



The adsorption of Ni on the Mo(111) crystal face

C. Tomas, S. Stepanovskyi, Sz. Klein*, J. Śliwiński, J. Kołaczkiewicz

Institute of Experimental Physics, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland

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ABSTRACT

STM, LEED, AES, TDS and $\Delta\phi$ measurements were performed to investigate the adsorption of Ni on the molybdenum (111) surface. The adsorption energy of Ni atoms on the Mo(111) surface was determined. At 300 K the layer-by-layer growth mechanism was observed. No faceting of the Mo(111) surface was observed after the annealing. Annealing leads to the adsorbate agglomeration and formation of Ni islands in the shape of pyramids.

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1. Introduction

The W(111), Mo(111) and Ta(111) substrates represent morphologically unstable atomically rough surfaces, which under the influence of an adsorption layer can be reconstructed. It is massive transformation from planar morphology to microscopically faceted surfaces with two types of micro-faces {211} or {110}. The faceting of the W(111) surface was studied by Madey et al. [1–9]. They found that this effect can be observed for metals used as adsorbate characterized by electronegativity equal to 2 or higher on the Pauling scale. The faceting is observed when the surface is covered by one ‘physical monolayer’ (in such a case all ‘visible’ atoms on the W(111) surface are covered by adsorbate atoms when we look down on the surface) after annealing to 700 K. Theoretical works show that faceting results from a decrease of the surface free energy [10–14]. In this case the surface free energy is lower than before reconstruction, although the

reconstructed surface exhibits larger area. According to Herring's theory [15,16], the transformation of surface from $\{hkl\} \rightarrow \{h'k'l'\}$ is favorable when $\gamma_{hkl} > \gamma_{h'k'l'}/\cos\theta$, where θ is the angle between the $[hkl]$ and $[h'k'l']$ directions and γ represents the surface free energy per unit of area. Guan et al. [5] suggested that the adsorbate electronegativity is a decisive factor, although they claimed that only such metals as Pd, Pt, Rh, Ir and Au whose atomic radii are close to the atomic radius of W, cause this process. The adsorption of atoms with radii more than 5% greater (Gd) or more than 5% smaller (Cu, Co, Ni) does not cause faceting of the W(111) surface. The investigations of the Mo(111) and Ta(111) surfaces [17–27] led to similar conclusions. The adsorbate atoms whose size is much bigger (Sm, Gd) or much smaller (Fe, Ni) than: W, Mo and Ta atoms – do not cause faceting of the substrate. However, it was found that neither Au nor Ag (with the atom radius size similar to that for Au) cause faceting of the Ta(111) and Mo(111) surfaces [5,19,22,26]. Authors [27] suggest that the surface morphology is determined by the interaction between the adsorbate and the substrate. Adsorbate atoms which interact very strongly with substrate atoms cause the substrate transformation. This can explain the

* Corresponding author. Tel.: +48 71 3759283; fax: +48 71 3287365.
E-mail address: szymon@ifd.uni.wroc.pl (Sz. Klein).

fact that there is no faceting in the case of Ag. However, there is no proof that the interaction of Au with the Mo(111) and Ta(111) surfaces is weaker than with the W(111) surface. The conclusion following from these investigations is that electro-negativity does not affect faceting. Very important is whether the adsorbate wets the surface or not. Two conditions must be fulfilled: (1) the adsorbate must wet the surface and (2) the free energy must decrease.

It was found that annealing of Fe and Ni layers on W leads to the adsorbate arrangement [27]. In thick Fe layers adsorbed on W(111), a non-wetting–wetting transition was observed. In the case of Ni on W(111) only the adsorption layer underwent reconstruction. The surface must consist of a more or less regular sequence of up and down steps within the limits of error for the width of three atomic row wide (111) terraces bounded by $[1\bar{1}0]$ steps. These conclusions were drawn from LEED patterns and the work function measurements. In this work the properties of Ni on the Mo(111) surface were investigated with the use of LEED scanning tunneling microscopy (STM), Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS) and work function measurements $\Delta\phi$. The question is whether the Ni adsorption on Mo(111) surface is similar to the W(111) case (Ni adsorption does not lead to faceting of W(111) surface) and whether the formation of the Ni–Mo alloy occurs after annealing up to 1175 K [8].

2. Experimental

The measurements were carried out in two metal UHV systems at the pressure lower than 1×10^{-10} Torr. One of them, Omicron apparatus, was equipped with a scanning tunneling microscope (STM) and a retarding field analyzer (RFA) used for Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) pattern observations. The other apparatus consisted of an OCI retarding field analyzer (RFA) used for LEED/AES measurements, a quadrupole mass spectrometer (QMS) for temperature-programmed desorption spectroscopy (TDS) and an additional electron gun for measurements of the work function changes ($\Delta\phi$).

