic applications without using critical raw materials. However, the maximum Power Conversion Efficiencies of kesterite-based solar cells is limited to 12.6%, which is far from the 23.4% achieved by the chalcopyrite-based ones. The main difference between these cousin technology lies into a much smaller Open Circuit Voltage (V_{OC}) for the CZTSSe-based solar cell. This V_{OC} deficit can be partially attributed to band tails in the kesterite absorber, which arises from a large amount of Cu_{Zn} antisites in the lattice. Replacing part of the Cu atom by Ag has been proposed as a solution to significantly reduce band tails in the absorber and thus the V_{OC} deficit [1].

In this work, optical spectroscopy studies were performed on $(Cu_{1-x}Ag_x)_2ZnSnSe_4$ thin films alloys with various Ag contents x, synthetized by vacuum-based processes: for x=1, epitaxial layers grown by molecular beam epitaxy were achieved following the optimization procedure developed for CZTSe epitaxy; for x varying between 0 and 0.5, CAZTSe absorbers are synthesized with a two-step selenization process of a Cu/Sn/Cu/Zn/Ag precursors stack sputtered onto a Mo coated SLG substrate [2].

The systematic optical investigation combines three types of spectroscopy measurements that allow us to determine the band gap of the alloys as well as the extension of their band tail of localized states: (i) the power dependence –and temperature one- of the photoluminescence spectra (PL), (ii) the photoluminescence excitation spectra (PLE), and (iii) the time resolved photoluminescence spectra (TR-PL).

A quantitative methodology will be presented [3] to precisely deduce the band gap Eg and the characteristic energy U for the extent of the tail of localized states, from the PLE and TR-PL data. Such an approach is different from the one usually used, namely measuring the energy shift between the steady-state PL emission and the absorption PLE threshold (the Stokes shift). The

advantage of the present method is that no arbitrary choice of the low power excitation has to be done to select the PL emission spectrum and its peak energy, which could vary widely.

All these data allow us to find the evolution of both the bandgap and the extension of the bandtail as a function of silver concentration. Regarding the latter, the band tail of these localized states is significantly reduced in an layer with Ag content x=1 compared to all other $(Cu_{1-x}Ag_x)_2ZnSnSe_4$ alloys.

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Investigation of wide band gap Cu2ZnGe(S,Se)4 thin-film formation during the sulfurization process

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Abstract

Kesterite-type compounds $Cu_2ZnSn(S,Se)_4$ has been shown as a promising material for absorber layer in thin-film solar cells due to earth-abundant and low toxicity of its constituent elements, *p*-type conductivity and a direct and tuneable band gap energy (E_g), which can be modified by substituting Se with S anions. The cations substitution of Sn with Ge also increases E_g up to 1.45 eV for $Cu_2ZnGeSe_4$ (CZGSe) and 2.25 eV for Cu_2ZnGeS_4, allowing to form wide band gap $Cu_2ZnGe(S,Se)_4$ (CZGSSe) absorbers that can open new market opportunities and increase the range of applications of photovoltaic devices. One of the key challenges to enhance the CZGSSe-based device performance is the distribution of [S]/([S] + [Se]) through the bulk of the absorber layer. Different routes have been proposed for the efficient control of the anion's ratio [1-4] allowing to reach the efficiencies of 3.2 % for the devices based on the wide band gap kesterites with E_g = 1.98 eV [2].

In this work, ~1 mm-thick CZGSSe thin films are obtained by sulfurization of co-evaporated CZGSe layers deposited onto Mo/SLG substrates. In order to understand the sulfurization mechanism of CZGSe thin films, break-off experiments are carried out at different temperatures and at different dwell times adding elemental S and GeS in Ar atmosphere. The structure and morphology of the obtained thin films with different anions ratio are studied by grazing incidence X-ray diffraction (GIXRD) and scanning electron microscopy (SEM). Raman spectroscopy yielded the information about the phase content. Depth-resolved compositional analysis is carried out via glow discharge optical emission spectrometry (GD-OES). The experimental results show that the increase of the temperature leads to a higher S incorporation into the CZGSe lattice, as well as allow to control the [S]/([S]+[Se]) depth gradient. Additionally, the concentration of incorporated S strongly depends on the cation's ratio in the initial CZGSe thin film. Moreover, the cooling rate is crucial to avoid the presence of Ge-Se-S secondary phases. These experiments reveal the key parameters to obtain high quality wide band gap CZGSSe thin films that, up to now, allowed to obtain solar cells with V_{oc} > 900 mV with absorber $E_g \approx 2.2$ eV. Moreover, this knowledge is being transferred to the growth of

CZGSSe on transparent substrates for the development of efficient semi-transparent solar cells for integrated photovoltaics and tandem solar cells applications.

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Lone pair driven anisotropy in antimony chalcogenide semiconductors

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Abstract

Antimony sulfide (Sb_2S_3) and selenide (Sb_2Se_3) have emerged as promising earth-abundant alternatives among thin-film photovoltaic compounds. A distinguishing feature of these materials is their anisotropic crystal structures, which are composed of quasi-one-dimensional (1D) $[Sb_4X_6]_n$ ribbons. The interaction between ribbons has been reported to be van der Waals (vdW) in nature and Sb_2X_3 are thus commonly classified in the literature as 1D semiconductors. However, based on first-principles calculations, here we show that inter-ribbon interactions are present in Sb_2X_3 beyond the vdW regime. The origin of the anisotropic structures is related to the stereochemical activity of the Sb 5s lone pair according to electronic structure analysis. The impacts of structural anisotropy on the electronic, dielectric and optical properties relevant to solar cells are further examined, including the presence of higher dimensional Fermi surfaces for charge carrier transport. Our study provides guidelines for optimising the performance of Sb_2X_3-based photovoltaics *via* device structuring based on the underlying crystal anisotropy.

Low Voc deficit kestertie solar cell from DMSO solution: how solution chemistry determines reaction path, defect property and device Voc?

