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Electronic surface structure of n-ML Ag/Cu(111) and Cs/n-ML Ag/Cu(111) as investigated by 2PPE and STS

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ABSTRACT We investigated the electronic structure of epitaxially grown silver films on Cu(111) with and without adsorption of cesium by means of scanning tunneling spectroscopy and two-photon photoemission. This system has been chosen as a model system to engineer and measure the dynamics of charge-transfer processes between an adsorbate and a heterogeneous substrate. Special emphasis has been laid on the investigation of the energy shift of the Shockley-type surface state and an excited cesium resonance as a function of Ag film thickness. For the cesium resonance we observe an increase in line width with increasing layer thickness.

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1 Introduction

The dynamics of excited electrons on adsorbate-covered surfaces determines many surface processes, in particular photon- and electron-stimulated reactions. The efficiency of these reaction mechanisms depends in a crucial way on the lifetime of intermediate electronic states. Recently, it has been demonstrated experimentally and theoretically that adsorbed alkali atoms on noble metals are an ideal model system to study the dynamics of charge-transfer processes between surface and chemisorbed adsorbates [1–3]. In a theoretical work, Borisov et al. showed that the substrate band structure is the most important parameter for the specific relaxation dynamics of the excited alkali state [3]. This knowledge opens the possibility to modify the adsorbate–substrate coupling and, hence, the dynamics of charge-transfer processes by the use of a properly adjusted heterogeneous substrate. Metallic thin-film overlayers, such as Co/Cu(111) or Ag/Cu(111), are ideal model substrates for this kind of study.

Cu(111) has a gap of ~ 5 eV around the Fermi level in the projected band structure at the Γ-point ($L_{2'}-L_1$ gap). As a result of the termination of the crystal at the surface an occupied Shockley-type surface state appears in this gap, which represents a quasi-two-dimensional electron gas. The existence of these states has been proposed by Shockley [4] and was exper-

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imentally identified first by Gartland and Slagsvold [5]. The localization of this state right at the surface makes it in general an ideal probe for the determination of surface conditions and properties [6]. In the few-monolayer (ML) regime a metallic overlayer of e.g. Na [7], Pd [8] or Ag [9] influences the binding energy of the surface state of Cu(111). For thicker films (more than 10 ML) discrete quantum well states (QWS) appear in the band gap, which have been observed by means of photoemission [10]. The energy of these states is determined by the film thickness and can be tuned quasi-continuously. Therefore, by adjusting the energetic position of relevant electronic states by means of metallic thin-film overlayers one has the potential to engineer the dynamics of charge-transfer processes on adsorbate-covered surfaces and, hence, can modify specific properties of chemical surface reactions such as efficiency and reaction channels.

The paper is organized as follows: in the first part we present two-photon photoemission (2PPE) and scanning tunneling spectroscopy (STS) measurements of the binding energy of the Shockley surface state of Ag/Cu(111) as a function of Ag overlayer thickness.

In the second part we investigate the effect of this interface on the electronic coupling between an adsorbate excitation, the Shockley-type surface state and the silver substrate and present first spectroscopic results for the model system Cs on Ag/Cu(111).

2 Experimental

Scanning tunneling microscopy (STM) and 2PPE experiments were performed in different UHV systems. The experimental setup for 2PPE spectroscopy has been described in detail elsewhere [11]. In short, the laser system used for the experiments is a mode-locked Ti : sapphire laser, pumped by about 6.5 W from a diode-pumped all-solid-state laser system. The system delivers transform-limited and sech^2 temporally shaped pulses of up to 15 nJ/pulse with a pulse width (FWHM) of 25 fs and a repetition rate of 82 MHz. The linear polarized output of the Ti : sapphire laser is frequency doubled in a 0.2-mm-thick beta barium borate (BBO) crystal to produce pulses of $h\nu = 3.1$ eV. The beam is oriented at 45° with respect to the surface normal of the sample. The sample is mounted in a UHV chamber equipped with standard surface analytical tools. Electrons photoemitted from the surface

are detected along the surface normal by a cylindrical sector electron energy analyzer with an energy resolution of 80 meV.