A sample of 5 N purity was cut perpendicular to the $[111]$ direction with an accuracy of $\pm 0.05^\circ$. The Mo sample was cleaned by prolonged heating at 1300 K in an oxygen atmosphere (1×10^{-7} Torr), which was followed by flashing to 2300 K. The sample was considered to be clean when the Mo (186 eV) amplitude peak was at least 300 times higher than the carbon peak C (272 eV). The sample temperature was determined in two different ways depending on the UHV system. In the STM apparatus, where the sample was moved from the preparation chamber to the STM, the temperature was determined by an optical pyrometer. In the second one UHV system the temperature was determined by the W5%Rh–W26%Rh thermocouple spotwelded to the bottom of the sample. The sample was heated resistively by passing constant current directly through it. In this way the sample temperature was increased till 1700 K. In order to reach higher temperatures the sample was flashed by electron bombardment at energy 1 keV.

The Ni was deposited from sources prepared from Ni wire (0.1 mm in diameter) wound onto tungsten wire (0.3 mm in diameter). Such a design of source is characterized by small thermal inertia and is relatively easy to degas. The measurements were performed after successive evaporations of the same adsorbate doses onto the sample. The thermal stability of the Ni layer was investigated by depositing a definite dose of adsorbate, which was followed by depositing time measurement. Then LEED and AES measurements were performed to verify the coverage and to check the sample cleanness. All STM measurements were carried out at 300 K. The tunneling current was usually 0.2 nA and the potential difference between the tip and the sample was usually

2 V. The STM images were processed by using the WSxM program [28]. The change of the work function ($\Delta\phi$) was measured by means of Anderson's method, where electrons at the energy of 12 eV were directed onto the sample. TDS spectra were measured by the linear increase of temperature with the heating rate of 2.7 K/s. The Auger signal was measured with a $\pm 2\%$ accuracy of a signal derived from the clean Mo surface, whereas the work function was measured with a ± 5 meV accuracy. For each coverage the desorption energy was determined by using the Arrhenius plot slope. The inaccuracy of measurement for specified coverage determined in several measurement series was ± 20 meV. The size of measurement points showed in the figures corresponds to the measurement error.

3. Results and discussion

Fig. 1 shows the Auger amplitudes (AA) of Ni(61 eV) and Mo(186 eV) and work function changes as a function of the deposition time at 300 K. For the used modulation voltage ($1 V_{pp}$) two initial Ni doses do not result in appearance of visible peaks, because the Ni(61 eV) peak lies on the slope of the secondary electron peak. Additionally in the same figure a variation of the Auger amplitudes for Mo(186 eV) is presented as a function of the deposition time at 300 K, but with a lower deposition rate.

The last dependence can be approximated by linear segments with the successively decreasing slope. The first slope-change occurs after 7.5 min and the Auger amplitude decreases to 75% of the initial value for the clean Mo surface (AA_0). The next kinetic breaks are visible after 15 min and 22.5 min of the deposition time. After 15 min of evaporation $AA(Mo)$ equals 56% of AA_0 , after 22.5 min $AA(Mo)$ equals 43% of AA_0 . The ratios of slope of the linear segments (S_{n+1}/S_n) have constant value equal to 0.7 with an accuracy of ± 0.01 . The first kinetic break of the (AA) 61 eV Ni and 186 eV Mo for a bigger deposition rate occurs after 3 min, and the next after 6, 9, 12, 15, 18 and 21 min. In the case of 3 min the (AA) 186 eV Mo peak equals 77% of the AA_0 value. In the case of an adsorbate on the surface with low surface density, the slope changes of linear segments are not as clear as in the case of layers with high surface density.

The work function initially increases and reaches the local maximum. It then decreases to reach the minimum after 3 min. Then the work function increases and after 11 min it reaches a value which is 0.7 eV higher than the value for the clean Mo(111) surface. For $t > 11$ min a decrease of the work function is observed, which depends on the layer deposition method. During deposition, the decrease grows with the value of a single dose. The largest decrease

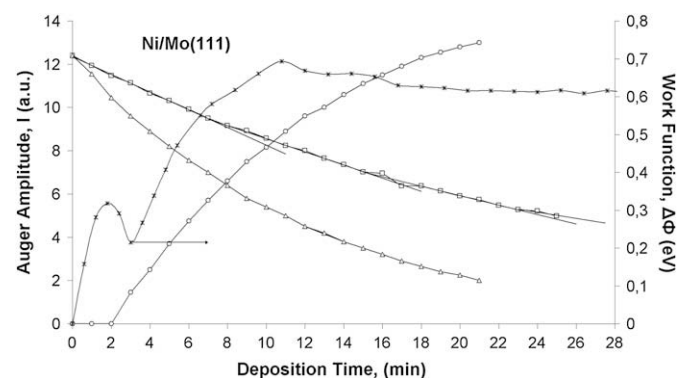


Fig. 1. Auger amplitudes of Ni(61 eV), Mo(186 eV) and work function changes as a function of Ni deposition time at 300 K. The measurement points marked as empty squares correspond to lower deposition rate.

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