Authors

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Abstract

Understand the origin of the large open-circuit voltage deficit ($V_{oc,def}$) of kesterite ($Cu_2ZnSn(S,Se)_4$, CZTSSe) solar cells is critical for further boosting their efficiency to commercialization level. CZTSSe solar cells fabricated from DMSO molecular solutions exhibit very different open circuit voltage (V_{oc}) when $SnCl_2{\cdot}2H_2O$ and $SnCl_4$ are respectively used as Sn precursor with Cu^+ and Zn^{2+} and thiourea (Tu) as Cu, Zn and S precursors. The chemical reactions in the solution, the reaction path from solution to precursor film, and the grain growth mechanism of the two CZTSSe films have been systematically studied to understand the V_{oc} difference. Results show the coordination of Sn^{2+} with S in Tu (forms $Sn(Tu)_2Cl_2$) leads to the formation of SnS during thermal annealing of the wet film, resulting in a multi-phase (SnS, ZnS, $Cu_{2-x}S$, and CZTS) composed precursor film, whereas the coordination of Sn^{4+} with DMSO (forms $Sn(DMSO)_2Cl_4$) facilitates direct formation of CZTS precursor film. The secondary sulfides composed Sn^{2+} precursor film took a multi-step phase fusion reaction path with $SnSe_2$ existing on film surface during the whole grain growth and forms in a very defective surface whereas the uniform kesterite structured Sn^{4+} precursor film took a direct transformation reaction path along with a top down and bottom up bi-direction grain growth that forms a uniform and less defective surface. Characterizations show that both absorber films exhibit similar bulk electronic property with comparable band and potential fluctuations, Cu-Zn disorder level and tail states, the much lower V_{oc} of Sn^{2+} device (0.42 V) than Sn^{4+} device (0.52V) primarily comes from the serious recombination near the junction. A CZTSSe solar cell with a total area efficiency of 12.4% (active area efficiency 13.6%) with a $V_{oc,def}$ of 0.297 V ($V_{oc}/V_{oc}^{SQ}=0.637$) was achieved from Sn^{4+} solution. Further, we have successfully fabricated $(Ag_xCu_{1-x})ZnSn(S,Se)_4$ solid solutions with a whole concentration of Ag (x=0-1) from Sn^{4+} based DMSO solution. The same coordination chemistry of Ag^+ and Cu^+ in the DMSO solution results in the same reaction path and grain growth mechanism from solution to absorber materials, resulting in significant suppression of Cu_{Zn} defects, defect cluster $[2Cu_{Zn}+Sn_{Zn}]$ and deep level defect Cu_{Sn}. A champion $(Ag_{0.05}Cu_{0.95})ZnSn(S,Se)_4$ device with an efficiency of 12.5% (active area efficiency 13.5% without antireflection coating) and a record low $V_{oc,def}$ ($V_{oc}/V_{oc}^{SQ}=0.642$) has been achieved. Our results demonstrate the large V_{oc} deficit of kesterite solar cell mainly comes from surface defects that originated from multi-phase fusion grain growth mechanism. A kesterite structured precursor film that can facilitate uniform phase transformation grain growth is a new and effective strategy to mitigate the defect property of kesterite and improve device V_{oc}.

Low-temperature, solution-based chalcogenide perovskites for PV

Authors

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Abstract

Chalcogenide perovskites – eponymously named for containing S, Se, or Te as the anion rather than a halide --- are an emerging frontier in Pb-free, inorganic perovskites. Common to many perovskite compounds, promising optoelectronic properties for PV have been identified from theoretical simulations of this material family. They also benefit from high optoelectronic tunability and through elemental substitution resulting in a large potential material space. Importantly, these materials can be comprised of all non-critical and earth-abundant resources and have demonstrated high stability. In fact, their stability ultimately results in a high crystallization energy barrier for their formation, particularly when converting from oxides to sulfides/selenides. As a result, current syntheses fail to realize the potential of chalcogenide perovskites by requiring high temperatures (c. 1000 °C) and/or long reaction times. Accordingly, there is a significant lack of relevant experimental syntheses of chalcogenide perovskites and powders/pellets are commonly reported rather than the thin-films required for device fabrication. To address this need, we have developed low-temperature (100 - 300 °C) solution-based chemistry for the direct synthesis of sulfide chalcogenide perovskites. Novel single source precursors for the reaction of alkali-earth metals with group IV and transition metal cations are key to this synthesis. Examples of $BaZrS_3$ and $BaSnS_3$ nanoparticles will be discussed; Figure 1 shows a nanocrystalline ink of $BaZrS_3$ and the obtained Raman spectra of the 110 \degree C synthesis in toluene. Current work is underway for the reactive grain-growth of these chalcogenide perovskite nanocrystals into thin-film sulfides and selenides. Ultimately, success in this research would result in a new class of PV absorbers which would combine the phenomenal optoelectronic properties in the perovskite crystal system with the stability and processing opportunities of thin-film chalcogenides.

Next generation solar devices: detailed electron nanoscopy investigations on Zn3P2 rotated domains

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Abstract

The interest towards abundant and renewable energy sources is rapidly increasing due to the risk anticipated by climate change. Zinc phosphide (Zn_3P_2) is an ideal candidate as material for photovoltaic applications thanks to its direct bandgap, earth-abundance, and optoelectronic characteristics, although it has not been extensively studied due to limitations in the fabrication of high-quality layers. It is possible to overcome these factors by growing the material into nanoscale objects, exploiting the selected area epitaxy approach (SAE), opening up new elastic strain relaxation mechanisms and minimizing the interface area [1].

Here we present our latest results for Zn_3P_2 nanowire-like structures epitaxially grown on InP substrates. We have explored different orientations to obtain a comprehensive picture of the main mechanism involved during the growth. By combining scanning transmission electron microscopy in high angle annular dark field (HAADF-STEM) mode, with modelling and simulation we could recognize the presence of two stable rotated crystal domains coexisting in the same nanowire structure. We deeply investigated these defects' structure to address their formation mechanism and effects reflected in their electronic properties, in order to comprehensively understand the final device performance of the synthetized material [2].

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Numerical simulation of earth abundant and non-toxic Kesterite-based solar cells using Solar Cell Capacitance Simulator

Authors

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Abstract

In this research work, the performance of Cu_2ZnSnS_4 (CZTS) based solar cells was analyzed and studied by the Solar cell capacitance simulator (SCAPS-1D) software. We chose Zn(S,O) as a solar cell buffer material in order to replace toxic Cadmium Sulphide (CdS). The photovoltaic parameters (the short-circuit current density, open-circuit voltage, fill factor, and efficiency) of the Mo/p-Cu_2ZnSnS_4/n-Zn(S,O)/i-ZnO/n-ZnO:Al structure have been simulated with different CZTS samples. According to the simulation results, we found that the efficiency Mo/p-Cu_2ZnSnS_4/n-Zn(S,O)/i-ZnO/n-ZnO:Al structure was around 10 %. We also studied the effect of the thickness of Cu2ZnSnS4 films and we found an increase of the efficiency from 10 to 17 % by increasing the thickness from 0.5 to 3 µm.

Over 6% efficient TiO2/Sb2Se3 solar cells via surface and bulk modification of TiO2 buffer layer

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Abstract

The emergence of new PV applications in the society requires design of materials and devices with a different set of properties. At this scale, for a new PV technology is not sufficient to be only competitive with the Si and CdTe technologies in efficiency and reliability but one should also rely on green, environmentally friendly, and earth-abundant materials. An emerging highly promising PV material currently under widespread investigation in the PV community is the inorganic Sb_2Se_3 compound showing an impressive achievement in less than five years of research and development. While CdS is the most widely used partner layer for Sb_2Se_3 solar cells, recent investigations showed TiO_2 as a good alternative to develop Cd-free based device as well as its high potential to improve the device performance. Although several reports showed promising results for TiO_2/Sb_2Se_3 cell architecture, there are a few critical questions that should be addressed in this direction. In particular, the mechanism by which the bulk and surface states in TiO_2 (usually deposited by chemical deposition methods) affect the TiO_2/Sb_2Se_3 heterojunction interface is not yet understood. Here we show post-deposition annealing in a controlled environment as an efficient technological approach to modify the bulk and surface chemistry of ultrasonic sprayed TiO_2 films, towards improving the TiO_2-Sb_2Se_3 heterojunction interface. It is demonstrated that implementation of such approach allows an impressive enhancement in the device performance from 4% to 6 %. Classical XRD, SEM, EDX in combination with advanced XPS, Kelvin Probe (KP), Photoelectron Yield Spectroscopy (PYS), I-V, EQE, and C-V-F are used for the analysis of layers and device properties. The mechanism of organic residuals and oxygen mobility in the chemically processed TiO_2 and their interrelation with the formation of TiO_2-Sb_2Se_3 heterojunction interface and hence device performance is provided.