STM and STS experiments were performed in a cryogenic STM operating at 77 K situated in a UHV chamber at a base pressure of 10^{-10} mbar. To obtain dI/dV spectra a small sinusoidal voltage (5–30 mV$_{rms}$, 2–3 kHz) was added to the sample bias and the derivative signal as a function of bias voltage was recorded using the standard lock-in technique.

The Cu(111) crystals were cleaned by sputtering and annealing cycles. The surface quality was characterized by low-energy electron diffraction (LEED), Auger spectroscopy, STM and 2PPE spectroscopy. Silver was evaporated in both chambers from a Knudsen-cell-type evaporation source at a rate in the range of 1 ML/min. During evaporation the sample temperature was held at 300 K.

3   Results and discussion

At room temperature silver grows in a Stranski–Krastanov mode on Cu(111): a layer by layer growth is observed for the first two monolayers; at higher coverages three-dimensional (3D) island growth appears, in agreement with published results [9, 12]. Figure 1 shows a topographic image of a nominally 3.5-ML-thick Ag overlayer on Cu(111). Whereas the first monolayer is completed the second and third monolayers still exhibit openings and the fourth and fifth monolayers have already nucleated. All layers display the 9×9 superstructure formed by the strain relief of the Ag film (see below).

In the 2PPE chamber, the thickness calibration of the evaporator was deduced from observation of the intensity ratio between Cu(111) surface state and Ag surface state at cover-
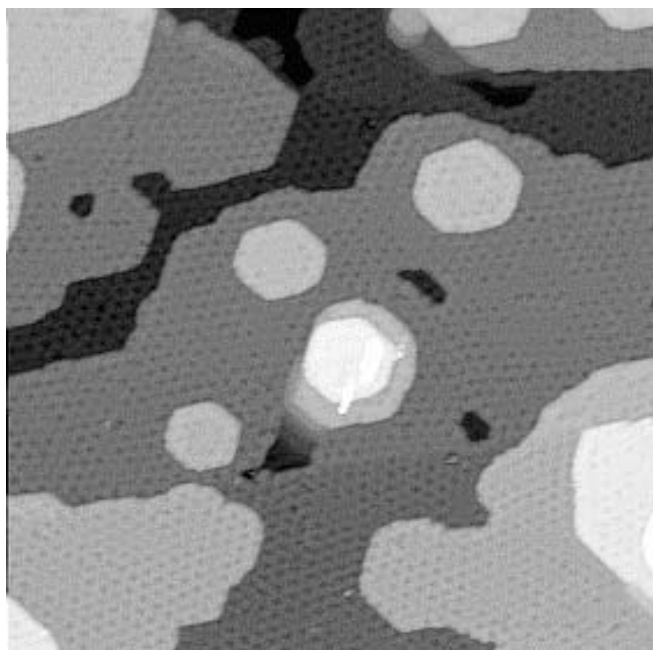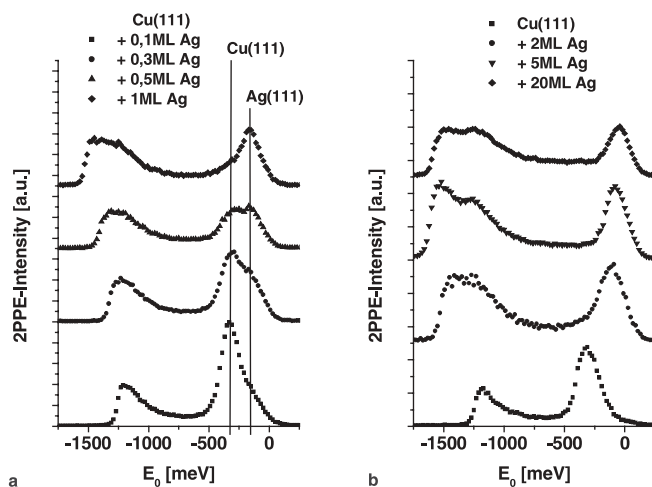

