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# Morphological modifications of Ag/Cu(111) probed by photoemission spectroscopy of quantum well states and the Shockley surface state

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**ABSTRACT** Epitaxial ultra-thin Ag films grown on Cu(111) have been investigated by angle-resolved photoemission spectroscopy. The thickness dependence of the binding energy for the Shockley surface state at 300 K could be determined accurately in films up to 5 ML thick. Furthermore, we observe drastic changes in the film morphology after annealing to 450 K. Spectral modifications in the shape of the quantum-well states (QWS), characteristic for these ultra-thin silver films, prove that the surface morphology is homogeneous. The photoemission spectra also indicate that the silver film bifurcates to form a film exhibiting two distinct film thicknesses. For all levels of silver coverage, we identify surface regions that are 2 ML thick, while the thickness of the remaining surface depends on the amount of deposited silver. The almost purely Lorentzian line-shape of the spectral features corresponding to the two different surface regions show that both surface areas are atomically flat.

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## 1 Introduction

The electronic structure of ultra-thin metal films on metals or semiconductors has been the focus of several photoemission experiments in recent years. Of particular interest are quantum size effects due to discrete quantum well states, which are caused by electron confinement in these films [1–7]. Other works focus on the surface electronic structure and how it changes due to the interaction of the metal film with its underlying substrate [8, 9]. In general, it is found that the film morphology is a very important parameter that determines both the electronic structure and the quality of the photoemission spectra. Therefore, one of the aims for these investigations is the preparation of macroscopically uniform and atomically flat films. Striking examples in this direction include Ag/Fe(100) [10], Ag/V(100) [11], and Pb/Si(111) [2, 4].

Another system that has been studied quite intensively with respect to its surface states and quantum well states is

Ag/Cu(111). Even though the morphology of the silver films in this system shows distinct deviations from what is considered “ideal” for films thicker than two monolayers, Shockley surface states, as well as defined quantum well states, have been observed for this system in numerous works, even for rather high film thicknesses [8, 12–14].

In this letter, we use the sensitivity of the electronic structure (both QWS and surface states) to the structural film properties to gain detailed information on the morphology of an Ag film evaporated on Cu(111). Angle-resolved photoemission shows that after short annealing at 450 K, the Ag-film (evaporated at 300 K) bifurcates to form a film exhibiting two distinct film thicknesses. The purely Lorentzian shape of the spectral features related to these two different thickness areas, show that uniform, atomically flat surfaces have emerged. An accurate determination of the dependence of the Shockley surface state energy on film thickness enables us, in particular, to identify the reproducible formation of areas of 2 ML film thickness independent of the amount of pre-deposited silver. However, in the remaining regions, the film thickness is governed by the level of silver pre-coverage.

This paper first describes the photoemission results for an Ag/Cu(111) surface that was not annealed and focuses on the dependence of the film thickness on the silver surface state. Next, the effects of annealing the surface at 450 K on the film morphology are evaluated.

## 2 Experimental

Our angle-resolved photoemission experiment was conducted using a 150 mm hemispherical energy analyzer (SPECS Phoibos 150). The total energy resolution of the analyzer at the pass energy used in these experiments, 20 eV, was less than 20 meV, with an angular resolution of less than 0.15°. The electrons were collected with a 2D-detection unit consisting of a microchannel plate, a phosphorus screen and a CCD camera. This two-dimensional detector is able to record the emission spectra between –6 and +6 degrees without rotating the sample. All photoemission spectra were recorded at 300 K using the p-polarized 4th harmonic ( $\approx 6$  eV) of a narrow band, pulsed Ti:Sapphire oscillator (Spectra-physics, Tsunami) created by sequential frequency doubling in two 0.2 mm thick beta barium borate (BBO) crystals. The incident light was fo-

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cused onto the sample with a 250 mm lens, which results in a beam diameter of approximately 150  $\mu\text{m}$  at the surface.