Photoluminescence of monocrystalline and polycrystalline zinc phosphide thin films

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Abstract

Zinc phosphide (Zn_3P_2) is an earth-abundant semiconductor material capable of addressing the rising demand for low-cost and efficient optoelectronic devices. Its 1.5 eV direct bandgap, long minority carrier diffusion length (5-10 µm), and high absorption coefficient make it very promising for applications as an absorber in thin-film solar cells.[1] Furthermore, it has the added benefit of being a binary phase over more complex multinary materials.

We have grown high-quality monocrystalline zinc phosphide thin films on (100) InP substrates by molecular beam epitaxy.[2] In this work, we discuss the characterization of the optical properties and electronic structure of the films with photoluminescence spectroscopy and show that the monocrystalline thin films have a high optical quality.

Temperature- and power-dependent measurements have revealed two sets of peaks. One set appears in the low energy region, around 1.3 eV, with a typical behavior of defect-related transitions. The second set is characterized by a double peak structure close to the bandgap energy of 1.5 eV. We will discuss in detail the double peak structure and explain its origin by systematically addressing different existing interpretations, including the coexistence of a direct and an indirect bandgap, recombination via different types of defects, different electronic states between the bulk and the surface, and finally self-absorption effects.

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Post deposition annealing effect on properties of chemically deposited CdS films and performance of CdS/Sb2Se3 solar cells

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Abstract

Continuous diversification of the PV market requires screening for new semiconductor materials which are earth-abundant, non-toxic, and have a high potential for next-generation cost-efficient solar cells. In this context, Sb_2Se_3 is identified as a promising absorber material owning a direct bandgap of 1.18eV and high absorption coefficient of 10^5 cm^{-1}. Its pseudo-1D orthorhombic crystal structure with $(Sb_4Se_6)n$ vertical ribbons bonded through weak van der Waals forces prevent the formation of dangling bonds at the interface between grains, making it a grain boundary defect tolerant compound.

Taking these advantages, efficiencies between 7-9% were reported for Sb_2Se_3 thin-film solar cells, most often when designed in combination with CdS heterojunction partner layer. For such device configuration, post-deposition treatment of CdS layer in presence of oxygen and $CdCl_2$, at 380-420^{o}C is widely used as a standard procedure before its application in the cell. Although this is a well-established processing step for CdTe thin-film technology (where the treatment is applied for the whole stack), the reason for such treatment for CdS layer before its application in a full Sb_2Se_3 cell stack is not yet understood. There is a contradiction in the literature regarding the intermixing effect which occurs at the interface between CdS buffer and Sb_2Se_3 absorber. Several groups reported intermixing as beneficial for the device while other groups treated the same phenomenon as a limiting factor for the performance of CdS/Sb_2Se_3 solar cells. The question which arises is whether this treatment is required or not and if needed then what should be the suitable processing temperature and environmental conditions.

Considering these aspects, the focus of this study was to systematically investigate the influence of post-deposition annealing in vacuum and air, over a wide range of temperatures (200-400 ^{o}C) on the properties of CdS thin films and CdS/Sb_2Se_3 solar cells. The aim was to identify the suitable annealing conditions which would allow optimal CdS-Sb_2Se_3 heterojunction formation and to obtain efficient solar cells.

Close spaced sublimation (CSS) and chemical bath deposition (CBD) were used for the deposition of the absorber and buffer layers, respectively. XRD analysis showed modification from hexagonal to cubic CdS with the increase of vacuum and air annealing temperatures from 200 to 400 ^{o}C. Air annealing at 400 ^{o}C leads to the formation of CdO. The bandgap of CdS

decreased systematically from 2.4 to 2.3 eV with increasing of the vacuum and air annealing temperature from 200 to 400 ^{o}C. SEM analysis shows homogeneous and compact CdS films as a result of 200 ^{o}C annealing in air. The same annealing conditions promoted formation of CdS layers with a carrier concentration of ~ 10^{18} cm^{-3}. CdS annealed films were applied in superstrate configuration CdS/Sb_2Se_3 solar cells. The device processed with 200^{o}C annealed CdS buffer exhibited the highest efficiency of ~2.8% - an enhancement of ~40% compared to the cell obtained with the untreated CdS layer. These results demonstrate that for highly efficient CdS/Sb_2Se_3 device configuration, CdS buffer layer requires annealing in oxygen ambient, however, the annealing temperature should not exceed 200 ^{o}C.

Raman tensor elements of Zn3P2

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Abstract

The development of earth-abundant-based solar cells is a realistic pathway to large scale solar energy harvesting, both economically and environmentally. In this regard, Zinc Phosphide (Zn_3P_2) has been investigated for decades since it boasts a collection of desirable features for photovoltaics: high absorption (10^4 cm^{-1}), ideal bandgap (1.5 eV), and long diffusion length (10 μm). Nonetheless, the achieved cells exhibit low efficiencies (< 6%) far from their theoretical potential, thus affecting the keen interest in Zn_3P_2 of the scientific community. In particular, the semiconductor is incompatible with industrial-scale substrates and controllable doping has not been achieved yet. But the successful adaptation of Zn_3P_2 into nanowires (1) and recent strides in growth-quality control of Zn_3P_2 (2) partly resolve the problem, bringing the material up to date with great hope for the next generation photovoltaic applications. Still some structural and defect formation properties that may affect the charge separation efficacy are not explored fully and hinder the further development of Zn_3P_2-based photovoltaic devices.

Raman spectroscopy is a relevant tool for structural characterization of semiconductors, as it provides insights into crystal quality, defects, and doping. The selective enhancement of certain modes is made possible through polarized Raman measurements, allowing for precise identification of peak properties, thus rendering rich information on changes in the material. The enhancement of modes is determined by the selection rules, which are conveniently summarized in the Raman tensors. The aim of this work is to deepen-in the fundamental knowledge of Zn_3P_2, by investigating the values of Raman tensor coefficients. Low temperature,

Raman polarization measurements with 488 nm excitation have been performed on monocrystalline Zn_3P_2 thin films, grown by molecular-beam epitaxy on InP substrates (3). Angle-dependent polarization measurements on a (001) basal plane, have allowed mapping out the intensity behavior of A_{1g}, B_{1g} and B_{2g} modes, resulting in total identification of 19 modes with their respective Raman tensor elements. These experimental results are compared to the theoretically expected values calculated from density functional theory simulations.

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Reactive annealing effect on Sb2Se3 thin film electrical properties

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Abstract

Traditional inorganic thin-film photo-absorber technologies such as CIGS or CdTe have already been developed to reach a PCE of over 22%. However, the use of toxic materials such as Cd can impact the environment making the absorbers undesirable, using rare elements such as In or Ga ramps up the price of manufacturing solar devices. Relatively recently, antimony selenide (Sb_2Se_3) was found to be a perfect material for low cost, low toxicity absorber material. The rapid growth of record efficiency indicates substantial attention to the Sb_2Se_3 (2.1% to >10% since the year 2014) [1].

All of the most developed inorganic absorber layers (CIGS, CdTe) are universally p-type semiconductors, an assumption automatically has been made that Sb_2Se_3 material is no exception. Device architecture of TCO/CdS/Sb_2Se_3 was applied, which is common to CIGS, CdTe, and CZTS solar devices. However, the carrier type of Sb2Se3 was rather assumed p-type, than measured. Work with single crystals showed the compound to be insulating, suggesting significant midgap pinning because of native defects [2]. Cyclic voltammetry and Hall measurements showing p-type conductivity were shown by Zhou et al. [3]. The work of D. Major et al. reported n-type conductivity in Sb_2Se_3 thin-films, the source of n-type doping was identified to be Cl impurities from the Sb_2Se_3 powder [4].

