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Growth of Au on Ag(110): electronic structure by photoemission

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Abstract

Au films, from the submonolayer range up to eight monolayers, have been deposited in situ at 300 K. The electronic structure has been probed by ultra-violet valence-band photoemission. The discussion of our findings is based on a detailed knowledge of the geometrical structure of each film. With increasing Au coverage the valence-band structure changes from Ag- to Au-bulk-like. At intermediate Au coverages an interface state is observed. It appears to be localized between the first and second surface layer of areas where Au and Ag atoms are inverted. Moreover, the sp-type surface state observed for emission along $\bar{Y}$ in the case of the clean Ag(110) surface is strongly influenced by these inverted Au/Ag areas in that it shifts to higher binding energies. For higher Au coverages this surface state gradually fades out.

Keywords: Au films; Electronic structure; Growth; Photoemission

1. Introduction

Predicting the morphology and atomic arrangement of a thin film grown on a single-crystal substrate is a continuing challenge. One goal of interface and thin film science is to understand the growth process in sufficient detail to manipulate the structure and interface of the film, permitting improvement in thin film devices. It is obvious that for this understanding a knowledge of both the geometrical and the electronic structure is of prime importance.

Au and Ag have almost the same lattice constants, comparable surface energies and similar electronic and structural properties because they are isoelectronic. Au is thus expected to follow a simple growth mode on Ag. The Au/Ag(110) system, however, turned out to exhibit unexpected growth phenomena. Results from medium-energy ion-scattering [1], scanning tunneling microscopy (STM) [2,3], total energy theoretical modeling [4], and molecular-dynamics (MD) cluster simulations [5,6] indicate that for submonolayer Au coverages (Θ) most Au atoms go below the surface via an atomic exchange mechanism, forming an Ag-on-Au inverted layer. However, since none of the above mentioned techniques directly identifies the atomic species on the surface, the inverted Ag/Au layer (i-Au/Ag) interpretation is still not definite.

Therefore, we reinvestigated the geometrical structure of Au layers on Ag(110) by means of X-ray photoelectron diffraction (XPD), low-energy electron-diffraction (LEED), low-energy ion-scattering (LE-ISS) and STM. Here, however, we just summarize the results relevant for the discussion of the electronic structure. The details

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of this extensive study will be published elsewhere [7]. Due to the chemical selectivity and the sensitivity to local order of XPD [8], a direct confirmation of the inverted Ag/Au layer was possible. In agreement with Ref. [2] we find that for higher coverages nearly pure three-dimensional (3D) Au islands, elongated along [$\bar{1}$10], grow on top of this inverted Ag/Au layer. Only after the deposition of more than eight monolayers (ML) Au are the Ag/Au inverted areas completely covered, and the Au films finally develop the expected (1×2) missing row reconstruction. For each film discussed below the relevant structural information is given in Table 1 (see Table caption).

Concerning the electronic structure of Au epitaxy on Ag(110), to our knowledge, only one ab initio electronic structure calculation based on ideal layer-by-layer growth is available [9]. Here, we apply ultra-violet (UV) valence-band spectroscopy to investigate the Au induced changes in the electronic structure.

2. Experimental procedures

Experiments were performed in a VG ESCALAB Mk II spectrometer modified for motorized sequential angle-scanning data acquisition [10], and with a base pressure in the low 10^{-11} mbar region. Photoelectrons excited with He I (21.2 eV) radiation were analyzed with a 150 mm radius hemispherical analyzer. Clean Ag(110) surfaces were prepared by cycles of 1.5 keV Ar^+ sputtering and annealing to 750 K. Care was taken to ensure that the Ag(110) sample reached room temperature before Au deposition. Au was deposited from a liquid-nitrogen cooled hot-filament evaporator using a 0.3 mm molybdenum wire with a 0.09 mm Au wire wrapped around it, at pressures below 4×10^{-10} mbar. Coverages were controlled by means of a water-cooled quartz oscillator and calibrated by core-level spectroscopy (Au 4d to Ag 3d ratio) [7].