FIGURE 2 Series of two-photon photoemission valence-band spectra for several silver coverages. **a** ≤ 1 ML: the two peaks result from two coexisting Shockley-type surface states from Cu(111) and from Ag-covered areas, **b** > 1 ML: the silver surface state shifts continuously to lower binding energies with increasing layer thickness

ages up to one layer of Ag. The two surface states appeared in the 2PPE spectra already in the low-submonolayer regime (see Fig. 2a). Due to the growth mode of the silver films, the first monolayer of silver corresponds to a coverage where the emission from the Cu surface state has just completely disappeared. In a similar manner, by monitoring the intensity of the copper- and silver-related image states, Wallauer and Fauster were able to accurately monitor the layer by layer growth of this system within the first two monolayers [12]. The appearance of a 9×9 overstructure of the deposited silver films has been reported in a number of papers [9, 13–15] and was also clearly observable by LEED and STM in the present studies (see Fig. 1). It results from the mismatch of about 12% in lattice constant between silver overlayer and Cu(111) substrate where the occurring strain is relieved by a lattice of dislocation loops in the Cu(111) substrate [15, 16]. In our experiment superstructure and silver surface states were clearly visible over the entire range of our investigated layer thickness (up to 20 ML). However, the intensity of the superstructure in the LEED images and the 2PPE intensity from the silver surface state decreased at larger layer thickness as a result of the 3D island-growth mode.

3.1   *Energy shift of the Shockley-type surface state with increasing Ag film thickness*

The dependence of the binding energy of the surface state on Ag overlayer thickness on Cu(111) for coverages up to 10 ML was studied by Bendounan et al. [9, 14] using photoemission spectroscopy (PES). It was also shown that different in-plane atomic structures exist, which modify the binding energy of the surface state [14]. We focus here on the properties of films exhibiting the 9×9 reconstruction, which appears upon growth at 300 K.

Figure 2 shows 2PPE spectra at normal emission obtained for different silver film thicknesses. The spectra were recorded at room temperature. In a 2PPE process excitation from an occupied electronic surface state occurs via sequential absorption of two photons involving resonant or

FIGURE 1 STM topography ($110\,\text{nm}^2 \times 110\,\text{nm}^2$) of a nominally 3.5-ML Ag film on Cu(111) grown at room temperature. At that coverage the first monolayer is closed whereas the second and third monolayers are not yet completed. The fourth and fifth monolayers have already nucleated. In all layers the 9×9 reconstruction is visible

off-resonant excitation of an unoccupied intermediate state. The binding energy of the involved states can be determined from the measured kinetic energy distribution and the photon energy used in correspondence to conventional photoemission spectroscopy. Below 1 ML Ag the two distinct peaks at energies of $E_0 = -320$ meV and $E_0 = -230$ meV are ascribed to two-photon photoexcitation from the two coexisting Shockley-type surface states of bare Cu(111) and Ag-covered areas, respectively.

The measured binding energy of 320 meV for the Cu(111) surface state is in reasonable agreement with reference values for room temperature ($E_0 = -375$ meV) [17]. The observed lower binding energy is due to the limited angular resolution of the detector used ($\pm 6°$), which gives rise to an averaging over a large energy range of the dispersing surface state ($\Delta E \sim 40$ meV). At a silver coverage of 1 ML no emission from the Cu surface state can be observed and a new state has built up at a binding energy of 230 meV. In agreement with earlier publications [9] we do not find any dependence of the peak position of this new state as a function of coverage between 0 and 1 ML (see Fig. 2a). In the present paper we extended these investigations to silver thicknesses beyond the 1-ML regime. Spectra for different coverages at 2 ML, 5 ML and 20 ML are shown in Fig. 2b. One can clearly see a successive shift of the silver surface state to lower binding energies with increasing layer thickness.