Because of the insulating characteristics, doping is one of the key ways to improve the efficiency of antimony selenide thin-film solar cells. In this work, we studied the electrical properties of as-deposited and post-deposition treated Sb_2Se_3 thin films. Films were deposited on SLG/TiO_2 and SLG/FTO/TiO_2 substrates (TiO_2 layer was determined to be insulating) using the VTD method in a three-zone tube furnace. Hot-Point probe technique to determine the type of conductivity, electronic transport measurements (including Hall effect) were performed, XPS and EDX was used to establish the elemental composition of the samples, current-voltage (J-V) measurements were performed for the characterization of the devices.

All of our investigated films had p-type conductivity. Post-deposition treatments were applied for doping thin films with O_2 and S. Both oxygen and sulfur-doped films showed an increase in conductivity by up to 5 to 10 times, respectively. Conductivity vs. Temperature (Fig. 1) measurements (under no illumination) showed no presence of shallow defects, only intrinsic conductivity with activation energy similar to E_g ($E_a \sim 570$ meV).

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Reducing indium use in silicon heterojunction solar cells through local contacts

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Abstract

Silicon heterojunction solar cells are one of the two envisioned next-generation technologies for mass-production of silicon photovoltaic modules. They rely on earth-abundant crystalline silicon wafer for light absorption and earth-abundant thin amorphous-silicon layers for selective charge extraction. Nevertheless, they usually employ indium-based transparent conductive oxides (TCO) to collect laterally the charges towards the silver grid. Both Ag and In are scarce, and sustaining a terawatt-scale production volume over two decades would bring supply challenges. There is therefore strong interest in suppressing the use of these materials. Focusing on indium, it was thought for a long time that a TCO is necessary for efficient collection of photogenerated charges in silicon heterojunction solar cells. However, recent simulation work [1] evidenced that lateral charge collection can be provided by the wafer itself, and efficient TCO-free devices were recently demonstrated experimentally [2].

We perform here simulation and experimental work, to elucidate the mechanism of charge transport in silicon heterojunction solar cells and assess the feasibility of TCO-free devices. By using simulations, we evidence that using local contacts with a reasonable metallization fraction

(<5%) requires to achieve low contact resistance between the silicon wafer and the metal electrode below 0.01 Ohm.cm^2. Such values was notably reported for Si/Al contacts, which would remove both scarce elements In and Ag. Additionally, removing the TCO not only relaxes supply and reduces cost, but it also improves efficiency by reducing parasitic light absorption. By fabricating localized-contact solar cells with various contacting area, we confront simulation results to experimental data to improve our modelling of charge transport, and guide us towards the fabrication of high-efficiency, fully earth-abundant silicon heterojunction solar cells.

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Semi-transparent back contacts based on sputtered MoS2:Nb for Silicon/CZTS tandem cells application

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Abstract

Photovoltaic devices based on kesterite absorbers (mainly $Cu_2ZnSn(S,Se)_4$) are quite interesting since these materials are composed by non-toxic and abundant elements only. On the other hand, their efficiency is not increasing above 13% since several years. The improvement of the absorber properties, by means of chemical composition changes or doping, is certainly important but the development of suitable buffers and contacts is also relevant. On p-type absorbers a back contact with a high work function would give a good hole collection and reduce electron recombination. If the material is transparent in the IR it will be also possible to develop semi-transparent devices for tandem application. Indeed, solar cells based on pure sulfide Cu_2ZnSnS_4 (CZTS) semiconductor can find a promising application as top-cell in CZTS/Silicon tandem devices due to its high bandgap value (up to 1.67 eV).

This work is centred on the development of such a back contact modifying the MoS_2/FTO/ZnO structure already used as intermediate contact in working monolithic CZTS/Si tandem cell [1]. First of all a new process route involving the direct RF sputtering deposition of MoS_2:Nb has been followed. The dual purpose is to ensure a better control of both thickness and transparency of this layer and to preserve TCOs from degradation, avoiding the sulfurization process previously required to convert Mo into MoS_2. In addition, Niobium doping should shift the material conductivity towards p-type, giving an improvement of hole transport at the CZTS/MoS_2 interface. The correlation between sputtering conditions and MoS_2:Nb optical and electrical properties has been investigated and thin films with proper stoichiometry and high transparency have been obtained. Another change in the trilayer is the replacement of the ZnO layer with a Tungsten doped Indium Oxide (IWO), since IWO exhibits higher conductivity and better transparency. The final CZTS/MoS_2:Nb/FTO/IWO stacks show a good transparency (total

absorbance around 20% with 30 nm of MoS_2) and the desired ohmic behaviour as confirmed by linear J-V curves measured between IWO and gold dots evaporated on CZTS (Figure 1).

Complete CZTS solar cells on MoS_2:Nb/FTO/IWO back contact have been fabricated and characterized. The performances on flat substrates are limited by bad adhesion between CZTS and MoS_2 layers, whereas no adhesion problems were found using textured substrates. Monolithic CZTS/Si tandem devices based on textured Silicon bottom-cell were produced using the MoS_2:Nb/FTO/IWO structure as intermediate contact, achieving an efficiency of 4.6% (Figure 1). The device performances are limited by the top-cell, which must be suitably optimized on the new contact and textured substrates.

This work has received funding from the European Union H2020 Framework Programme under Grant Agreement no. 952982 (Custom-Art).

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Shedding light on defect states of (AgxCu1-x)2ZnSnSe4-based absorber solar cells

Authors

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Abstract

Thin-film solar cells have achieved great progress and offer more opportunities in terms of photovoltaic (PV) performances to convert solar light into electrical power at low cost. To prevent the losses of V_{OC}, partial or total replacement of the cations with other isovalent elements with different ionic sizes has drawn significant attention due to their promising results to solve the V_{OC} deficit issues. In this paper, by combining the experimental and simulation work, we demonstrated the effectiveness of cation substitution by altering the formation energy of different cationic defects. We partially substituted Cu^{1+} with larger ionic radius Ag^{1+}, to work on the recombination mechanism for the complex Ag-alloyed CZTSe ($(Ag_xCu_{1-x})_2ZnSnSe_4$ (ACZTSe) system. In order to gain access to the recombination pathway of the ACZTSe system, a systematic analysis has been done by intensity-dependent photoluminescence (PL) at low temperature. It shows that defect density and depth of potential fluctuations (Υ) were reduced after Ag-alloying. Our DFT analysis shows that Ag promotes favorable defects whereas it suppresses the detrimental defects. Here, we showed that the complex Ag-alloyed CZTSe system does show improvement in terms of voltage deficit issues with efficiency 7% efficient baseline CZTSe, while Ag-alloyed CZTSe increase the efficiency up to 9.1%.

Sol-gel deposition of Cu2XYS4 thin-films with tunable bandgap as absorbers for photovoltaic applications

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Abstract

In current days, the PV research is focused on finding low cost and easily processable materials. Here we propose a simple chemical procedure for the synthesis and characterization of earth-abundant chalcogenide thin-films with tunable bandgap, leading to well-defined phases of Cu_2XYS_4 (with X = Zn, Fe, Mn; Y = Sn, Ge). The deposition process is straightforward and very cheap, based on the sol-gel technique, where the thin films are produced thanks to a direct drop-casting of the precursor solution, followed by a gelation process and heat treatment in Ar atmosphere for short time to generate the desired crystalline phase of the quaternary alloy. Metal acetate precursors were proved to have a primary role in creating a network in the sol-gel transition by coordinating and so pre-organizing the metals in solution, together with thiourea (as the only source of sulfur) and DMSO or DMF as solvents. [1] Moreover, the addition of dopant amounts of KCl into the precursor solution was experimentally demonstrated to be beneficial for the grain growth and material quality, both crucial for the final solar device performance.