3. Results and discussion

Fig. 1 shows electron energy distribution curves obtained in normal emission as a function of Au coverage. With increasing coverage the valence-band structure changes from Ag- to Au-bulk-like. In the submonolayer regime ($\Theta=0.4$ ML) the characteristic Ag(110) d-peaks [11], labeled A and B, respectively, are slightly shifted towards lower binding energies. Moreover, two new peaks at $\sim$3.0 eV (label D) and $\sim$4.7 eV (label E) are detected. At intermediate coverages ($\Theta=1.2$ ML, 2.4 ML) peaks A, B, and D are no longer visible. Feature E, however, is unshifted with respect to the submonolayer film. For the two new peaks F (at $\sim$2.3 eV) and G (at $\sim$3.5 eV) a general shift towards lower binding energies is observed when going to the thick film regime ($\Theta=6.1$ ML, 7.9 ML), until, after deposition of about 8 ML, a spectrum is obtained whose characteristic d-band peaks are identical in position to those observed from Au(110) single crystals [11]. In order to achieve also agreement in relative intensities, even thicker Au films are needed. Feature C is noteworthy in that it is not concerned with the general

Table 1
Observed LEED patterns, distribution (in per cent of the surface area) of three possible surface terminations, and the average height H of 3D Au islands (in layers) as a function of the Au coverage Θ. The data is based on a simple model and obtained from the best fit to LE-ISS data [7]. A similar surface composition is predicted by the MD simulations of Ref. [6]

Θ (ML)	LEED	Bare Ag bulk (%)	Inverted i-Ag/Au (%)	3D Au on i-Ag/Au (%)	H (1.44 Å)
0	(1×1) sharp	100	0	0	0.00
0.4	(1×1) sharp	66	30	4	1.50
1.2	(1×1) broad	29	48	23	2.13
2.4	(1×1) striped	9	39	52	2.86
6.1	(1×3) or (1×2)?	0	7	93	5.48
7.9	(1×2) sharp	0	3	97	7.11

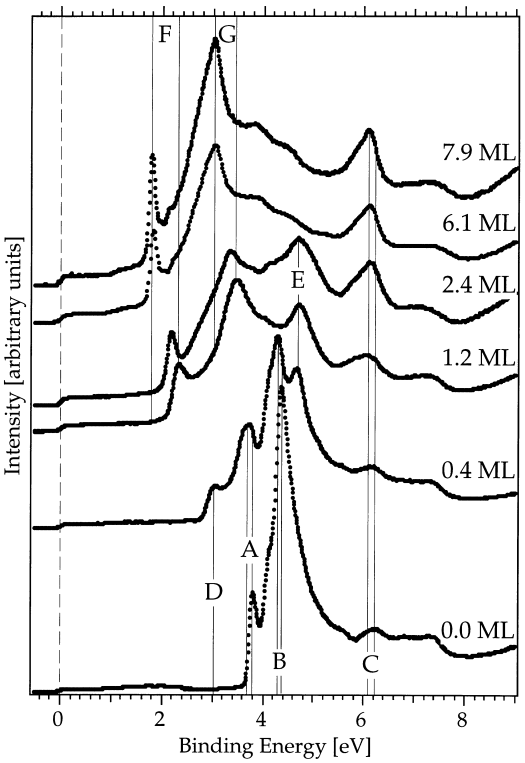

Fig. 1. Normal emission photoelectron spectra (He I, $h\upsilon =$ 21.2 eV) taken from Au deposited on Ag(110) at different coverages. Binding energies are referred to the Fermi level. The lines indicate shifts of the labeled peaks (see text).

shift, but is characterized by a gradual intensity increase during Au deposition.

There is ample evidence from many metal-on-metal systems [9,12] that bulk-like photoemission features are observed after about three to four layers, provided a layer-by-layer growth occurs without intermixing at the substrate surface and without growth of adsorbate clusters. In our case both conditions are not fulfilled (see Table 1), consistent with the fact that Au(110) bulk-like features are not clearly defined before a nominal coverage of more than 8 ML is reached.

Comparison with Table 1 reveals that feature E is present only in spectra taken from samples with a large portion of inverted Ag/Au. By comparing our data with the density of states (DOS) obtained from ab initio electronic-structure calculations using Ag(110) slabs covered with none, one, or two Au layers [9], we assign feature E to an interface state. Layer-resolved DOS calculations reveal that a DOS peak appearing at a similar binding energy ($\sim$5.2 eV) as feature E ($\sim$4.7 eV), is localized in the second layer from the top. Remarkably its intensity is found to be enhanced for adjacent Ag/Au layers. This effect, therefore, may even be increased by the inverted Ag/Au geometry of our case, where one Au layer faces two Ag layers.

The first layer restricted DOS of Ref. [9] has a rather steep rise at about 2.7 eV for Ag and at 2.2 eV for Au, and is explained in terms of antibonding orbitals towards the vacuum. In the case of our submonolayer film a large area of the surface is composed by inverted Ag/Au, i.e. by an isolated Ag surface layer (Table 1). This accounts well for peak D, located at $\sim$3 eV binding energy. Correspondingly, feature F in the intermediate regime of coverages may be caused by the surface layers of the two to three layer high Au islands. For thick Au films, further support for Au surface layers contributing to feature F is given by the work of Xu et al. [13]. Using self-consistent first-principles calculations they calculated the projected bulk band structure of Au together with the dispersion of surface related bands for (1×2) reconstructed Au(110). The predicted surface resonance at a binding energy of 1.8 eV at $\bar{\Gamma}$ agrees nicely with feature F for the (1×2) reconstructed Au film ($\Theta = 7.9$ ML). According to Ref. [13], the wavefunctions of the states in this band are localized in the first three surface layers.