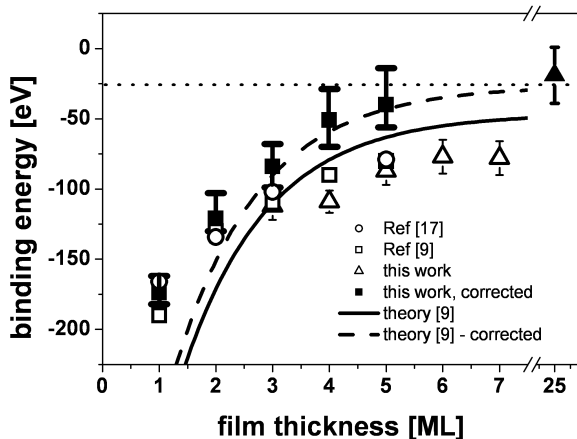
The Cu(111) crystal was cleaned by repetitive sputtering (10 min, 500 eV) and annealing cycles (15 min, 500  $^{\circ}\text{C}$ ). The surface quality was checked by low energy electron diffraction (LEED), Auger spectroscopy, and the photoemission characteristics of the Shockley surface state of the Cu(111) surface. Silver was evaporated from a Knudsen cell type evaporation source at a rate that was in the range of 1 ML/min. During evaporation, the sample temperature was held at 300 K. Ag-film thickness calibration was performed by monitoring the change in the intensity ratio of the two Shockley-type surface states in the photoemission spectra corresponding to a bare Cu(111) surface and a Cu(111) surface covered with 1 ML Ag, as described previously in [14].

### 3 Experimental results and discussion

#### 3.1 Photoemission from non-annealed silver films

The electronic structure of silver films on Cu(111) has been the topic of several photoemission experiments in recent years. These studies focused particularly on two main spectral features in the valence band regime, specifically, the occupied Shockley-type surface state resulting from the termination of the crystal by the (111)-oriented surface [8, 9, 14], and the quantum well states (QWS) due to the quantum confinement of the *sp* valence electrons within the silver film [12, 15, 16].

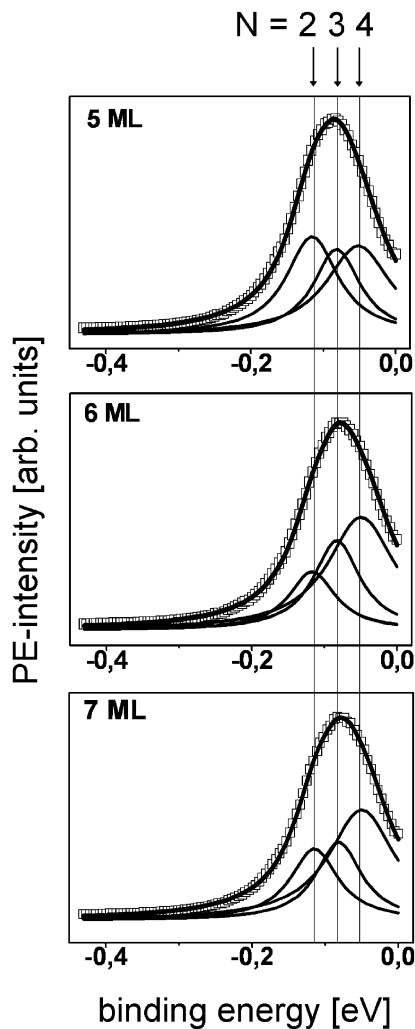
The binding energy of the Shockley state for the Ag/Cu(111) surface depends critically on silver film thickness, where the highest sensitivity is observed for films between 0 and 5 ML [9, 14, 17]. This energy shift results from a finite entrance depth of a few ML of the surface state into the bulk and the consequent interaction with the Ag/Cu(111) interface in this thickness regime [9, 14]. Figure 1 summarizes



