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Discussion

Comment on “Ag organisation on Ni(1 1 1) surface” [Surface Science 602 (2008) 2363]

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In a recent paper [1], Chambon et al. have reported on the early growth stages of Ag on the Ni(1 1 1) surface by means of scanning tunneling microscopy (STM). The authors have concluded that Ag on Ni(1 1 1) (at 300–625 K) forms mostly bilayer islands, even for a low coverage of 0.1 monolayer (ML). The interpretation of Chambon et al. is based on the assumption that the first atomic layer of Ag on Ni(1 1 1) is imaged with a very low apparent height of 1 Å [1], compared to the separation of the Ag(1 1 1) planes in the bulk crystal structure which is 2.36 Å. In the present Comment we will demonstrate that this assumption is not consistent with the STM images of the authors reported in Ref. [1], nor with our own STM investigations of the early growth of Ag on Ni(1 1 1). We will show that 1 ML thick Ag islands form on Ni(1 1 1) in the submonolayer regime due to the high Ag mobility on the surface above room temperature. This Ag growth mode is well explained by Bauer’s criterion [2] and the difference in surface energy between Ag(1 1 1) and Ni(1 1 1).

The experiments discussed in the following were performed in ultrahigh vacuum with a low-temperature STM system from Omicron [3] operated at 77 K. The STM images were recorded in the constant-current mode (with the stated voltage referring to the electric potential of the sample with respect to the tip), and they have been processed with the WSxM software [4]. The clean Ni(1 1 1) single crystal surface was prepared by several cycles of room temperature Ar-ion sputtering followed by annealing at 1000 K. Surface crystallographic order and absence of surface impurities were checked by low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy, respectively. STM images of the as-prepared Ni(1 1 1) surface showed clean terraces (atomically resolved) with several 100 nm widths, separated by monatomic steps showing a measured height of 2.05 Å which corresponds to the Ni(1 1 1) interlayer spacing in the bulk structure (2.03 Å). Silver was evaporated from a home-built evaporator using electron-bombardment heating and thickness was monitored by a quartz microbalance.

Fig. 1a shows the three-dimensional rendering of an STM image with a coverage of roughly 0.5 ML Ag on Ni(1 1 1) estimated from different large scale STM images (not shown). This preparation was obtained by depositing 1.5 ML Ag on Ni(1 1 1) at room temperature followed by annealing to 850 K (for 10 min) resulting in a partial desorption of Ag [5], as attested in our LEED patterns by clear diffraction spots of the Ni(1 1 1) substrate (not shown). Three terraces can be readily distinguished in Fig. 1a, where one, labeled Ag(1 1 1), exhibits a pronounced hexagonal superstructure, namely a moiré pattern which forms due to the large lattice mismatch of 16% between Ag and Ni. The moiré structure has a periodicity of 17.5 Å and therefore can be regarded as a close to (7 × 7) superstructure with respect to the Ni(1 1 1) lattice, as observed in our LEED patterns. The atomic resolution STM image displayed in Fig. 1c shows that the Ag(1 1 1) layer atomic lattice adopts the Ag bulk parameter (2.89 Å) and is rotated by 13° with respect to the moiré hexagonal lattice. The moiré orientation results from a misorientation angle between the Ag(1 1 1) and Ni(1 1 1) lattices amounting to 1.8°, which is very close to what is found by calculations to minimize the interface energy [6]. The apparent corrugation of the moiré structure is about 0.15 Å.

