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Growth and electronic properties of ultra-thin Ag films on Ni(1 1 1)

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ABSTRACT

We studied the growth mode and electronic properties of ultra-thin silver films deposited on Ni(1 1 1) surface by means of scanning tunnelling microscopy (STM) and angle resolved photoemission spectroscopy (ARPES). The formation of the 4*d*-quantum well states (QWS) was analysed within the phase accumulation model (PAM). The electronic structure of the 1 ML film is consistent with the silver layer which very weakly interacts with the supporting surface. The line-shape analysis of Ag-4$d_{xz,yz}$ QWS spectrum support the notion of strong localization of these states within the silver layer. The asymmetry of the photoemission peaks implies that the decay of the photo-hole appears to be influenced by the dynamics of the electrons in the supporting surface.

1. Introduction

Detailed understanding of structural and electronic properties of ultra-thin metallic films is important from both fundamental and technological point of view. A vast number of metal-on-metal systems has been studied with the aim to learn how different combinations of constituents exhibit novel properties. Particularly attractive are low dimensional systems which exhibit a strong size dependence of their electronic structure. Such systems are ultra-thin metallic films deposited on well-defined metallic or semiconductor surfaces where the electronic structure perpendicular to the surface, through the formation of stationary states is strongly quantized [1,2]. The discretization of the electronic structure is usually associated with discrete variation of a wide range of physical properties: density of states [3], work function [4], electron–phonon coupling [5–8], etc. The attractiveness of ultra-thin layers is in the fact that supported structures of reduced dimensionality (quantum wells) provide a broad ground for manipulation of geometrical and electronic properties.

There is a large difference (16%) between lattice constants of Ag and Ni and therefore no pseudomorphic growth of Ag on Ni(1 1 1) may be expected. LEED studies have shown epitaxial silver growth at room temperature [9] with the lattice constant equivalent to the bulk silver value. In some studies a small rotation of the layer main axes away from the substrate main axes was found [10,11]. Within the first layer silver forms 2D islands. Shapiro et al. [12] have concluded that the second Ag layer starts to grow when the coverage of 0.7 ML is reached. Mroz and Jankowski [9] have found that the first layer was completed at a nominal coverage of 1.4 ML while the saturation of the first layer is followed with the growth of the islands in the third layer.

The only published STM study of this system [13] was focused on the formation of the first monolayer and the formation of silver nanoclusters on top of it. This study shows that the first Ag atomic layer grows by coalescence of large 2D islands. These islands are attached to the step edges and have irregular shape. They do not cross the terrace edge and have a moiré structure that fits a model of a regular Ag(1 1 1) layer positioned over the Ni(1 1 1) layer.

It has been shown that the Ni(1 1 1) surface supports formation of QW states of *s-p* and *d*-symmetry in epitaxially grown ultra-thin silver films [14]. An early study of Miller et al. [15] was focused on interface effect on formation of *sp*-derived quantum well (QW) resonances in the 14-ML-thick film. More recent work of Senkovskiy et al. [16] explored a range of silver films proving the existence of the *s-p* QW states. The states were successfully modelled using an extended phase accumulation model. Quantum well states of *s-p* and *d*-symmetry in silver films were used by Varykhalov et al. [14] to probe the ground state electronic structure of the Ni(1 1 1) surface. The effective energy band gap of Ni(1 1 1) was determined in the energy range between 2.6 and 4.8 eV.

In this work we use STM, and high-energy and high-angle resolution ultraviolet photoemission spectroscopy to study ultra-thin silver films formed on the Ni(1 1 1) surface, in particular the quan-

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tization of the Ag-4*d* electron system. We confirm the STM results for the first monolayer from Ref. [13] and present new photoemission data from ultra-thin Ag films. We have studied in detail electronic properties of the 1 ML silver film and have shown that 4*d* electrons within silver film very weakly interact with the supporting surface as if they are decoupled from the nickel substrate, behaving as a non-interacting 2D system.

2. Experimental

The experiments were carried out in an ultra high vacuum chamber with base pressure in the range of low 10^{-8} Pa. The chamber was equipped with the scanning tunnelling microscope (STM), Specs He discharge lamp, and Scienta SES-100 hemispherical analyzer which simultaneously collects photoelectrons at a range of energies and angles (12° or less). The ultimate instrumental resolution of the analyzer is around 5 meV while in these experiments the total energy resolution was 25 meV. The angular resolution was 0.2°. The photon excitation energy used in these experiments was 21.2 eV. The STM experiments were performed in the constant-current mode.

A monocrystalline Ni disc, (1 1 1) oriented and cut, was mechanically and electrochemically cleaned and polished prior to insertion into the vacuum chamber. The initial cycles of 3 keV Ar^+ sputtering and annealing at 925 K removed most of contaminations with exception of small amount of carbon, oxygen and sulphur. Further cycles removed carbon and oxygen. In order to remove sulphur the annealing was performed at 850 K and the cycles of sputtering and annealing were performed several days. Eventually a clean and well-ordered Ni(1 1 1) surface (as checked by LEED and STM) was formed.