**FIGURE 1** Experimental and theoretical values for the Shockley surface state binding energies for Ag/Cu(111) as a function of film thickness. *Open symbols*: experimental data from [17] (circles), [9] (squares), and from this work (triangles). *Full squares*: experimental data from this work evaluated with consideration of the 3D growth mode of the Ag/Cu(111) system and the modification of the spectral distribution by the Fermi–Dirac distribution. For more details, see text. *Solid line*: theoretical data from [9]; *dashed line*: same data corrected for the value of the surface state binding energy for bulk Ag(111) found in this experiment (*full triangle*) in agreement with [18] (*dotted line*)

experimental photoemission data for the binding energy as a function of silver film thickness at 300 K, where the data is compiled from different references [9, 17] and compared to data collected in this work. While the values for one and two monolayer films can be obtained from the photoemission data with high accuracy [9], the deconvolution of the correct binding energies for film thicknesses,  $\theta$ , greater than 2 ML (shown as open symbols in Fig. 1) is more difficult as the result tends to be an overestimate of the actual binding energy [9, 14]. This systematic deviation arises from the Stranski–Krahanov growth mode of Ag on Cu(111), where layer by layer growth is only observed for the first two monolayers and three-dimensional island growth appears at higher coverages [14]. Thus, a laterally integrated photoemission spectrum recorded for a film with a nominal thickness of 5 ML, for example, contains information from regions of varying film thicknesses. Therefore, the determination of the correct binding energy requires a careful and consistent multi-peak fitting procedure for the experimental photoemission data that accounts for all the contributions from the different Ag-thicknesses at each location. Furthermore, due to the close proximity of the surface state to the Fermi-edge,  $E_F$ , ( $\sim 26$  meV binding energy for bulk Ag(111) at 300 K [18]), a considerable portion of the surface state lies beyond  $E_F$ , which means that its spectral shape is significantly distorted by the Fermi distribution. Multiplication of the measured spectra by  $f(E_i, T) = 1 + \exp[(E_i - E_F)/kT]$  compensates, at least partly, for this effect and improves the accuracy of the determined binding energies significantly, as shown for bulk Ag(111) in [18]. For example, the solid squares in Fig. 1 correspond to the corrected binding energies obtained from our experimental data using these two corrections. Here, the consistency of the multi-peak fits was assessed by analyzing the photoemission data for films that spanned the nominal thickness regime between 3 and 11 ML (see Fig. 2). The fitting function consisted of three to four Lorentz profiles where, in a first approach, all peak positions were set as free fitting parameters. These fits resulted in rather consistent peak positions, which were independent of nominal film thickness and only varied in their relative intensities. Next, fixing the position of the lowest peak to its value when it first appeared resulted in further improvements to the consistency of the data. In this way, in addition to the peaks associated with 1 and 2 ML, which are spectrally clearly resolved, three more discrete energy positions can be identified and assigned to silver films of three, four and five ML thicknesses.

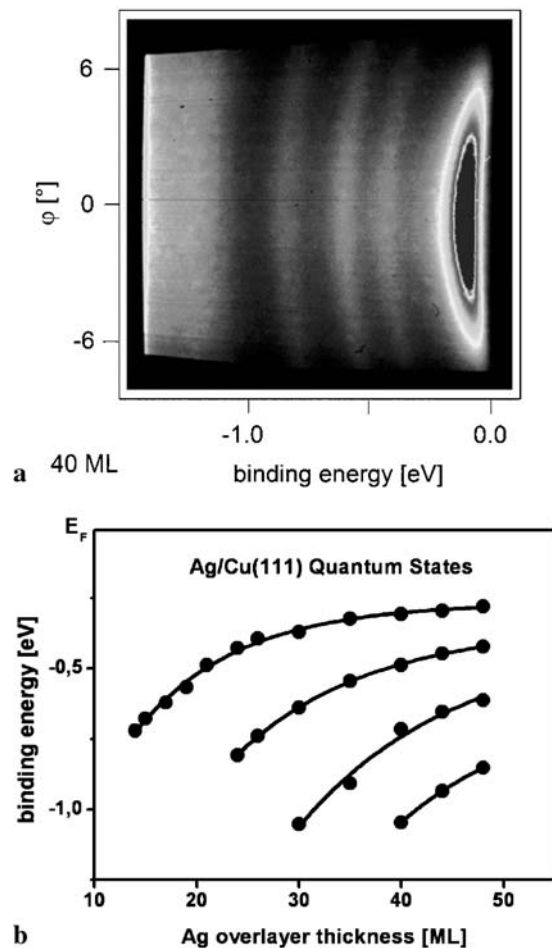
The binding energies for 1 and 2 ML thick films obtained in this way are very consistent with the values reported by Bendounan, et al. [9]. However, for  $\theta$  greater than 2 ML, they deviate significantly and the values reported here are shifted 25 meV to 50 meV lower. A less pronounced, but still observable, systematic deviation at these thicknesses is also visible when this data is compared to theoretical data for the Ag/Cu(111) system (solid line) also taken from [9]. A relevant boundary condition for these calculations is the asymptotic value of the surface state binding energy at infinite Ag film thickness, which was set to  $E_B = 45$  meV. This value was deconvoluted from experimental data without correcting for the Fermi distribution. A more correct analysis of the Ag(111) surface state energy by Panagio, et al. gives