The so-synthesized layers have been characterized by UV-Vis, µ-Raman, XRD, EDX spectroscopy measurements and their morphology was studied by SEM imaging proving the very good quality of the material. The band gap, obtained from transmittance measurements, ranges from 1.4 to 2.1 eV depending on the combination of the chosen metal precursors, suggesting this class of materials as suitable candidate as top absorber in a tandem device architecture. Promising single-junction prototypes of working solar-devices have been produced even with semi-transparent substrate leading to a bifacial activation of the *p-n* junction.[2,3,4]

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Solvent Selection for Printable, Green, Non-toxic Perovskite Solar Inks

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Abstract

Perovskite Solar Cells (PSCs) are an attractive next-generation, low-cost and solution processable solar technology that can facilitate large-scale manufacturing of photovoltaics. PSCs utilise a thin-film perovskite as the solar absorber layer, which has highly tunable properties by altering the chemical composition of the perovskite itself. However, the majority of current PSCs use toxic lead and harmful chemical solvents such as dimethyl formamide (DMF) in their production, leading to issues of user and environmental safety throughout the lifetime of the cell. Other issues associated with PSCs are their stability and scalability.

Here we present our work on safe and green solvent selection for inkjet printing lead-free, tin-based perovskite solar inks. We aim to minimise the safety concerns and environmental burden of our solar inks, while maximising their stability, accessibility, and cost-effectiveness. Several key parameters have been identified which require further investigation, the most pressing of which being the selection of an appropriate solvent or solvent system. In addition to being a good solvent for the perovskite precursor materials and displaying an acceptable solution stability, our solvent systems are required to be compatible with the rheological demands of inkjet printer technologies. We have chosen inkjet printing as our method of deposition because it is a scalable next-generation additive manufacturing technique that minimises waste and allows a high degree of process control and optimisation. As such, we have tested a variety of different solvents and solvent mixtures for use in our solar inks and assessed their compatibility with inkjet technologies. Some examples of these solvents include amides (diethyl formamide {DEF}), diamides (dimethylpropyleneurea {DMPU}), heterocyclic cycloalkanones (dihydrolevoglucosenone {Cyrene™}, gamma-valerolactone {GVL}), and ionic liquids (methylammonium acetate {MAAc}, methylammonium formate {MAF}). Z-number printability was calculated using measured viscosity, surface tension, and density. Printable solvents were further investigated to determine experimental droplet size, perovskite precursor solubility, ink stability, and ability to form a continuous thin-film. Finally, optimisation of printer parameters such as print speed, interdroplet distance, number of passes, and stage temperature were investigated for well-performing solvent systems.

Our findings suggest there are several potential solvent systems suitable for inkjet printing thin-film perovskite absorber layers, with different advantages and disadvantages associated with each one. We have categorised these solvents based on their printability, ability to dissolve the perovskite precursor materials, and subsequent precursor solution stability. Overall, we believe that a mixture of DEF:DMPU in a 6:1 ratio provides the greatest suitability for inkjet printing of solar inks due to its safety, cost-effectiveness, printability, and ability to fully dissolve high

concentrations of perovskite precursors. For the 6:1 DEF:DMPU mixture a printability Z-number of 21 was calculated, giving a mean jetted droplet size of 62.0 ± 2.5 μm experimentally. Optimum print parameters were found when printing at a 10 mms^{-1} print speed, 0.075 mm interdroplet distance, 3 printed passes, and a stage temperature of 100°C onto a glass substrate. This work could lead to printable, green, non-toxic perovskite solar inks and facilitate scalable and accessible manufacture of safe PSCs which are cost-effective and have minimised environmental burden.

Structural characterization of the solid solution Cu2Mn(GexSn1-x)S4

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Abstract

The research of quaternary Cu-based chalcogenide semiconductors has caught a large interest for photovoltaic applications, because these materials consist of non-toxic and earth abundant elements [1]. While being environmentally friendly and low cost, materials like Cu_2MnGeS_4 or Cu_2MnSnS_4 are very promising candidates for use in tandem solar cells, because they can cover a wide bandgap range of 1.52-1.72 eV [2-4]. This study presents new insight into the crystal structure of the solid solution $Cu_2Mn(Ge_xSn_{1-x})S_4$.

$Cu_2Mn(Ge_xSn_{1-x})S_4$ has already been studied earlier [4, 5]. In these studies, the structural analysis of the solid solution based on X-ray powder diffraction data. Because Cu, Ge and Mn are electronic similar elements, they cannot be differentiated in a structural analysis based on X-ray powder diffraction data. But their neutron scattering lengths are different, that is why we apply neutron diffraction to analyze the crystal structure of the $Cu_2Mn(Ge_xSn_{1-x})S_4$ mixed crystals. Moreover, the basis of our investigations is a careful determination of the chemical composition of the mixed crystals by WDX spectroscopy. This is important, because it was shown for other quaternary chalcogenides (e.g., Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$) that even small deviations in composition (off-stoichiometry) can have a critical influence on the band gap energy of the material [7].

The endmembers of the $Cu_2Mn(Ge_xSn_{1-x})S_4$ solid solution crystallize in different structures: Cu_2MnSnS_4 crystallizes in tetragonal stannite type structure (space group), whereas Cu_2MnGeS_4 adopts the orthorhombic wurtz-stannite structure (space group $Pmn2_1$). Thus, within the solid solution a structural transition from the tetragonal to the orthorhombic crystal structure can be expected. In the presented study $Cu_2Mn(Ge_xSn_{1-x})S_4$ mixed crystals were synthesized by solid state reaction of pure elements in evacuated silica tubes at temperatures of 800°C. The chemical composition and homogeneity of the synthesized polycrystalline powder materials were determined by WDX spectroscopy using an electron microprobe system. The lattice parameters of the mixed crystals were obtained by LeBail refinement of powder X-ray diffraction data. It can be shown that Sn-rich mixed crystals ($0 \leq x \leq 0.3$) adopt the stannite type structure, whereas Ge-rich mixed crystals ($0.6 \leq x \leq 1$) of this series adopt the wurtz-stannite type structure. Within $0.3 > x > 0.6$ two quaternary phases coexist, adopting the tetragonal and the orthorhombic structure, respectively.

The results of the chemical composition study in combination with structural characterization and optical bandgap evaluation from diffuse reflectance of $Cu_2Mn(Ge_xSn_{1-x})S_4$ mixed crystals will be presented providing special attention to the phase transition from the stannite to the wurtz-stannite crystal structure.