Feature C for $\Theta = 0$ ML and $\Theta = 7.9$ ML corresponds to transitions from pure Ag and Au surfaces, respectively [11]. The gradual intensity increase at higher coverages, therefore, is related to the average height of the Au islands. The general shift of G and F towards lower binding energies may be such an effect as well. This interpretation also compares favorably with photoemission studies of the valence band features of polycrystalline bulk Au_xAg_{1-x} alloys [14]. There the Au d-band width increases with x and is accompanied by a characteristic shift of the upper d-band edge towards the Fermi level E_F.

Occupied surface states were reported at the $\bar{Y}$ point of the (110) surface Brillouin zone for Cu

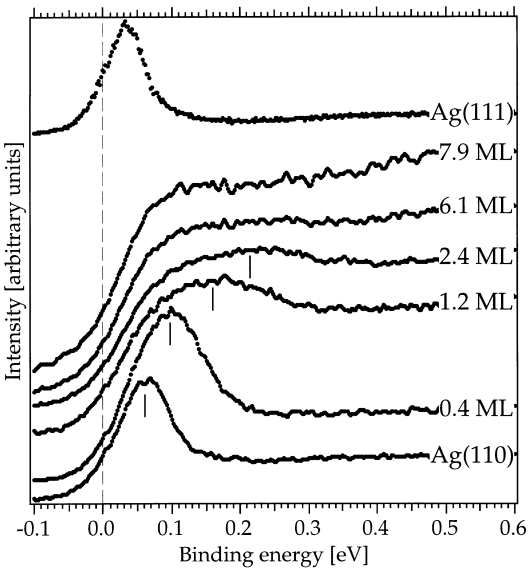

Fig. 2. Photoelectron spectra along $\bar{Y}$ (He I, $h\nu = 21.2$ eV, energy resolution ≤ 50 meV, angular resolution 0.5°) taken for different Au coverages. The top curve shows the Ag(111) $\bar{\Gamma}$ surface state. Binding energies are referred to the Fermi level and markers indicate peak positions of the observed surface state.

and Ag [15], and were associated with the sp hybridization gap in the calculated projected DOS at the $\bar{Y}$ point of the (1×1) surfaces. In Fig. 2 we focus on the behavior of the Ag(110) Shockley surface state for emission along $\bar{Y}$ during Au deposition. With increasing coverage the surface state shifts to higher binding energy, broadens and finally fades out for thick Au films.

At 0 ML we observe a binding energy of approximately 60 meV. This value is smaller than that reported by Bartynski (~ 100 meV) [15]. However, the reliability of our result is supported by the agreement of our findings for the binding energy of the Ag(111) $\bar{\Gamma}$ surface state (top curve in Fig. 2) with that determined by Matzdorf and coworkers (25 meV) [16]. Broadening and disappearance of the surface state upon Au deposition may be caused by the increasing disorder on the surface (see Table 1). Indeed, sputtering experiments on Cu(111) reveal that the $\bar{\Gamma}$ surface state broadens, shifts to lower binding energies, and finally fades out with sputtering time [17]. In our case, however, the increasing disorder cannot account for the present shift. As explained in the following, the observed shift can be qualitatively traced back to the Au-induced shift of the bulk band gap: recently, Paniago et al. demonstrated that the energy position of the noble-metal fcc(111) $\bar{\Gamma}$ surface state reacts most sensitively to variations of the lower edge ($L_{2'}$) of the $\bar{\Gamma}$ band gap [16]. In very good agreement with their experiment it is found that with increasing temperature the thermally induced lattice expansions shift $L_{2'}$ closer to E_F, and this in turn shifts the surface states towards E_F. We use similar arguments to explain the Au-induced shift of the Ag(110) $\bar{Y}$ surface state. $L_{2'}$ at the $\bar{Y}$ gap of the unreconstructed Ag(110) and Au(110) surfaces is located 0.3 eV and 0.9 eV below E_F, respectively [18]. Therefore, $L_{2'}$ is expected to move away from E_F with increasing Au concentration, going along with a shift of the surface state towards higher binding energies. In view of the sharp (1×1) LEED pattern found in the 0.4 ML experiment, the width of the corresponding surface state is surprising. One may speculate that the observed surface state contains unshifted contributions from bare Ag bulk areas as well as a shifted component originating from inverted Ag/Au areas (see Table 1). The exact knowledge of the surface composition together with the detected surface state could then provide a tool to determine the position of the lower band gap edge ($L_{2'}$) as a function of the Au concentration.

