Depopulation of the Ag(111) Surface State Assigned to Strain in Epitaxial Films

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Photoemission spectra from epitaxial Ag(111) films on Si(111)-(7 × 7) show that the $\overline{\Gamma}$ surface state in Ag(111) is depopulated in films deposited on the silicon surface when compared with ideal Ag(111) surfaces. This is interpreted as a shift of the surface state up in energy, beyond the Fermi level, since it can be partly reversed by a lowering of the work function, in accordance with phase-accumulation model calculations. This shift is ascribed, through band structure calculations, to the strain in the Ag layers induced by film growth. [S0031-9007(97)02408-3]

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Shockley-type surface states on noble metals have received considerable attention in the past. They arise from special boundary conditions introduced by the metal/vacuum interface. The surface states on the (111) faces have been the subject of photoemission studies after their discovery on Cu(111) by Gartland and Slagsvold [1]. They occur in gaps of the surface-projected bulk band structure, being trapped, in a one-dimensional model, in the potential well formed by the crystal edge, where the energy gap reflects the electrons, and the surface potential barrier. Thus any modification of (a) the substrate band gap or (b) the surface potential barrier will consequently have an influence on the surface state energy. Here we report on the surface energy in Ag(111) epitaxial films on Si(111)-(7 × 7) as determined by photoemission. An observed depopulation of the $\overline{\Gamma}$ surface state on Ag(111) is interpreted as due to an upward shift of its energy, in terms of strain-induced movement of the L_2' band edge [process (a)]. In order to demonstrate the depopulation of the surface state by this process, we reduce the vacuum barrier (by alkali metal adsorption) and effect a gradual downshift of the surface state [process (b)].

The experiments were performed at the BESSY storage ring in Berlin. Photons with energy of 47 eV were obtained from the monochromators TGM4 and TGM6. Electrons were detected by a VG ADES400 spectrometer system with a base pressure of 10^{-10} mbar. The overall resolution of 0.1 eV was determined from the width of the Fermi edge, and, for the work function, the low-energy cutoff in the photoelectron spectra was used. Epitaxial layers with a uniform thickness were produced, resorting to a *kinetic pathway* during MBE deposition. This means cooling the substrate to 130 K, evaporating layers of 50 Å thickness, and subsequent annealing to good crystalline quality at temperatures of 300–500 K. The crystallinity was checked by the observation of clear LEED patterns generated by the Ag(111) surfaces. Silver films on Si(111)-(7 × 7) showed only diffuse spots before and sharp hexagons after annealing, as shown in the inset of Fig. 1. For comparison, Ag films have also been prepared on highly oriented pyrolytic graphite (HOPG), which have the properties of ideal Ag(111) surfaces [2]. Their LEED pattern consisted of sharp rings similar to the rings generated by the rotationally disordered substrate.

In order to compare the electronic structure of an ideal Ag(111) surface and that of Ag(111) films on Si(111)-(7 × 7), consider the spectra shown in Fig. 1. These

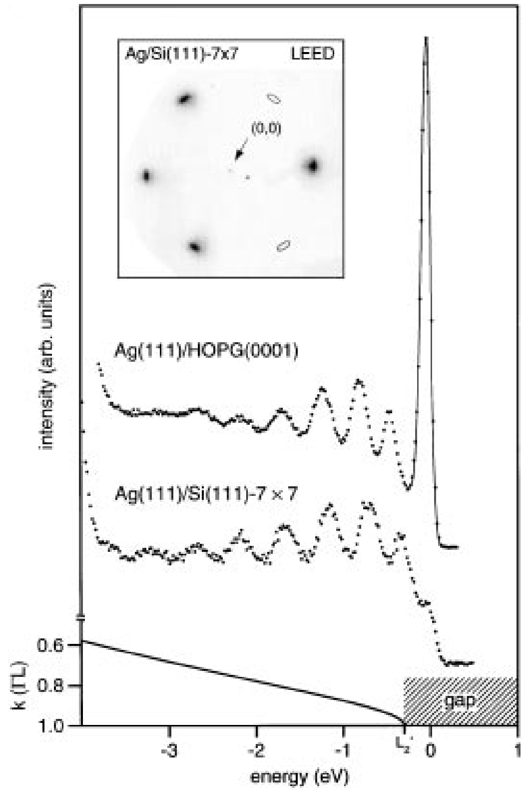

FIG. 1. Comparison of photoelectron spectra taken at 47 eV photon energy in normal emission from approximately 50 Å thick Ag(111) layers on HOPG and Si(111)-(7 × 7). The diagram below the spectra shows the relevant part of the Ag-band structure. The wave vector is given in fractions of the Brillouin zone radius (ΓL). The inset shows the LEED pattern generated by an Ag(111) film on Si(111)-(7 × 7) at an energy of 140 eV. Two additional spots obscured by the sample holder are indicted by rings.