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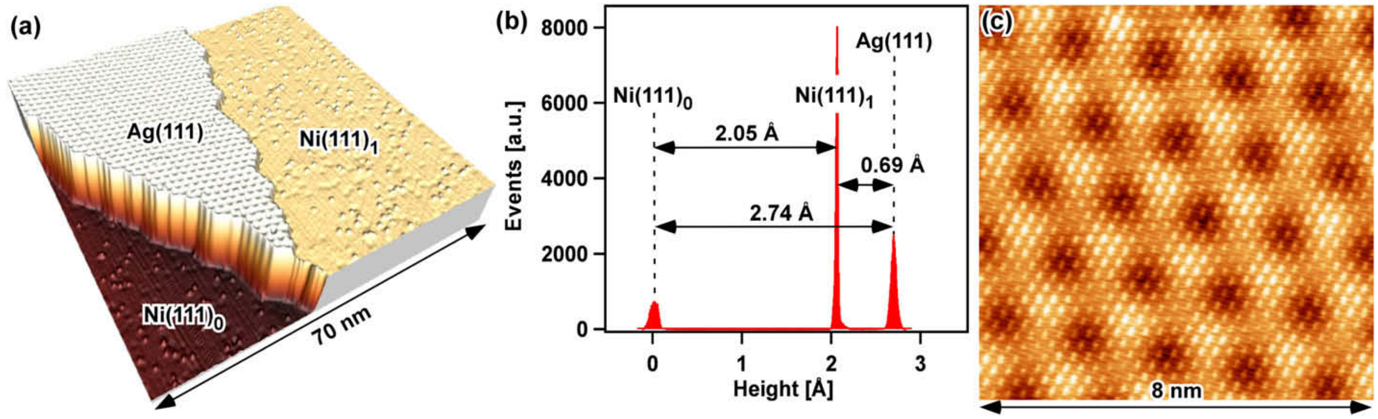

Fig. 1. (a) STM image of about 0.5 ML Ag/Ni(1 1 1) (+1 V, 0.5 nA). Are clearly seen two terraces of Ni, Ni(1 1 1)$_0$ and Ni(1 1 1)$_1$, with Ni(1 1 1)$_0$ lower than Ni(1 1 1)$_1$ by a monatomic step, together with an Ag(1 1 1) terrace showing a moiré structure. (b) Apparent height histogram of the distinct terraces seen in (a) with respect to Ni(1 1 1)$_0$. Very similar results were obtained with a tunneling voltage of −1 V. (c) STM image showing the Ag/Ni(1 1 1) moiré structure together with the Ag(1 1 1) atomic lattice (−5 mV, 120 nA).

In Fig. 1a, one can see two Ni terraces labeled Ni(1 1 1)$_0$ and Ni(1 1 1)$_1$ with Ni(1 1 1)$_0$ lower than Ni(1 1 1)$_1$ by an apparent height difference of 2.05 Å (see Fig. 1b) which corresponds to a monatomic Ni(1 1 1) step. Now there are three possible configurations for the Ag(1 1 1) terrace showing the moiré structure:

(i) 1 ML Ag on the lower Ni(1 1 1)$_0$ with an apparent step height of 2.74 Å,
(ii) 1 ML Ag on the upper Ni(1 1 1)$_1$ with an apparent step height of 0.69 Å,
(iii) 2 ML Ag on the lower Ni(1 1 1)$_0$ with an apparent step height of 2.74 Å.

We will show in the following that the situations (ii) and (iii), argued by Chambon et al. [1], can be reasonably excluded and only the situation (i) is true. Consequently, as will be discussed later, a 1 ML Ag island on Ni(1 1 1) appears with a 16% increased STM imaged height as compared to the Ag(1 1 1) plane separation in the bulk crystal which is 2.36 Å, a value we find in our measurements within less than 1% error for the height of the second Ag layer on the first Ag layer (not shown).

Chambon et al. [1] have observed two apparent heights, 1.0 ± 0.2 Å and 3.0 ± 0.2 Å, and interpreted them as those of 1 ML and 2 ML Ag islands, respectively (corresponding in our case to the possibilities (ii) and (iii)). According to the authors, the STM imaging height of the first Ag layer would be much lower than expected from the Ag bulk structure, and they claim that this lowering "should be ascribed to the difference in the local density of states between the clean Ni(1 1 1) and the Ag/Ni(1 1 1) surfaces" [1]. To clarify this, we like to compare the Ag/Ni(1 1 1) system to a similar system which is Ag/Pt(1 1 1). The similarity arises because Ni(1 1 1) and Pt(1 1 1) are characterized by large density of states close to the Fermi energy dominated by d-bands (see, for instance, Refs. [7–9]). The valence band of Ag(1 1 1) is very different with the d-bands far from the Fermi edge (see for instance [10]). In the case of Ag/Pt(1 1 1), 1 ML Ag islands on Pt(1 1 1) appear in STM not with a decreased but with an increased height of 2.9 Å presumably due to the strong decrease of the work function by Ag adsorption [11]. Indeed, the work function of Pt(1 1 1) (5.7 eV [9]) is much higher than that of 1 ML Ag/Pt(1 1 1) expected to be nearly the same than the one of bulk Ag(1 1 1) (4.5 eV [10]). The case of Ag/Re(0 0 0 1) is also interesting to mention here, because 1 ML Ag islands have been observed in STM again with an increased apparent height of 3.2 ± 0.4 Å argued by a decrease of the work function by 0.7 eV when the Re(0 0 0 1) surface is covered by 1 ML Ag [12,13].