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STUDY OF THE OPTICAL PROPERTIES OF Sb2(Se1-X,SX)3 (x= 0 - 1) SOLID SOLUTIONS

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STUDY OF THE OPTICAL PROPERTIES OF Sb_2 $(Se_{1-x}S_x)_3$ (x = 0 - 1) SOLID SOLUTIONS

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Antimony selenide (Sb_2Se_3) is a binary compound from the V_2-VI_3 group with anisotropic optoelectronic properties. It gained research attention in the last decade as absorber material in thin-film solar cells due to optimal bandgap energy of 1.2 eV at room temperature, a high absorption coefficient of 10^4 cm^{-1} at visible wavelengths. However, Sb_2Se_3 has a quasi-1D ribbons-like crystal structure, which results in 3 and 2 non-equivalent lattice sites for Se and Sb, respectively. Such low symmetry configuration of atoms in the lattice leads to a large variety of point defects and complicated defect chemistry overall**.** **I**t is crucial to collect more information about the electronic band structure of such highly anisotropic semiconductor material. Moreover, Sb_2Se_3 is isomorphous to antimony sulfide (Sb_2S_3) as both are from Pnma(62) space group, so we can follow a strategy of varying the x = S/(S+Se) value in $Sb_2(Se_{1-x}S_x)_3$ solid solutions to learn more about the electronic structure of this promising group of materials. This study presents a detailed analysis of the optical properties of the $Sb_2(Se_{1-x}S_x)_3$ (x = 0–1) polycrystals. Four antimony selenosulfide solid solutions $Sb_2(Se_{1-x}S_x)_3$ together with Sb_2Se_3 and Sb_2S_3 were synthesized from elemental precursors at the same synthesis conditions, only varying the x = S/(Se + S) value with a step of Δx = 0.2. Successful formation of the $Sb_2(Se_{1-x}S_x)_3$ solid solutions was determined by Raman spectroscopy and X-ray diffraction. As expected for the same type of crystal structure of Sb_2Se_3 and Sb_2S_3, the bimodal behavior of Ag Raman mode

in $Sb_2(Se_{1-x}S_x)_3$ was detected. Temperature and excitation power-dependent photoluminescence (PL) analysis of $Sb_2(Se_{1-x}S_x)_3$ was performed in order to look into the electronic and defect structure of these promising semiconductor materials for optoelectronic applications. The shift of the near band edge PL emission in $Sb_2(Se_{1-x}S_x)_3$ towards higher energies from 1.309 eV to 1.728 eV with increasing sulfur content was detected at $T = 3$ K. A change in the radiative recombination mechanism was detected being of excitonic origin in samples with $x \leq 0.2$ and resulting from deep donor-deep acceptor pair recombination in samples with $x > 0.2$.

Superior Optoelectrical Properties of Cerium-Doped Indium Oxide Thin Films for Solar Cell Applications

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Abstract

Indium tin oxide (ITO) is the most commonly used front contact material for a variety of photovoltaic technologies. However, the presence of a high free carrier concentration in ITO thin films results in the well-known phenomenon of free carrier absorption in the near-infrared (NIR) region of the solar spectrum. This causes optical losses especially in those solar cells where the active layer is designed to preferentially absorb NIR photons. Therefore, a combination of high carrier mobility and high NIR transparency is desired for advanced transparent conductive oxides for substituting ITO in solar cells. Following this approach, various transition metals including Mo, Ti, W, Zr, and Nb have been found as potential dopants for inducing high mobility in indium oxide films. However, the doping effect of inner transition metals on the structural, optoelectrical and chemical properties of the host In_2O_3 films still remain largely unknown. In this work, we explore cerium (Ce), which is a member of the lanthanide group, as a potential dopant in In_2O_3. It is important to note that Ce has a higher relative abundance in the earth's upper crust than most other dopants studied before. Accordingly, thin films are prepared on glass by industrially relevant pulsed DC magnetron sputtering with high deposition rates. XRD and Raman measurements revealed the poly-crystalline nature of the deposited films, and the corresponding peaks are in close agreement with those of pure bixbyite In_2O_3. The highest mobility of ICeO achieved in this work is 71 cm^2/Vs, for a film deposited at a substrate temperature of 160 °C and oxygen content of 1.4 vol% followed by post-deposition vacuum annealing at 500 °C for 30 minutes. This mobility value is almost four times higher than that of the standard ITO film prepared in this work, and more than two times higher than the value previously reported in the literature (30 cm^2/Vs) for DC magnetron sputtered ITO: Ce films on glass. Comparison of the measured mobility values with those calculated using the BHD model and Erginsoy approximation revealed that neutral impurity scattering is the most dominant scattering mechanism in the fabricated ICeO films. However, the density of these neutral defects can be strongly reduced with post-deposition vacuum annealing. In addition, the optical transmission of ICeO is comparable to ITO in the visible region, but the former clearly outperforms the latter in terms of its NIR trans-parency. Together with a smooth surface (RMS roughness ~ 2-5 nm), pulsed DC magnetron sputtered ICeO/glass substrates therefore demonstrate significant potential to replace the most commonly used ITO/glass substrates for emerging solution processible photovoltaic

technologies, such as organic solar cells and perovskite solar cells with low bandgap absorbers. For more information, please refer to: https://doi.org/10.1016/j.ceramint.2020.09.006

Surface modification of Cu2ZnSnS4 and Cu2ZnSn(S,Se)4 films during plasma treatment

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Abstract

The processes of surface modification of Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) films under ion-plasma treatment have been studied. Films were deposited on SLG and Mo-coated SLG substrates. Plasma treatment was carried out in argon plasma in a high-density low-pressure RF inductively coupled plasma reactor. Argon plasma was ignited by applying RF power of 800 W (frequency 13.56 MHz) on the inductor. The plasma-treatment parameters were an argon rate of 10ncm^3/min, a working pressure of 0.08 Pa, an average Ar^+ ion energy of 120, 200 eV and the ion current density of 5.2 mA cm^{-2}.
The plasma treatment duration was varied in the range of 60–180 s.

Fig.1. The initial surface of CZTS film (left) and its modification after plasma treatment at argon ion energy of 120 eV for 3 minutes (right).

As a result of plasma treatment, an ensemble of nanocones appeared on the surface of CZTS and CZTSSe films (Fig. 1). The height of the nanocones varied in the range of 50-400 nm. The geometric parameters of the cones and their surface density depended on the energy of the argon ions, the time of the process, initial morphology of the films and S/Se ratio. The changes in the chemical composition of the surface after plasma treatment and the physical models for the nanostructures formation have been discussed.

Synthesis and characterization of thermally evaporated Ag2ZnSnS4 semiconductor

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Abstract

Over the past few years, there has been considerable interest about the quaternary Cu_2ZnSnS_4 (CZTS) material for its suitable direct bandgap and the high absorption coefficient. Nevertheless, this absorber layer is ineffective in comparison to CIGS as it suffers from a severe open circuit voltage deficit Voc which results from the generation of the antiste CuZn defect. Significant work has been carried out to overcome this problem through the replacement of copper with other elements such as silver. This research involves the introduction of a new method for the synthesis of Ag_2ZnSnS_4 (AZTS) thin films by vacuum thermal evaporation. AZTS thin films were deposited on glass substrate by the vacuum thermal evaporation method at a pressure 10^{-5} Pa. Structural characterization of AZTS, conducted by X-ray diffraction and Raman spectroscopy, revealed the presence of the stannite phase of AZTS with a preferential orientation along the (112) plane with a secondary phase Ag_8SnS_6. EDS analysis confirmed the occurrence of the four constituent elements in AZTS in their respective stochiometric compositions. Optical measurements determined from transmittance and reflectance spectra show that AZTS thin film had high absorption coefficients close to 10^5 cm^{-1} in the visible range and exhibits a direct optical band gap of 2.05 eV. The wavelength dependence of the refractive index was assessed using the Swanepoel model. An analysis of the electrical characteristics performed using the hot probe method indicated a conductivity type n.