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were recorded at a photon energy of 47 eV in normal emission, i.e., with the **k** vector along the Γ-L direction in reciprocal space. The diagram underneath the spectra shows the relevant part of the silver band structure, which consists of the s-p band leveling off close to the Fermi level E_F, at the L point at the Brillouin zone boundary. From this point a band gap extends up to an energy of 3.9 eV above E_F, shown as the cross-hatched region in the schematic band structure in the bottom of Fig. 1. If the Si layer is regarded as a quantum well for its valence electrons, the wave vectors of stationary states in the well can only take quantized values given by

$$k = \frac{n}{N}\,\frac{\pi}{a} + C\,, \tag{1}$$

where Na is the layer thickness expressed by the layer distance a and the number of layers N. The correction C arises from the finite height of the walls forming the well. This quantity can be treated theoretically and varies only little in this energy range [3,4]. Therefore, Eq. (1) describes the condition for quantized k-values which, by virtue of the monotonous band structure, leads to the discrete energy levels first observed in photoelectron spectroscopy by Wachs *et al.* [5]. The energetic position of the quantum-well peaks in the s-p-band and their distances via Eq. (1) depend strongly on the layer thickness, giving an independent measure of this quantity. Thus, it can be inferred that the two silver layers compared in Fig. 1 have approximately the same thickness of 50 Å. For Ag/HOPG this means that the layer consists of islands with a very narrow height distribution [2], while for Ag/Si(111) extremely flat closed films are observed [6].

In the band gap along the Γ-L direction (cross-hatched region at the bottom of Fig. 1) a Shockley-type surface state exists, which gives rise to the prominent peak near E_F in the Ag/HOPG spectrum in Fig. 1. Its energy is about 50 meV below E_F at a temperature of 130 K [7]. Clearly, this peak is missing in the Ag(111) layer on Si(111)-(7×7) prepared under identical conditions. We use the so-called phase-accumulation model for an explanation of the difference in the spectra in Fig. 1. In this model the surface state is a stationary state in the one-dimensional quantum well comprised of the image potential barrier on the vacuum side and the band gap in the crystal on the other [8]. The quantum-mechanical solutions are found by calculating the phase shifts for the reflection of the electron wave functions at these barriers [3,4]. It is simple to show that the energy of the Shockley surface state, which is the lowest eigenstate of this well, depends on the height of the vacuum barrier, i.e., the work function [3], and the energies of the band edges adjacent to the gap [7].

We have verified the dependence of the surface state energy on the magnitude of the work function experimentally. Adsorption of submonolayer quantities of alkali metals leads to a considerable lowering of the work function. The effect of a decreasing work function on the surface state is shown in Fig. 2. The left side shows spectra of an ideal Ag(111) surface prepared on HOPG. The top trace from a clean surface shows the quantum-well peaks and the intense surface state emission close to E_F. With increasing amounts of deposited Cs, the work function decreases as indicated. From the position of the surface state peak maximum (indicated by gray bars), it is obvious that its energy decreases with the work function. This behavior has previously been observed for Cs/Cu(111) [9] and Na/Cu(111) [10]. The intensity decrease of the surface state with Cs deposition is due to a redistribution of its charge in energy/momentum space [11] such that the unperturbed wave function is only found on a reduced area, and to the fact that, as the surface state approaches and crosses the L_2' band edge at 0.3 eV below E_F, its wave function extends further into the bulk, and electrons accommodated in this state are less efficiently detected by surface sensitive photoemission.

In order to quantitatively evaluate the shift of the surface state energy with work function change, both the surface state peak and the quantum-well peaks were modeled by Voigt peaks over a constant background enveloped by a Fermi function with experimentally determined parameters. On the left of Fig. 3 the results of such an analysis for the spectra of Ag(111) on HOPG are shown as circles. Included are the confidence intervals of the least-squares-fitting procedure as error bars. For most points the symbol size exceeds the error. The solid line shown represents the prediction of the surface state energy from the phase-accumulation model, where we assume that the only effect of the adsorption of Cs is to change the work function [3]. Evidently, the simple model well describes the behavior of the surface state.