In STS the differential conductance dI/dV at constant tip height is recorded, which is proportional to the local density of states (LDOS). The two-dimensional surface state causes a step-like increase in the LDOS. Figure 3 shows spectra taken on Cu(111) with increasing Ag thickness, measured at 77 K, from which the binding energy of the surface state is determined as the mid-point energy of the steep rise in the dI/dV signal. The first monolayer of Ag shifts the surface state of the Cu substrate from 420 meV to 230 meV binding energy.
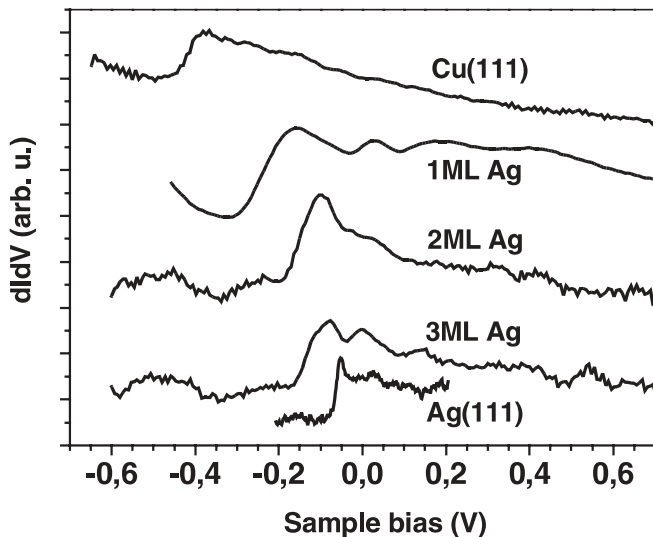
We note that only for small islands (or small silver patches at step edges) with < 10 nm could a lateral confinement affecting the binding energy be detected [18]. This is in agreement with a thickness-independent peak position for coverages < 1 ML in 2PPE.

Figure 4 summarizes the binding energies for 1 ML–20 ML of Ag obtained by STS and 2PPE. In addition the value of the Ag(111) surface state at 30 K from [19] is added to the data. The error bars for the STS data reflect the fact that due to the reconstruction the onset energy depends slightly on position; the error bars for the 2PPE data account for the limited angular resolution of the detector as well as for the scatter of different experimental runs. A systematic mapping of the underlying potential landscape will be addressed in future studies.

Comparing our results with the previous PES studies at room temperature [9, 14], we find an excellent agreement with the STS data for the binding energy of 1 and 2 ML Ag considering a temperature coefficient of the binding energy of 0.17 or 0.18 meV/K as found for Ag(111) and Cu(111) respectively [17]. The difference in binding energies for 4 ML as measured at 77 K by STS and for 5 ML at 300 K by PES is only 20 meV instead of more than 40 meV expected from the temperature difference alone. This discrepancy can be traced back to 3D island growth of the silver film starting at coverages of 3 ML. PES and 2PPE integrate over a macroscopic area so that different layer thicknesses with different surface-state energies contribute to the signal (e.g. contributions from 3 ML, 4 ML and 5 ML). The contributions from areas of lower Ag coverage give rise to an average surface-state binding energy which is larger than the actual one at e.g. 4 ML. In addition to that effect, the remarkable quantitative agreement between our STS and our 2PPE data requires some comments. Due to the different temperatures used for the STS and 2PPE experiments a downward shift of the binding energy for the 2PPE experiment similar to the Cu(111) result is expected. However, one has to consider that besides
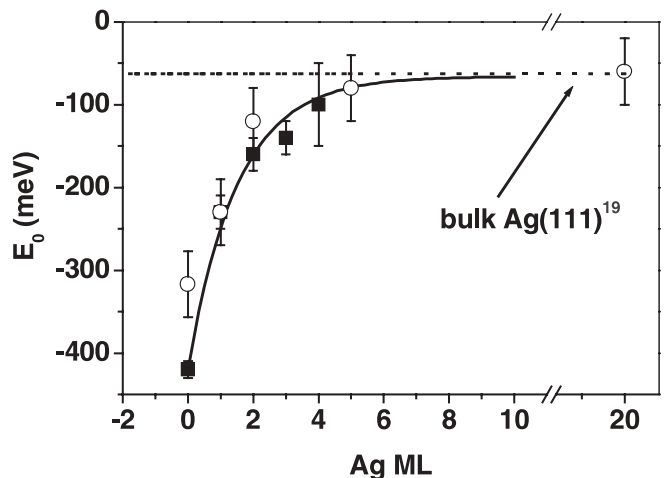