**FIGURE 2** Photoemission spectra of the Shockley surface state for nominal film thicknesses of 5, 6, and 7 ML (*open squares*). The binding energies of the surface states that correspond to the effective film thicknesses contributing to the PE-signal are determined from multi-peak fits into the data (*solid lines*). Independent of nominal film thickness we obtain very consistent values for the binding energies (see *vertical lines*). The results are summarized in Fig. 1

a room temperature value for  $E_B$  equal to  $26 \pm 5$  meV [18], which is in good agreement with our data for a thick Ag film (see Fig. 1). The dashed line in Fig. 1 displays the calculated data shifted upwards by 20 meV to correct for this difference in the surface state bulk value. After comparing this curve again to the experimental data of the present work we now find an excellent agreement for the values of  $\theta$  greater than 2 ML. The deviation for one and two monolayers is still obvious, but this difference agrees with the findings of [9] where it was attributed to lattice relaxation of the Cu-substrate due to a lattice mismatch of about 13% between silver and copper. This lattice mismatch was not considered in the calculation. Because of the restricted analysis method applied to the experimental data in [9], it could only be speculated that these substrate distortions do not affect the surface state binding energy for  $\theta > 2$  ML. However, the almost perfect agreement between theory and our experimental data for the three, four and five monolayer values do indeed confirm this assumption.

For silver film thicknesses beyond 5 ML, additional spectral features appear in the photoemission spectra in the energy regime between  $E_B = -850$  meV and  $E_B = -300$  meV [18] at the  $\bar{\Gamma}$  point, where these features are related to the well-known quantum well states for this system [19]. In the present case, the potential well that confines the Ag *sp* valence electrons is formed by the band-gap along the  $\Gamma$ -L direction of the Cu(111) substrate and a potential barrier associated with the image potential at the vacuum side. The energy of these peaks are uniquely related to the thickness of the silver film and can be calculated rather accurately using the so-called phase-accumulation model [19, 20]. After evaporation of the silver films at 300 K and without any further treatment, these QWS-features appear inhomogeneously broadened in the photoemission spectra, indicating that the morphology of the silver films exhibits a certain degree of inhomogeneity, and also indicating that a number of different



**FIGURE 3** (a) Photoemission map (intensity in gray scale as function of energy and emission angle) of a silver film of nominally 40 ML prior to annealing; the spectrum shows a dominating signal from the Shockley surface state right at the Fermi-level. At higher binding energy, a series of three quantum well states is visible. Due to the structural inhomogeneity of the non-annealed surface, all four peaks are Gaussian shaped. (b) Energy of the  $\nu = 1$  to  $\nu = 4$  quantum well states and resonances as a function of nominal film thickness as determined from photoemission spectra from non-annealed silver films. The energy spacing between the states and the overall general trend are in very good agreement with the data in [12]. However, the assignment of the quantum well states to the silver film thickness has to be performed with care as discussed at the end of the paper