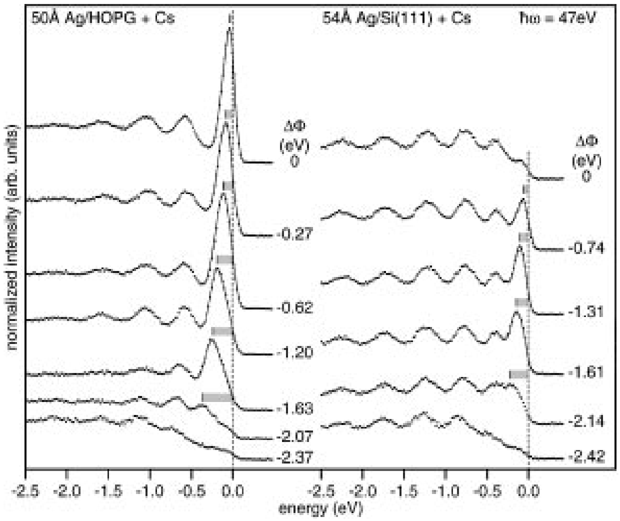

FIG. 2. Photoelectron spectra of the Ag(111) surface state of Ag films on HOPG (left) and Si(111) (right) substrates covered by submonolayer quantities of Cs. The gray bars indicate the position of the peak maxima, clearly showing the decrease in energy of the emission by the lowering of the work function.

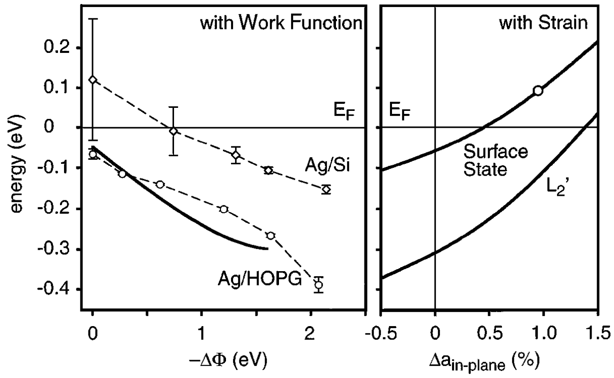

FIG. 3. Shift of the surface state with the change of work function and with strain. Shown at left are the surface state energies extracted from the spectra of Fig. 2 as compared to the energies from the phase-accumulation model (solid line). On the right, the calculated energies of the s-p-band edge L_2' and the surface state under volume-conserving strain in the (111) plane of the Ag crystal are displayed. The circle marks the point on the theoretical curve where the surface state energy is shifted by 150 meV from its equilibrium value, as observed for Ag(111)/Si(111)-(7 × 7).

The effect of Cs adsorption on an Ag(111) surface of a 54 Å film prepared on Si(111) is shown on the right hand side of Fig. 2. Again, the top trace shows the spectrum obtained on a clean surface. As in Fig. 1 only the quantum-well peaks in the s-p band are visible. No sign of a surface state is detected in the vicinity of the Fermi edge. With the decreasing work function by Cs adsorption, however, there is a clear rise in intensity immediately below E_F. This peak becomes most pronounced in the spectrum of $\Delta\Phi = -1.31$ eV. With larger decreases in work function the intensity decreases again, as in the case of an ideal Ag(111) film. After its first pronounced appearance at $\Delta\Phi = -0.74$, the energies of the peak maxima continuously fall with the work function as visualized by the gray bars. Thus it is already evident by inspection that the absence of surface state emission from clean thin Ag(111) layers prepared on Si(111)-(7 × 7) is due to a shift of the surface state into the unoccupied region. The downshift induced by Cs adsorption causes it to cross the Fermi level, and to become accessible to photoelectron spectroscopy. The surface state energies extracted from the spectra by the procedure described above are displayed as diamonds in the left part of Fig. 3. They are consistently found at higher energies as compared to the corresponding state from Ag(111)/HOPG. In order to model the spectrum from the clean Ag(111)/Si surface with the same restricted parameter set as those from Ag(111)/HOPG, it is necessary to place the surface state almost 120 meV above E_F. The surface states of Ag(111)/Si(111)-(7 × 7) are, on average, displaced by 150 meV with respect to the states of Ag(111)/HOPG. This value is sufficient to completely depopulate the surface state on the clean Ag(111) surface at this temperature [7].

Several effects can cause a shift of the surface state. In very thin epitaxial Ag layers the Ag(111)-surface state shows substantial shifts, which are explained in terms of the interaction of the weakly decaying surface state wave function with the substrate [12]. Thicknesses on the order of 50 Å, such as used here, exceed the decay length of 28 Å [13] by far, rendering this explanation of our above observations implausible. Lateral localization of the surface state wave function on top of islands, as reported for image states on Ag islands [14], is equally unlikely since the island size required to introduce a significant shift is far below the lateral coherence length of our LEED system. Since the Ag/Si(111)-(7 × 7) interface is incommensurate [15], this should lead to a vanishing of the LEED pattern; the sharp LEED spots (inset of Fig. 1) demonstrate that the localization of the Ag(111)-surface state cannot contribute significantly to the observed energy shift.