FIGURE 3 LDOS of Cu(111) with increasing Ag film thickness as measured by STS (dI/dV spectroscopy) at 77 K. For comparison the spectrum of a clean Ag(111) crystal is also shown. At the onset of the surface state the LDOS rises step-like according to the density of states of a two-dimensional state. The spectra are offset vertically for clarity

FIGURE 4 Surface-state binding energy ($E_F = 0$) of Ag/Cu(111) as a function of Ag coverage as measured by STS (*solid symbols*) at 77 K and 2PPE (*open symbols*) at 300 K. For 5 ML 2PPE data are influenced by the growth mode of the thin film (see text). The *solid line* is a fit to the STS data using the exponential decay given in ((1)). It yields the decay length of the surface-state wave function inside the crystal (see text)

the above-mentioned limited angular resolution of the detector used, the 2PPE data are affected by the strong asymmetry in the peak shape of the surface state for an Ag thickness > 5 ML. This indicates a significant Fermi-edge crossing of the surface state at low binding energies and is characteristic for the Ag(111) surface state at elevated temperatures [17]. As a consequence the binding energy of the surface state cannot be determined accurately and tends to be overestimated.

The perfect agreement with the low-temperature STS measurements is accidental and related to the compensation of the upshift when going to higher temperatures by the downshift as described above. Reference photoemission investigations starting at 10 ML silver film thickness are available from [20]. Even though a value for the measured binding energy of the surface state is not given in this reference, no shift in energy can be observed in the investigated coverage regime between 10 ML and 43 ML.

The occurrence and the binding energy of a surface state are influenced by the charge distribution at the surface, which determines the potential experienced by an electron at and in front of the crystal surface, and by the position of the band edges of the projected bulk band structure. A simple one-dimensional model using few free parameters to describe the surface potential was shown to explain the energetic position of surface and image states of a variety of crystal surfaces [21]. Based on the obtained wave functions further properties like the lifetimes of the surface [22, 23] and image states [24] could be calculated. From the success of this model some conclusions can be drawn concerning the surface states in overlayer systems. The first monolayer of the overlayer material influences the potential in the vacuum region outside the crystal, as can be seen by the great sensitivity of the work function to adsorbates on the surface. In a hypothetical Cu(111) crystal with Ag(111) surface potential the binding energy of the surface state shifts towards the L_2 band edge. Hence, in the case of Ag overlayers on Cu(111) the major contribution to the new binding energy of the overlayer surface state comes from the potential step at the interface of the two materials. This was also shown in a calculation in [14] using the model potential [21] for the Ag/Cu system. The experiments can also be understood in first-order perturbation theory where the change in binding energy of the state is proportional to the state's intensity (i.e. proportional to the envelope function of $|\Psi|^2$) at the interface [25]. This results in an exponential decay of the binding energy E_0:

$$E_0(d) = E_0(\infty) + (E_0(0) - E_0(\infty)) \, e^{-2\beta d}, \qquad (1)$$

where d is the overlayer thickness and E_0 is the surface-state binding energy equal to the binding energy of the Cu surface state for $d = 0$ and to that of the Ag surface state for $d = \infty$. Thus the decay length β^{-1} of the surface state into the bulk crystal can be obtained, which is related to the positions of the band edges of the host crystal. From the fit to our data (see solid line in Fig. 4) we obtain a decay length of 3–4 ML (6–8 Å). However, this simple law holds in the low-coverage regime only, where the host crystal's bulk band structure remains unchanged. From the observation of quantum well states (QWS) for coverages in excess of 10 ML, which allow the mapping of the Ag bulk band structure [26],

one can conclude that beginning at this Ag thickness the near-surface electronic structure is Ag-like. Therefore, from 5 ML Ag onwards the surface state is entirely residing in the Ag overlayer at first due to the short decay length governed by the positions of the band edges of the Cu(111) crystal and at higher coverages when the state is a true Ag(111) surface state due to the fact that the increased decay length (12 ML was reported for Ag(111) [25]) can now be accommodated into the overlayer. Of course, this discussion neglects the influence of the observed reconstruction, which has been studied in great detail recently [14].

3.2   Cs *on* Ag/Cu(111)

Our observations for the silver Shockley-type surface state show that the electronic properties of surface localized states can be modified by the interaction with the thin silver film substrate and the copper/silver interface. In case of excited adsorbate resonances such modifications can be an effective source for changes in the charge-transfer rate between substrate and adsorbate. In the following we present first spectroscopic results obtained for cesium adsorption on n-ML Ag/Cu(111). Our results indicate that the decay dynamics of an excited cesium state actually depends on the thickness of the underlying silver film.

The Cs was deposited by resistive heated getter sources. The pressure during evaporation was maintained in the low 10^{-10} mbar range. Previous 2PPE measurements [1, 27] showed that a long-lived excited adsorbate state A exists in the energy range 2 eV to 3 eV above E_F for both Cs/Cu(111) and Cs/Ag(111).

Figure 5 shows the 2PPE spectrum for different Cs coverages on (a) 2 ML and (b) 5 ML Ag film. In order to study the energy of excited (unoccupied) states, the 2PPE spectrum is plotted as a function of the intermediate-state energy $E - E_F$. As the work function of the substrate is very sensitive to alkali adsorption (see left onset of the 2PPE spectra in Fig. 5), its characteristic change served as a measure of the alkali coverage.