One may wonder why no surface state is found for the 7.9 ML thick Au film, for which the sharp (1×2) LEED pattern indicates long-range order on the surface. However, our result agrees with Xu's calculations for (1×2) reconstructed Au(110) [13]. Xu et al. predict a band gap at $\bar{\Gamma}_{(1\times 2)}$ containing an unoccupied surface state located just above E_F. On the one hand this result is confirmed by inverse photoemission data which at $\bar{\Gamma}_{(1\times 2)}$ identify an unoccupied surface state 0.1 eV above E_F [15]. On the other hand it is inconsistent with a photoemission study, which around $\bar{\Gamma}_{(1\times 2)}$ reported an unusual broad, non-dispersive surface state 0.1 eV below E_F [19]. This inconsistency may be explained by the very weak (1×2) LEED pattern observed in the study of Ref. [19]. The related disorder seems to introduce

a broadening of the unoccupied surface state, so that the tail end of its distribution extends below E_F and gives rise to a photoemission signal.

4. Summary

In summary, we have probed the Au induced changes of the electronic structure during Au on Ag(110) epitaxy by means of UV valence-band spectroscopy. With increasing Au coverage the valence-band structure changes from Ag- to Au-bulk-like. However, the fact that Au(110) bulk-like features are not clearly defined below a nominal coverage of more than 8 ML is consistent with the formation of 3D Au islands on the Ag/Au inverted surface. At intermediate Au coverages we identify an interface state, localized between the first and second surface layer of Au/Ag inverted surface areas. Finally, the sp-type surface state observed for emission along $\bar{Y}$ in the case of the clean Ag(110) surface is strongly influenced by this inverted Au/Ag area in that it shifts to higher binding energies. In agreement with the prediction of Ref. [13], the surface state is not observed in the case of the (1×2) reconstructed Au(110) film for emission along $\bar{\Gamma}_{(1\times 2)}$.

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References

[1] P. Fenter, T. Gustafsson, Phys. Rev. Lett. 64 (1990) 1142.
[2] S. Rousset, S. Chiang, D.E. Fowler, D.D. Chambliss, Phys. Rev. Lett. 69 (1992) 3200.
[3] E.S. Hirschorn, D.S. Lin, E.D. Hansen, T.-C. Chiang, Surf. Sci. 323 (1995) L299.
[4] C.T. Chan, K.P. Bohnen, K.M. Ho, Phys. Rev. Lett. 69 (1992) 1672.
[5] M.I. Haftel, M. Rosen, T. Franklin, M. Hettermann, Phys. Rev. Lett. 72 (1994) 1858.
[6] M.I. Haftel, M. Rosen, Phys. Rev. B 51 (1995) 4426.
[7] J. Hayoz, Th. Pillo, R. Fasel, L. Schlapbach, P. Aebi, submitted to Phys. Rev. B.
[8] C.S. Fadley, R.Z. Bachrach (Ed.), Synchrotron Radiation Research: Advances in Surface Science, Plenum Press, New York, 1990, p. 421.
[9] H. van Leuken, A. Lodder, R.A. de Groot, Phys. Rev. B 45 (1992) 4469.
[10] J. Osterwalder, T. Greber, A. Stuck, L. Schlapbach, Phys. Rev B 44 (1991) 13746.
[11] P. Heimann, H. Neddermeyer, H.F. Roloff, Phys. Rev. Lett. 37 (1976) 775.
[12] K. Jacobi, in: S.D. Kevan (Ed.), Angle-Resolved Photoemission, Elsevier, Amsterdam, 1992, p. 371.
[13] C.H. Xu, K.M. Ho, K.P. Bohnen, Phys. Rev. B 39 (1989) 5599.
[14] H. Ebert, P. Weinberger, J. Voigtländer, Z. Phys. B: Condens. Matter 63 (1986) 299.
[15] R.A. Bartynski, T. Gustafsson, Phys. Rev. B 33 (1986) 6588 and references cited therein.
[16] R. Paniago, R. Matzdorf, G. Meister, A. Goldmann, Surf. Sci. 336 (1995) 113.
[17] P.O. Gartland, B.J. Slagsvold, Phys. Rev. B 12 (1975) 4047.
[18] S.H. Liu, C. Hinnen, C. Nguyen Van Huong, N.R. De Tacconi, K.M. Ho, J. Electroanal. Chem. 176 (1984) 325.
[19] R. Courths, H. Wern, U. Hau, B. Cord, V. Bachelier, S. Hüfner, J. Phys. F 14 (1984) 1559.