The danger of isovalent substitution: Revealing excitonic behaviour in vacancy-ordered titanium perovskites (Cs2TiX6)

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Abstract

High-performance, lightweight solar cells with low-cost and non-toxic substituents are a major target in the field of solar photovoltaics.[1–3] Nanocrystals of lead-free vacancy-ordered perovskites (A_2MX_6) have recently been placed under the spotlight as auspicious candidates for this goal, exhibiting suitable electronic bandgaps, strong optical absorption, benign defect properties, long carrier diffusion lengths and high stability.[4–8]

Despite many theoretical studies of this material, there remains a significant discrepancy between the predicted electronic structure and experimental observations. Accurate hybrid Density Functional Theory (DFT) calculations consistently over-estimate the experimental electronic bandgap, with lower levels of theory (semi-local DFT) being commonly employed in order to yield agreement with the experimental value.[4,7,9–14] We show that this behaviour is the result of a non-trivial error cancellation, where the major errors in the electronic structure obtained by semi-local DFT sum to produce a bandgap matching experiment, neglecting crucial physical properties of these materials.

Through in-depth beyond-DFT computations (QSGW+BSE), we reveal the presence of strong excitonic effects in this 0D system, resulting in a significant renormalisation of the bandgap energy. We discuss the physical and chemical origins of this behaviour, and highlight the major implications of these findings for the broad field of researchers investigating these materials for opto-electronic applications.

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The role of lead precursors in driving competitive crystallization reactions during the formation of 2D perovskites

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Abstract

Two-dimensional (2D) lead halide perovskites are an exciting class of materials currently being extensively explored for both photovoltaics and optoelectronic applications. The ionic nature of these materials makes them ideal candidates for solution processing into both thin films and nanostructured crystals.

Based on prior works on 3D LHPs, we know that the formation of reaction intermediates and the presence (or not) of solvent complexes play a pivotal role in determining the crystallization pathway (e.g. topotactic reactions, dissolution/ re-crystallization, and ion-exchange reactions) and thus the crystal quality. Recent works have shown that tuning intermediate complex formation through solvent engineering is also crucial in controlling 2D perovskite growth. However, we note that all prior works on the transformation of lead solid precursors into LHPs employ the same solvent (i.e. IPA). Therefore the difference in reported crystallization dynamics cannot be attributed to the solvent. As already suggested by prior works on perovskite nanocrystals, a closer look at the role of lead precursors is necessary to fully leverage the potential of solution processing of 2D perovskites. This highlights the incompleteness in the understanding of 2D LHPs crystallization dynamics.

Here, we investigate the role of different solid lead precursors (PbO_2, PbI_2, $PbCO_3$) on the crystallization of pure-phase, n=1, Ruddleson-Popper 2D perovskite BA_2PbI_4, during a two-step drop-cast-based synthesis. While BA_2PbI_4 is formed in all cases, the nucleation and resulting morphology are strongly dependent on the choice of precursor, where the three lead precursors differ from each other in terms of their Pb-ion oxidation state, crystal structure, and material class. We use in-situ optical live imaging during synthesis to reveal clear differences in crystallization kinetics of the same 2D perovskite as a function of the lead precursor. We discern three competing mechanisms in the Pb-precursor for the formation of BA_2PbI_4: dissolution/complexation, BAI intercalation, and solid-state conversion. The differences in the oxidation state and solubility of the starting lead precursor in halide-rich solution play a key role in defining the crystallization pathway(s). This work demonstrates the importance of lead precursors in defining the nucleation and growth of perovskites thereby advancing the existing solution-processing techniques. Understanding how 2D perovskite crystals form in solution is

key to full control over their growth and optoelectronic properties, which will enable new types of physical phenomena and devices.

Ultrathin a-Si:H/oxide UV-selective transparent solar cells

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Abstract

The photovoltaic (PV) market is dominated by mono- and polycrystalline silicon modules (~90% of the market) and thin-film technologies like $Cu(In,Ga)Se_2$ and CdTe (~10%). Despite being consolidated technologies, the devices present important caveats, namely: high weight, low flexibility, and are opaque, leading to poor applicability in building integrated photovoltaic (BIPV) applications. State-of-the-art (semi-)transparent photovoltaic (TPV) devices are focused on the partial absorption of the visible spectrum and/or multiple conversion mechanisms of ultraviolet (UV) and/or infrared (IR). By selectively absorbing UV and NIR wavelengths the theoretical Shockley–Queisser (SQ) limit for the efficiency of a TPV single junction with 100% Average Visible Transmittance (AVT) is 20.6%, compared to 33.1% for an opaque PV.

UV-selective harvesting is a novel topic under development, showing promising results in the last years. Most of the work relies on using wide bandgap (WBG) materials, mainly oxides, as many present bandgaps >2.7eV, making them strong candidates for UV optoelectronic applications and other applications requiring optical transparency. Their bandgap guarantees these optical properties due to non-absorption below its bandgap (i.e. visible range). With this approach, we recently demonstrated a UV-selective device using Zn(O,S) as UV-selective absorber showing a PCE=0.5% under AM1.5G illumination with an Average Visible Transmittance (AVT) close to 70%. Another interesting approach relies on the use of ultrathin materials with WBG <2.7eV with high absorption coefficients. This unnatural move in PV is necessary to ensure that UV-blue absorption occurs within the ultrathin film while letting the rest of the visible light through. A candidate material for this approach is a-Si, with a 1.7-2.1 eV bandgap.

In this work, we report on the fabrication of functional TPV devices with ultrathin a-Si:H and oxide carrier selective contacts and transparent electrical contacts. We present devices with PCE=0.6% (AVT=60%) and a record PCE=1.95% (AVT=35.4%) using a device with structure Glass/FTO/AZO/a-Si:H(8, 31 nm)/MoO3/ITO, with total thickness below 100nm (excluding TCO contacts). In this work, we study the impact of the a-Si:H thickness and its compromise in terms of AVT vs. PCE and provide a complete characterization in terms of TPV parameters.

Photothermal Deflection Spectroscopy has been used to study optical properties of the nanometric a-Si:H films, obtaining experimental absorption coefficient values and allowing for a precise bandgap and Urbach energy through fitting using the Cody Model. UV-VIS spectrophotometry was used to calculate the transmittance profile of complete devices and to obtain their AVT and CRI. J-V characteristics were obtained under AM1.5G illumination and UV and Blue illumination, as well as in the dark. Two-diode circuit model fitting was performed on the best device. Spectral Response was obtained at different electrical biases (with and without light bias) as well as unbiased for the best device. The results and insights obtained from these studies will be presented. This complete characterization allows identifying potential limitations of this alternative wavelength-selective PV technology. This work has received funding from the European Union H2020 Framework Programme under Grant Agreement no. 86002 (Tech4Win).

Understanding the effect of soft thermal treatment on CZTSe/CdS based solar cells: absorber disordering versus buffer improvement

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Abstract

Photovoltaic devices based on kesterite compounds remain one of the most attractive thin film technologies derived from the toxicity or scarcity in the Earth crust of the constituent elements of other technologies. In addition, kesterites provide some advantages as photovoltaic absorber materials such as high flexibility in controlling their physicochemical properties resulting in tunable optical and electronic features. However, the presence of several limitations recently studied by advanced characterization techniques [1] make necessary to continue investigating the complex mechanisms involved in the synthesis and fabrication of kesterite-based devices. These processes usually require high (500-600°C) and low (100-200°C) temperature annealings, for the synthesis and post-deposition treatments, respectively. While high temperatures are employed in the synthesis of the absorbers and are expected to only influence the initial layers of the device, softer temperatures are applied at the final production or even at the post-production stages and, therefore, can influence the whole device. Several groups have reported beneficial effects of low temperature post-deposition annealings in kesterite solar cells [2,3]. However, the available information about the mechanisms behind the observed effects remains quite limited.