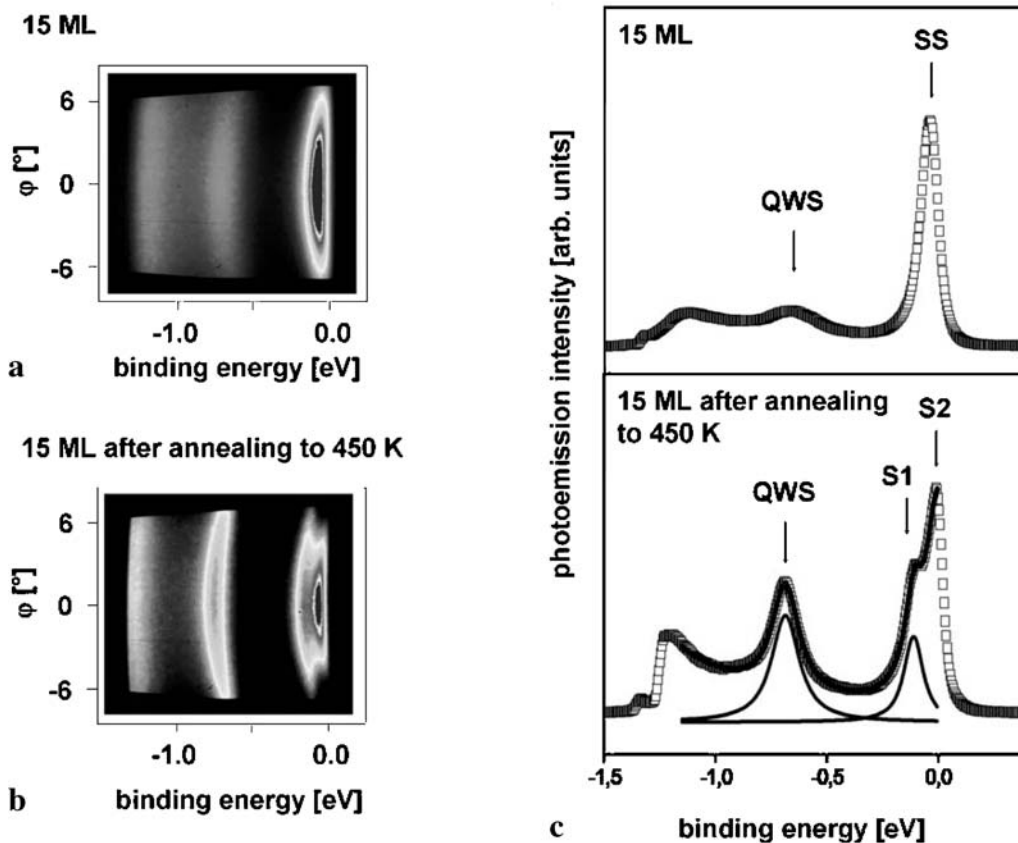
local film thicknesses contribute to the photoemission signal. Figure 3a shows a photoemission spectrum for a silver film of nominally 40 ML where the dominant spectral feature close to  $E_F$  corresponds to the Shockley surface state. At higher binding energies, the  $\nu = 1$  to  $\nu = 3$  quantum well states can be clearly distinguished. Figure 3b summarizes the experimentally determined energy positions for the first four QWS (or resonances) as a function of the nominal film thickness. Our results are in qualitative agreement with data published before by Mueller, et al. [12]. Unfortunately, a perfect quantitative agreement taking into account our thickness calibration could not be found. However, this disagreement is nicely resolved by taking into account the specific film morphology as described in the following section.

### 3.2 Photoemission from silver films after annealing to 450 K

Short-time annealing of the Ag/Cu(111) surface at a temperature of 450 K results in drastic changes to the spectral distribution of the photoemission spectra. As an example, Fig. 4 shows photoemission data recorded at room temperature for a silver film of nominally 15 ML, both before and after the annealing procedure. The originally broad and Gaussian shaped quantum well (QW) peak for the  $\nu = 1$  QW state of the silver film (see Fig. 4a) was transformed into a narrow and almost purely Lorentzian shaped peak (see Fig. 4b). In addition, the peak position was shifted slightly to a higher binding energy. These results show that the homogeneity of the surface regions was improved significantly. A similar enhancement in

the film uniformity for the Ag/Cu(111) system was also reported by Mueller, et al. [12]. The Lorentzian shape of the peak in the present example strongly indicates that the surface now exhibits large areas of uniform silver films with a defined single thickness.