The feature A as seen in the energy region between 2.5 eV and 3 eV is due to photoemission from the excited unoccupied Cs resonance A. A striking feature of alkali adsorption is the downward shift of this resonance with increasing coverage as a result of the dipole interaction of the adsorbed alkali atoms. The energy of the alkali resonance and the slope of the downward shift are predominantly determined by the adsorption distance of the alkali. The free-electron density r_S of the substrate and interaction of the resonance with surface-located substrate states are generally of minor importance [28–30]. The increase in the photoemission intensity from state A at an intermediate-state energy $E - E_F$ of about 2.75 eV is the result of resonant excitation of the Cs state from the occupied surface state, which also shifts down in energy with increasing alkali coverage [31] and disappears when the low-energy edge of the $L_{2'}-L_1$ Ag(111) band gap located at about 300 meV [17] binding energy is crossed. It is noteworthy to mention that for bulk Ag(111) we observed for the same photon energy a distinct feature in our 2PPE spectra at $E - E_F = 2.5$ eV arising from a direct initial- to final-state excitation [27, 32]. This broad peak remains after
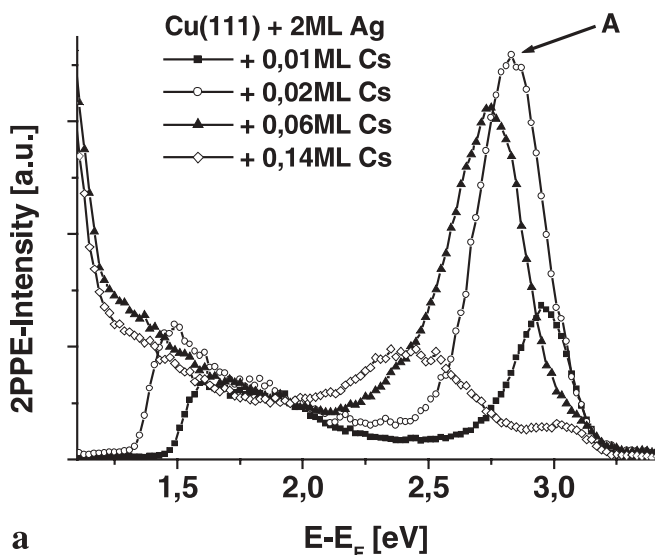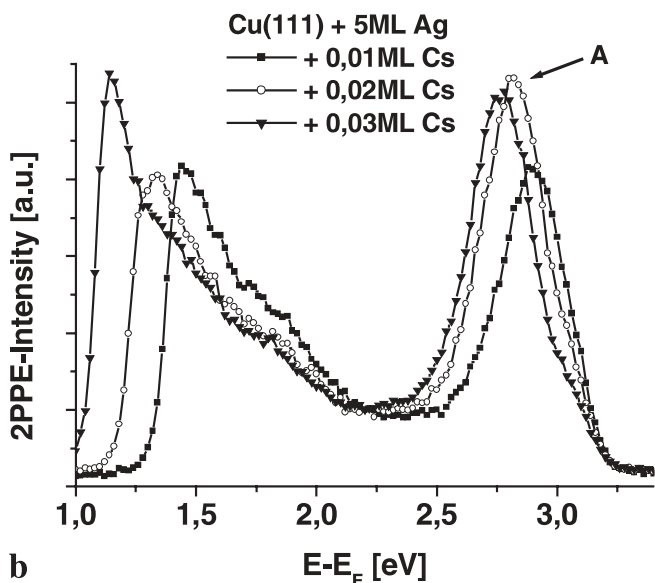
FIGURE 5 Series of 2PPE spectra (normalized to $E - E_F = 2$ eV) of **a** 2 ML and **b** 5 ML Ag on Cu(111) with increasing Cs coverage. Feature A is associated with an excited unoccupied Cs resonance

FIGURE 6 Energy dependence of the Cs resonance A relative to the change in the work function $\Delta\varphi$ for different silver film thicknesses. The *dashed lines* correspond to a $\Delta\varphi^{3/2}$ dependence as suggested by Borisov et al. [29]

Cs adsorption and overlaps with the electron-emission signal from the cesium excitation, restricting severely an investigation of the Cs resonance. The spectra in Fig. 5 show that this direct bulk excitation channel is absent in an ultra-thin Ag film, caused by the missing bulk structure perpendicular to the surface.