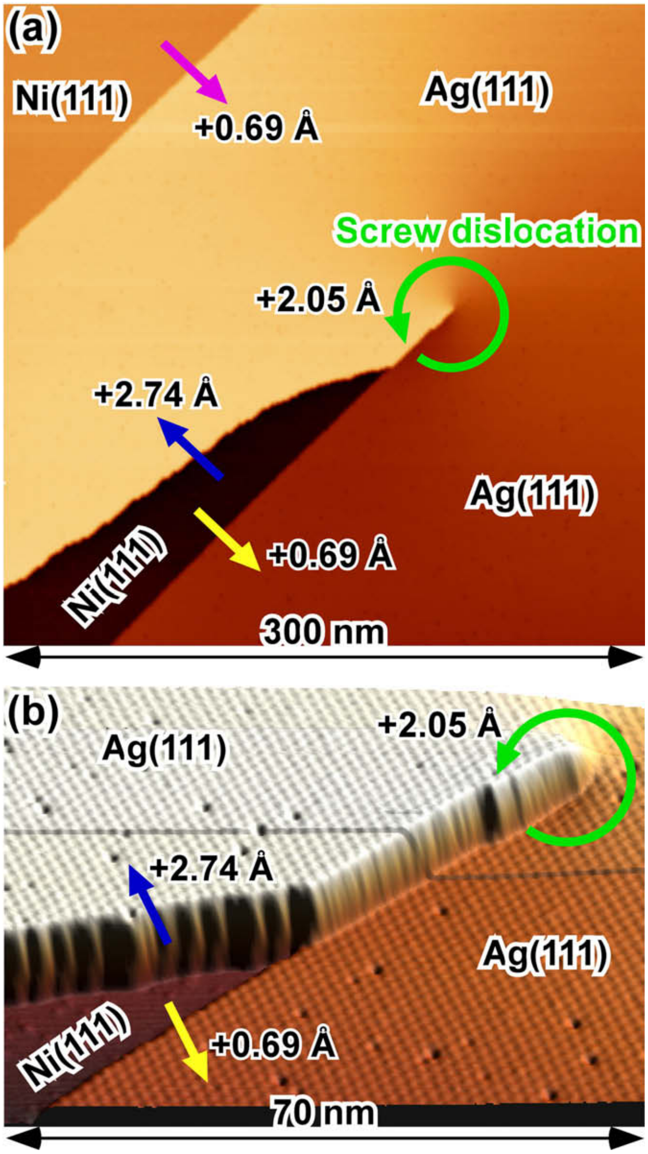

Fig. 2. STM images (of the same sample preparation as in Fig. 1a) showing a Ni screw dislocation covered with 1 ML Ag, together with domains of bare Ni(1 1 1) (−1 V, 0.5 nA). Image (b) is a close-up observation of the region around the Ni screw dislocation seen in (a).

Similarly, in the present case, the work function of Ni(1 1 1) (5.5 eV [14]) is higher by 1.0 eV than that of Ag(1 1 1) [10]. For this reason, we see that there are very good arguments from the literature that 1 ML Ag on Ni(1 1 1) is imaged here with a height of 2.74 Å (16% larger than the expected height of 2.36 Å), opposed to an apparent height of 0.69 Å (71% smaller than 2.36 Å). Therefore the Ag(1 1 1) moiré structure seen in Fig. 1a corresponds to 1 ML Ag/Ni$(1\,1\,1)_0$.