Silver films were prepared by resistive heating of tungsten basket filled with pure silver while the substrate was at room temperature. Prior to the silver deposition the cleanness and order of the Ni(1 1 1) substrate was checked by photoemission spectroscopy and the quality of the LEED pattern.

3. Experimental results

3.1. STM

In Fig. 1 an overview of the room temperature growth of Ag on Ni(1 1 1) substrate is given by typical constant-current STM images recorded for different coverages. The STM image of the clean nickel surface shows large terraces divided by monoatomic steps (see Fig. 1a). The obtained results nicely agree with the previous measurements [17]. The scan taken along the line indicated in (a) reveals the step height of 1.9 ± 0.1 Å (Fig. 1b) which is the value reported also in Refs. [17,18]. We have used the reported interatomic distance on the Ni(1 1 1) surface [17] of 2.49 Å to calibrate lateral distances in STM topographs throughout this work.

Silver grows in the form of a number of islands starting at terraces and step edges. With the increasing coverage the growth of silver film goes dominantly through the increase of the size of islands at the step edges. The vacancies within the islands can be found up to the saturation of the first silver layer. An example is given in Fig. 1c for a submonolayer coverage. The height of monoatomic Ag islands, measured from the line scans across the island edge, is found to be 2.9 ± 0.1 Å (Fig. 1d). The Ag islands appear 1 Å higher than Ni(1 1 1) monoatomic steps and can easily be distinguished.

At the nearly saturation coverage most of the surface is covered with silver, forming a homogenous Ag monolayer with the fuzzy step edges (Fig. 1e). Occasionally, a small vacancy islands in a monolayer are observed, as well as the small fraction of a second Ag layer that emerges as an extension of the first layer across a step edge.

The atomically resolved STM image in Fig. 1f shows hexagonal moiré superstructure that is a result of 16% mismatch between the Ag(1 1 1)-film and Ni(1 1 1)-crystal lattices [13]. The interatomic distance of 2.87 ± 0.05 Å is determined from the images. The linescan analysis of the patterns shows a buckling of 0.40 ± 0.05 Å. The buckling periodicity is 17.40 ± 0.05 Å which fits the periodicity of 6 Ag atoms along 7 Ni atoms. The same periodicity was confirmed by LEED measurements (not shown here).

At coverage above 1 ML the system shows more complex growth pattern. At temperatures around 200 K silver was reported to grow in a layer-by layer mode [9]. At the room temperature we find mixed thicknesses, as shown in Fig. 1g which presents STM image of a nominally 2 ML coverage silver film. The second layer grows in a similar way as the first one starting at the step edge but continuing to grow over the terrace edge and over the underlying silver layer. Such a growth mode results in a film where the third layer grows simultaneously with the second layer as indicated by STM image in Fig. 1g. The measured height of the second Ag layer with the respect to the first one is 2.3 ± 0.1 Å (Fig. 1h). The same value is found for the height of the third layer with respect to second one.

3.2. ARPES

3.2.1. Multilayer films

Fig. 2 shows the normal emission spectra of the Ni(1 1 1) surface covered with different silver films taken with HeI (21.2 eV) photon excitation. The spectrum at the bottom of Fig. 2a is obtained from the clean Ni(1 1 1) surface. The spectrum is characterised by strong Ni 3*d* maxima just below the Fermi level and a weak satellite at 6 eV.

The photoemission spectrum of the 1 ML Ag film shows additional two peak structure between 4 and 5 eV. In principle, each silver monolayer should contribute five peaks, associated with five spin-independent Ag-4*d* states containing 10 electrons, to the photoemission spectrum (see Fig. 1 in Ref. [19]). However, at the excitation photon energy of 21.2 eV, used in this work, we observe only two peaks while the emission from other states is suppressed. The absence of the emission from other states can be attributed to the variation of the excitation-cross-section with photon energy [20,21] and light polarization [22] which significantly affect the photoemission intensity from the Ag-4*d* bands. Fig. 2b shows spectra of submonolayer and monolayer silver coverage. The constant binding energy for both states was determined for all submonolayer coverages.

Additional atomic layer brings in additional 5 (spin-independent) d-states which further complicates the corresponding photoemission spectrum. The 2-ML normal emission spectrum is characterised by the set of new states labelled C–I. Besides two distinctive peaks at high binding energy side (H and I at energies 5.5 eV and 6.0 eV, respectively) there is also a characteristic shift of the leading peak towards the Fermi level (in Fig. 2a peak C with respect to peak A). The leading peak (J) is even more pronounced for the 3-ML spectrum. This contrasts with the situation of QW states of s-p symmetry which can generally be easily associated with a particular film thickness [1,2]. The 4*d* bands produce, due to their weak dispersion, a large number of states within a narrow energy window prohibiting thus the possibility to distinguish them already for films thicker than 2 ML. The leading peak energy could be used as a fingerprint of a specific film thickness when dealing with layer-by-layer-grown uniform films [20]. Although in the case of the Ag/Ni(1 1 1) system we find multilayer growth at coverages exceeding 1 ML the *d*-QW states can be effectively used to detect when the first silver layer is saturated and when the second starts