Next to the spectral changes related to the quantum well peak, we observe another, rather striking modification to the PE-spectrum in the vicinity of  $E_F$ , which has not been reported before. For the non-annealed surface, the photoemission peak associated with the Shockley state is located at a binding energy of 34 meV and shows a purely Gaussian shape (see Fig. 4c, top graph). As expected, the observed inhomogeneities in the film thickness also result in a broadening of the surface state that is in conjunction with the broadening of the QW state. After annealing at 450 K, the surface state has now split into two peaks  $S_1$  and  $S_2$ , which are just below and above the original peak (see Fig. 4c, bottom graph). Both peaks exhibit an almost perfect Lorentzian shape that indicates significant homogenization of the film morphology, similar to the result for the QW states. Regarding the left peak ( $S_1$ ), the binding energy corresponds almost exactly to the Shockley surface state for a silver film of 2 ML thickness ( $E_B = 120$  meV, see Fig. 1). The second peak ( $S_2$ ) at a lower binding energy points instead to a rather thick film of at least 15 ML. Therefore,  $S_2$  can be related to the film thickness, which is also responsible for the pronounced quantum well state in the spectrum. As our photoemission spectrum does not indicate the presence of any other silver film thicknesses, we conclude that the annealing procedure results not only in a greater degree of homogenization in the local



**FIGURE 4** (a) Photoemission map of a 15 ML thick silver film (nominal thickness) before (a) and after (b) annealing at 450 K; (c) normal emission spectra taken from (a) and (b) clearly visible are the modifications in the spectral shape of the quantum wells state (QWS) and in the energy region, where the Shockley surface state (SS) is observed.  $S_1$  and  $S_2$  indicate the two distinct Shockley surface states appearing in the spectrum after annealing; the two Lorentzians in the bottom graph result from a fit into the QWS-peak and  $S_1$ -peak of the bottom spectrum. Also shown as a solid line is the total fit result. A Gaussian was used to reproduce the low energy tail of the spectrum and a Lorentzian to fit the peak  $S_2$

film morphology, but also in a bifurcation of the film into areas characterized by two distinct, but well-defined thicknesses. These two areas obviously strongly dominate the film morphology.

PE spectra from a silver wedge evaporated onto a Cu substrate demonstrates that both the homogenization of the film morphology and the bifurcation are rather independent on the initial nominal silver coverage. The small spot size of the focused laser light used in our experiments allows us to probe a distinct silver film thickness within the wedge. Next, translation of the sample enables us to make a quasi-continuous scan over different thicknesses, both before and after annealing. Figure 5a shows three photoemission spectra for nominal film thicknesses of 13, 17, and 35 ML recorded at 300 K after a brief heat treatment at 450 K. For all three cases, we observe the narrowing of the QW features, which are characterized

by an almost Lorentzian peak shape, and we also observe the splitting of the original surface state peak. Again, the peak positions of the final QW peak(s) remain almost unchanged compared to their original positions, but the film thickness of the corresponding area is obviously governed by the initial silver coverage.

Regarding the two surface states  $S_1$  and  $S_2$ , which we observe simultaneously, we find that the binding energy of peak  $S_1$  coincides in all cases with the energy characteristic for the 2 ML thick silver film. In addition, this peak appears after annealing for all film thicknesses tested in this study, up to a nominal film thickness of 35 ML. However, we observe that the relative intensity of the 2 ML surface state peak  $S_1$ , decreases with increasing film thickness relative to the intensity of the second surface state,  $S_2$ , (see Fig. 5b), which indicates that the lateral extension of the thicker film regions increases