Observing the Ag layer at a Ni screw dislocation, as shown in Fig. 2, we can completely rule out the possibility that the 0.69 Å step height would correspond to 1 ML Ag on Ni(1 1 1). The Ni screw dislocation in Fig. 2 induces a monatomic Ni(1 1 1) step of 2.05 Å height. As can be seen from Fig. 2b the dislocation center is covered by an Ag layer (hexagonal moiré pattern), whereas the lowest terrace is bare Ni(1 1 1). This means that the yellow[1] arrow in Fig. 2b crosses a descending Ni step of the substrate, where the lower terrace is covered with Ag and the upper terrace is not. The height difference of 0.69 Å corresponds therefore to the height of 1 ML Ag on Ni(1 1 1) of 2.74 Å (see blue arrow) minus 2.05 Å of the Ni step height. The assumption that Fig. 2 would show a 2 ML thick Ag layer, as suggested in Ref. [1], cannot reasonably hold, because it would mean that we never observe 1 ML Ag on Ni(1 1 1) in all our experiments.

Our STM measurement of the apparent height of 1 ML Ag on Ni(1 1 1) of 2.74 Å is in accordance with previous studies, where it was found in the range of 2.7–3.0 Å [8,15,16]. Therefore the apparent height of 3.0 ± 0.2 Å observed by Chambon et al. [1] has to be ascribed not to 2 ML but to 1 ML Ag on Ni(1 1 1). The authors have reported small "triangular" Ag islands formed in the middle of Ni(1 1 1) bare terraces which have an apparent height of 1.0 ± 0.2 Å. In contrast to the interpretation of Chambon et al., we believe that the "triangular" Ag islands are grown not above the topmost layer of the Ni(1 1 1) bare terraces but are actually embedded in this topmost layer. The apparent height of 1.0 ± 0.2 Å must thus correspond in our case to the apparent height of 0.69 Å (height difference between 1 ML Ag/Ni$(1\,1\,1)_0$ and Ni$(1\,1\,1)_1$ in Fig. 1a).

Our STM investigations show that Ag on Ni(1 1 1) grows initially by forming ML islands, in agreement with several previous works [5,7,8,15,16], except Ref. [1], where the authors have argued for a bilayer growth. In Figs. 1a and 2, one can see that big ML Ag islands grow from the step edges of the Ni(1 1 1) surface. This is due to the high mobility of the Ag atoms above room temperature resulting from a rather flat surface potential landscape on the bare terraces of Ni(1 1 1), as in the case of other comparable systems such as Ag on Pt(1 1 1) [11], Ag on Cu(1 1 1) [17] and Au on Ni(1 1 1) [18]. Of major importance, the growth mode of Ag on Ni(1 1 1) can be explained thermodynamically by Bauer's criterion [2] based on Young's equation $\Delta\gamma = \gamma_{\mathrm{Ag}(1\,1\,1)} - \gamma_{\mathrm{Ni}(1\,1\,1)} + \gamma_{\mathrm{Ag}(1\,1\,1)/\mathrm{Ni}(1\,1\,1)}$, where $\gamma_{\mathrm{Ag}(1\,1\,1)}$ and $\gamma_{\mathrm{Ni}(1\,1\,1)}$ are the surface free energies of the adlayer and substrate, respectively, and $\gamma_{\mathrm{Ag}(1\,1\,1)/\mathrm{Ni}(1\,1\,1)}$ is the interface energy. Calculations show that $\gamma_{\mathrm{Ni}(1\,1\,1)}$ is about twice $\gamma_{\mathrm{Ag}(1\,1\,1)}$ [19–22] and $\gamma_{\mathrm{Ag}(1\,1\,1)/\mathrm{Ni}(1\,1\,1)}$ is much lower than $\gamma_{\mathrm{Ag}(1\,1\,1)}$ [6,21]. Therefore $\Delta\gamma$ is largely negative, which implies that Ag will wet the Ni(1 1 1) surface and will initially grow on it by forming ML islands.

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[1] For interpretation of color in Fig. 2, the reader is referred to the web version of this comment.