This study presents an investigation on the effect of a controllable soft thermal treatment (~200°C) on the properties of a 50×50 mm^2 $Cu_2ZnSnSe_4$ sample consisting of 225 individual 3×3 mm^2 solar cells, which was fabricated following the standard IREC technology [1,2]. A comprehensive study of the solar cells was made combining XRF, Raman, photoluminescence and I-V characterizations, comparing the properties of the devices before and after the annealing. The high number of devices analyzed allowed working with high statistics and

detecting small variations in specific layers. Multi-wavelength Raman and photoluminescence spectroscopies revealed small changes in the absorber surface, associated mainly with Cu/Zn disordering. The comparison with reference samples containing different Cu content (thin film samples) and different Cu/Zn order-disorder (powder samples) enabled to develop a Raman-based methodology for the differentiation and evaluation of V_{Cu} and Cu/Zn defects. In addition, changes in the CdS buffer layer were also detected by resonant Raman spectroscopy and related, mainly, to an improvement of its crystalline quality. Additional experiments (see figure), allowed to conclude that the main beneficial effect of the soft thermal treatment is related to the improvement in the CdS layer while changes in the absorber surface are less relevant, or even harmful, for device performance. Combination of different techniques and high statistics allowed to apply Machine Learning algorithms as a fast-feedback tool for monitoring of the soft annealing process. The results of this work prove the importance of understanding the effect of low temperature production stages in device performance and represent one step forward for developing fabrication strategies that allow the kesterite PV technology to reach higher efficiency levels.

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Universal current losses in perovskite solar cells due to mobile ions

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Abstract

Efficient mixed metal lead-tin halide perovskites are essential for the development of all-perovskite tandem solar cells, however they are currently limited by significant short-circuit current losses despite their near optimal bandgap (~1.25 eV). Herein, we investigate the origin of these losses, using a combination of voltage dependent photoluminescence (PL) timeseries and various charge extraction measurements. We demonstrate that the Pn/Sn-perovskite devices suffer from a reduction in the charge extraction efficiency within the first few seconds of operation, which leads to a loss in current and lower maximum power output. In addition, the emitted PL from the device rises on the exact timescales due to the accumulation of electronic charges in the active layer. Using transient charge extraction measurements, we show that these observations cannot be explained by doping-induced electronic charges but by the movement of mobile ions towards the perovskite/transport layer interfaces, which inhibits charge extraction due to band flatting. Finally, we generalise these findings to lead-based perovskites, showing

that the loss mechanism is universal. This elucidates the negative role mobile ions play in perovskite solar cells and paves the path towards understanding and mitigating a key loss mechanism.

Utilising cation disorder to achieve bandgap tuning in Zn-group IV-nitride and oxide nitride

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Abstract

Recently, there has been significant interest in Zn-group IV-nitrides $ZnM^{IV}N_2$ (M^{IV}: Si, Ge, Sn) since they are earth-abundant. These ternary nitrides provide excellent bandgap tunability and have been considered as promising candidates for an absorber material in solar cells.[1]

Zn-group IV-nitrides are structural analogues to group III-nitrides, where the group III element is replaced by Zn and a group IV element. Having two different cations raises the question of their ordering. Computational studies show that the ß-$NaFeO_2$ type crystal structure (space group: $Pna2_1$) , with the two cations ordered on two different $4a$ Wyckoff sites, is thermodynamically stable.[2,3] Nonetheless, a certain degree of cation disorder, such as Zn_{IV} and IV_{Zn} anti-sites, is possible as an intrinsic disorder of the material. In case of full cation disorder, the material crystallises in the wurtzite-type structure (space group: $P6_3mc$). Herein, cations share one $2b$ Wyckoff site, similar to the binary group III-nitrides.[4] Utilising a variable degree of intrinsic disorder is being investigated as a novel strategy to engineer material properties.[5]

This work presents a comprehensive study of the oxygen-containing system $Zn_{1+x}Ge_{1-x}(N_{1-x}O_x)_2$ synthesised through ammonolysis of Zn_2GeO_4.[4,5] A certain oxygen content, which was unavoidable, necessarily results in a Zn-rich off-stoichiometric composition (Zn/Ge>1) and hence in the formation of Zn_{Ge} anti sites. This compositional disorder is different from the intrinsic disorder through cation permutation. The chemical composition of the material was successfully controlled during the synthesis by varying the reaction conditions (particular temperature and time). Applying XRF and hot gas extraction the cation ratio Zn/Ge and the anion ratio O/N has been determined, respectively. In this way we could conclude on the reaction mechanism model and thereby form the preparative basis for a thorough investigation of the material system.[6, 7]

We are using diffraction techniques to investigate the crystal structure and structural disorder of $Zn_{1+x}Ge_{1-x}(N_{1-x}O_x)_2$. While X-ray powder diffraction allows to determine accurate lattice parameters, neutron diffraction permits to distinguish between the isoelectronic cations Zn^{2+} and Ge^{4+}. Especially the cation site occupancy factors determined by Rietveld analysis of neutron diffraction data allowed us to investigate the distribution on the two cation sites of the ß-$NaFeO_2$-type crystal structure. In this way, we can distinguish between intrinsic and compositional cation disorder. While both types of disorder depend directly, but different on the synthesis conditions, there is no correlation between oxygen content and intrinsic disorder.

Finally, we combine our findings concerning cation disorder and band gap energy determined by UV-VIS spectroscopy to enlighten the relationship between the two disorder mechanisms and an optoelectronic materials property.

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Zn3P2 growth on graphene via van der Waals epitaxy for photovoltaic applications

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Abstract

Zinc phosphide (Zn_3P_2) is a promising earth-abundant solar cell material. Zn_3P_2 has a direct band gap transition of 1.5 eV [1], which is close to the optimum solar energy conversion range. It has a large optical absorption coefficient of $>10^4$ cm^{-1} near its band edge [2], and a minority carrier diffusion length reported ~10 μm [1, 3]. Additionally, as both zinc and phosphorous are earth-abundant elements it could potentially make solar cells more economical for large-scale deployment.

Due to the large lattice parameter and a high coefficient of thermal expansion of Zn_3P_2, the choice of substrate for epitaxial growth is limited and this largely affects the thin film quality. In order to obtain Zn_3P_2 growth independent of substrate lattice parameter, we use van der Waals epitaxy using commercial graphene as a substrate. We demonstrate the growth of single-crystalline flakes and propose a growth mechanism [4]. We investigate the influence of various growth parameters on the Zn_3P_2 growth on graphene, such as temperature, flux and V/II ratio. We use Raman spectroscopy to confirm the stoichiometry and crystalline quality of the material and to detect the presence of impurities. Scanning electron and atomic force micrographs of the crystalline seeds show their triangular structure, most of them keeping a preferred orientation with respect to the underlying graphene. TEM further confirms the single-crystalline nature of the material. XRD is conducted to identify the phase of the grown material. Finally, we discuss the optical behaviour of the Zn_3P_2 obtained on graphene.