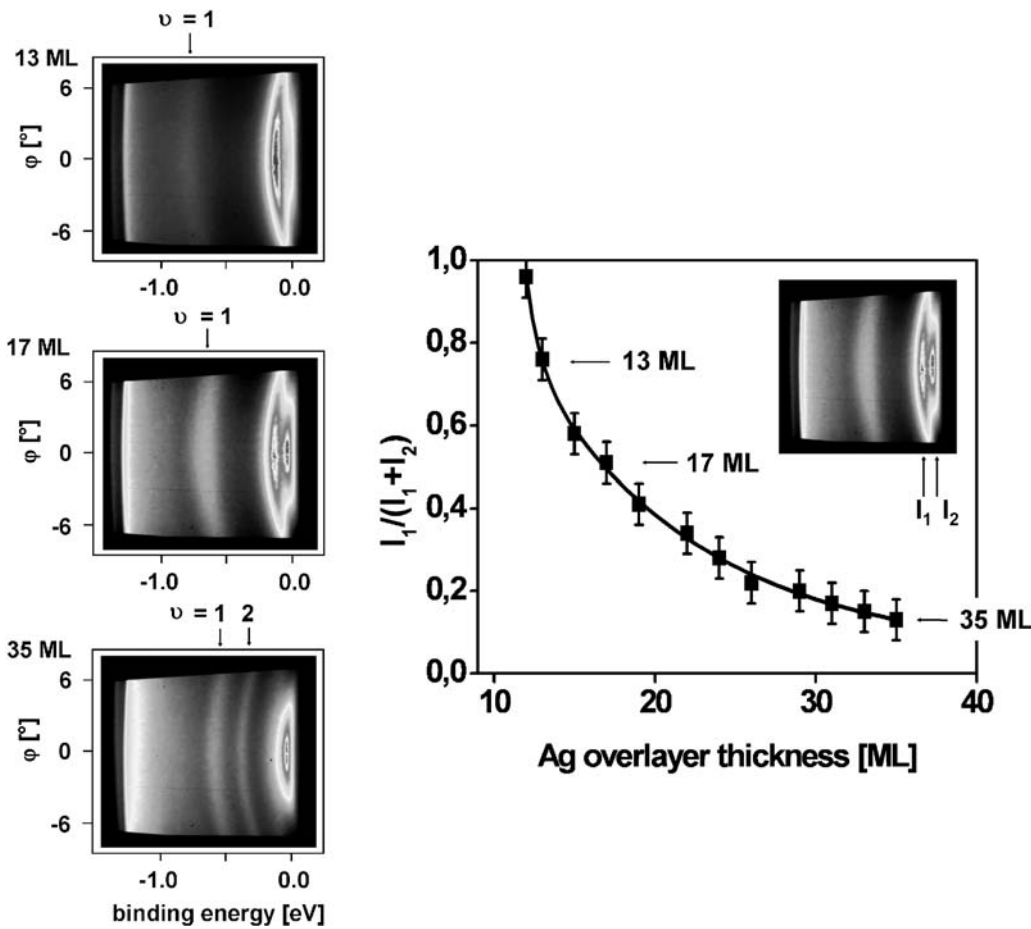


FIGURE 5 Left: photoemission maps of annealed silver films for three different thicknesses. For all three cases a splitting of the surface state is observed as well as a narrowing of the QWS. For 13 ML thickness the  $S_1$  peak dominates the spectrum, the intensity from the  $S_2$ -peak and the QW state is rather weak. For increasing film thickness this behavior is inverted so that at 35 ML the  $S_1$ -peak can be clearly distinguished only for large emission angles; right: normalized PE-intensity from the  $S_1$  peak as function of nominal film thickness