The influence of the band edges on the energy of the surface state provides a straightforward explanation for the shift of the surface state in Ag/Si(111)-(7 × 7). Because of its close vicinity, the lower band edge labeled L_2' has the larger influence. It is therefore sensible to suspect this quantity to be responsible for the observed shift. This view is corroborated by the observation that the highest quantum-well peak, corresponding to a quantum number $n = N - 1$ [cf. Eq. (1)], has a higher energy in Ag/Si(111) than in Ag/HOPG. Since the number of Ag layers is approximately 21 in both cases, this peak should show up in the same position relative to the band edge. The observed energy difference then points to a shift in the band edge L_2'. However, a variation of the correction C in Eq. (1) for Ag films on the two substrates may have an influence on the quantum-well state energies.

Since strain is a widespread feature in thin film growth on lattice-mismatched substrates and has been observed in epitaxial silver films of the same thickness as those of the present study [16], its influence on the energy of L_2' must be considered. We have thus calculated the band structure of Ag for distorted (strained) lattices within the nonlocal empirical pseudopotential method (EPM) as described in Ref. [17]. This straightforward scheme is sufficient to describe the properties of the simple band structure of the Ag-s-p electron. In order to reproduce the experimental value of -0.3 eV for the energy of L_2' [18] in an unstrained lattice, the bands were rigidly shifted by 225 meV after the calculation. Once the value for L_2' is determined by the EPM, the energy of the surface state follows from the phase-accumulation model. This scheme can be tested using the recent measurement of the temperature dependence of the energy of the surface state by Paniago *et al.* [7]. The coefficient of thermal expansion links the temperature of the sample to an isotropic distortion of the silver lattice. If a value of 19×10^{-6} K^{-1} [19] is used, a rate of 0.12 meV/K is calculated for the temperature dependent shift of the surface state by the described procedure. This is in good agreement with the experimentally determined rate of 0.17 meV/K [7]. The remaining discrepancy can be due to a narrowing of the *L* gap by lattice vibrations as calculated by Larsson and Pendry [20].

Strain exerted on the lattice concomitant with the formation of epitaxial Ag(111) films is expected to change the (111)-in-plane lattice constant. As a consequence, the lattice constant perpendicular to these planes changes also. To lowest order, the volume of the crystal will be conserved at the deformation. We used this condition to describe the lattice distortion in the calculations for the present experiments. Figure 3 shows the results of the theoretical treatment on the right side. As can be seen, the calculated surface state energy is already strongly shifted for small tensile strains in the (111) plane (compressive along [111]). In order to explain the observed shift of 150 meV, the Ag(111) lattice grown epitaxially on Si(111) needs to be strained by only 0.95%. Tensile strain in this magnitude observed in silver films of comparable thicknesses on MgF_2, Si(100), and mica [16] has been attributed to a polycrystalline Vollmer-Weber growth. Its origin was suggested to lie in the relaxation of grain boundaries and recrystallization effects in the silver layer. This growth mode is most likely present in our silver layers on Si(111)-(7 × 7) during the low temperature deposition as well, since only diffuse LEED spots are seen before annealing, and a continuously rising tensile stress has been observed by the cantilever beam method in recent measurements on Ag/Si(111) at low temperature [21]. The enhanced recrystallization due to the subsequent annealing step might lead to a further increase in the tensile strain. Additionally, the lattice order is improved, as signaled by the sharp LEED spots, and the surface is leveled, a prerequisite to the observation of quantum-well states in the *s*-*p* band (Figs. 1 and 2). A difference in the thermal expansion of Si and Ag cannot contribute to the strain present in the system, since evaporation and measurement are carried out at the same temperature.

Because of its limited decay length of 28 Å [13], the energy of the surface state is determined by the strain in only the topmost atomic layers of the film. Measurement of this local strain, which may differ from the value found by macroscopic stress measurements of the complete film by the cantilever beam method, is a distinct advantage of our above analysis.

Silver layers produced similarly on GaAs(110) substrates also show quantum-well peaks, indicating a uniform layer morphology, but no surface state. This is in line with recent scanning tunneling microscopy studies [22,23], which showed that the silver surfaces are not of a simple Ag(111) structure. Thus, the corresponding surface state may not be expected. Nevertheless, there are indications [23] that strain is an issue in these films as well.

In conclusion, we have shown that the epitaxial formation of thin Ag films can lead to changes in the electronic structure which depopulate the Ag(111)-surface state. Tensile strains common to thin epitaxial layers provide a plausible explanation for these changes, and band structure calculations for differently strained Ag(111) films serve to deduce quantitatively the amount of strain in the surface layer.

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