Borisov et al. showed show that for alkali adsorption at low coverages the energy dependence of the alkali resonance follows a $\Delta\phi^{3/2}$ law, in agreement with experimental data for Cs/Cu(111) [29]. Following the representation chosen in [29], we plot in Fig. 6 the measured resonance energies as a function of the work-function change for different silver film thicknesses. The results prove that the electronic structure of the adsorbed cesium can be tuned in a similar manner as the surface-state structure by the silver film thickness. For the investigated systems we find the highest binding energy of the Cs resonance (with respect to the vacuum level) for
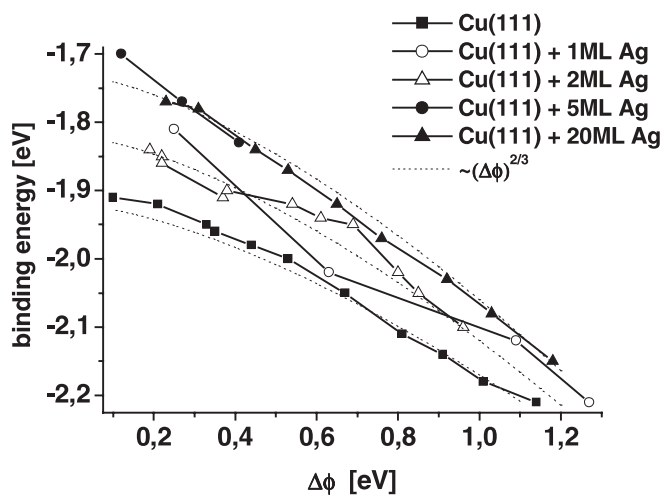
Cs/Cu(111). The energy decreases with increasing silver film thickness, where for 1 and 2 ML an upward shift of about 0.1 meV is observed, which is further increased for higher coverages (5 and 20 ML). In addition a clear indication for a change in the slope of the work-function dependence is visible: the dashed lines in Fig. 6 correspond to a calculated $\Delta\phi^{3/2}$ dependence where slope and energy have been adjusted to match the experimental data. In particular for the 5 and 20 ML data the change in energy is obviously steeper than for the pure Cu(111) and also in comparison to the data obtained for the 1 and 2 ML silver surface. For a chosen substrate the resonance energy and the resonance energy slope depend critically on the alkali–surface distance [29]. Even though the bond lengths of Cs on Cu(111) and Ag(111) are almost identical (3.08 Å for Cu(111) [33] and 3.02 Å for Ag(111) [33, 34]) the different adsorption sites (atop for Cu(111) and fcc hollow for Ag(111)) result in an effectively reduced alkali–surface distance in the case of Cs/Ag(111). This would qualitatively agree with the smaller binding energy and the steeper slope as measured for the Cs/Ag(111) system. It is, therefore, tempting to state a successive modification in the alkali–surface distance as a function of silver film thickness which may also correlate with structural modifications of the overlayer. For a detailed analysis, however, additional effects due to the interaction with the modified surface state and the change in the free-electron density of the substrate may have to be taken into account.

For the line width of peak A we observe a monotonic increase from a value of about 275 meV at 1 ML silver to about 450 meV at 20 ML. For the line width of Cs adsorbed on bulk Ag(111) we reported a value of about 420 meV in an earlier work [27]. For any film thickness the resonance shows a strong inhomogeneous contribution to the broadening possibly arising from the high mobility of the alkalis on the surface. The 3D growth mode starting at three monolayers of silver may enhance this effect and result in the observed increase in the line width. In addition, changes in decay dynamics of the resonance, e.g. due to an enhanced charge-transfer rate between adsorbate and substrate, may also partly account for these changes. An enhanced coup-

ling of the Cs resonance to the silver film may be the result e.g. of modifications in the electronic structure of silver QWS which are modified up to film thicknesses of several tens of ML [26]. However, the strong non-Lorentzian shape of the resonance in our spectra does not allow a quantitative analysis of such an effect, yet. Real-time investigations based on time-resolved 2PPE experiments are in progress and will give a more detailed insight into the coupling mechanisms important for the dephasing and population decay of the cesium resonance.

4   Summary

We investigated the electronic surface structure of epitaxially grown silver films on Cu(111) as a function of layer thickness by means of scanning tunneling spectroscopy and two-photon photoemission spectroscopy. Upon deposition of 1 ML of silver the Cu(111) Shockley-type surface state disappears and a new occupied state appears in our spectra. We observe a shift in the energy of this state toward the Ag(111) Shockley-type surface state with increasing film thickness.

In addition, our investigation demonstrates that Cs adsorbed on Ag/Cu(111) is an excellent system to study the charge-transfer dynamics into a heterogeneous substrate. Even though experimentally not verified yet by a real-time experiment, the decay dynamics of excited adsorbate states may be altered by the interaction with the Cu/Ag interface. Especially when the overlayer thickness is comparable or even smaller than the electron mean free path, quantum well states perpendicular to the film will influence the electron charge transfer dynamics quite considerably. Future time-resolved photoemission studies of Cs/n-ML Ag/Cu(111) should provide further insight on the dynamics of electron-charge transfer between adsorbate and metallic substrates.

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