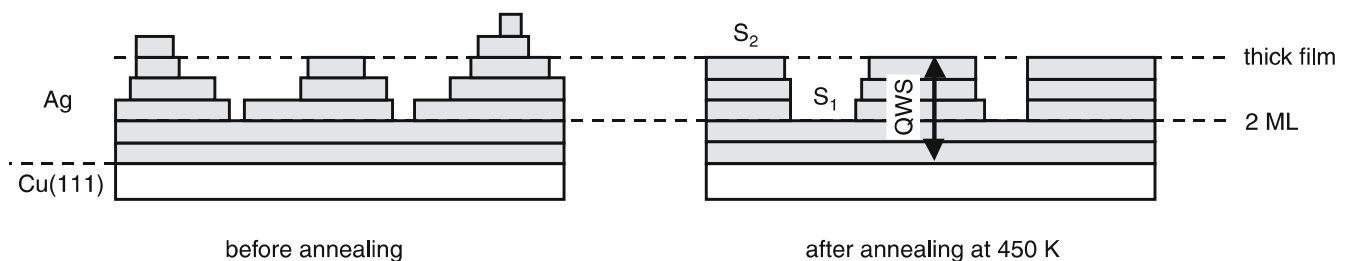


FIGURE 6 Schematic summary of the morphological changes induced by the heat treatment of the silver film that were identified in this photoemission study; film areas representative for the spectral features observed are indicated

at the expense of the 2 ML areas. Figure 6 summarizes in a schematic the morphological changes induced by the heat treatment of the silver film that were identified in this photoemission study.

One obvious result of these experiments is the high stability of the 2 ML thick silver film on Cu(111) which is not affected by the annealing procedure compared to films with a thickness,  $N$ , greater than 2 ML. Indeed, this observation is not too surprising as it reflects the specific Stranski–Krastranov growth mode of this system, which favors layer by layer growth up to the second silver layer and then changes into the 3D growth mode starting with the third layer. This behavior results from the competition between the interfacial and stress energies acting on the film due to the large lattice mismatch (13%) between silver and copper, and the surface energy of the silver film. This energy balance stabilizes the 2 ML film, but increasing strain caused by subsequent layers destabilizes thicker films and induces clustering [21]. However, an interesting question that arises for the Ag/Cu(111) system is whether the stabilization of the 2 ML film is considerably influenced by contributions from the electronic surface energy related to the Shockley surface state. This question is motivated by recent findings that discrete electronic states in thin metal films, particularly quantum well states, can have a dramatic influence on film morphology [2, 3, 5–7]. This phenomena, which is referred to as electronic growth, can result in the stabilization of a specific film thickness, for example. One factor that promotes such a process is the dispersion of these states with increasing film thickness accompanied by a Fermi-level crossing. Whereas the Shockley surface state shows a strong energy dependence in the relevant thickness regime (see Fig. 1), a Fermi-level crossing is not necessarily obvious. However, as discussed above, the close vicinity of the Shockley surface state to the Fermi-edge gives rise to, at least, a fractional crossing and, therefore, to a reduction of occupancy in the surface state depending on the silver film thickness. In addition, the upwards shift of the surface state towards the Fermi-edge with increasing temperature [18] will further support its depletion, resulting in enhanced stabilization of the thin film during the heating cycle.

At this point, we are now able to address the previously mentioned discrepancy regarding the calibration for the quantum well as a function of thickness obtained in this work compared to data published in [12] (see Sect. 3.1). Even though we find that the measured energy differences of the QW states for a specific spectrum in these two works are in perfect agreement, the absolute scale relative to the film thickness deviates by several monolayers. Our studies have revealed that the reason for this discrepancy lies in intrinsic, systematic errors within both sets of experiments. In our experiments, the energy of the QW states, as shown in Fig. 3b, is determined from photoemission spectra taken from non-annealed films where, due to the morphological inhomogeneity (3D growth for  $N > 2$ ), different film thicknesses contribute to the spectral QW feature(s) appearing in the photoemission spectrum. Therefore, an exact calibration for the QW state energy as a function of thickness for this data set is not possible. The energy position of the peak maximum is likely governed by a non-trivial weighting of the QW state ener-

gies from different film thicknesses, which is a result of the undefined film morphology as well as the film thickness dependent photoemission cross-section [19]. A determination of the quantum well energy from an annealed film, as performed in [12]<sup>1</sup>, will, in contrary, give an energy value that is indeed characteristic for a very specific, well-defined film thickness. However, a correct calibration of the local film thickness (where the QW states originate) is, in this case, impossible due to the fact that, after annealing, the surface does not consist entirely of a closed film, as shown by our photoemission results. For the bifurcated film, the nominal film thickness measured, for example, by a flux measurement during evaporation, systematically underestimates the actual thickness of regions where the film is thicker and it is these regions that are responsible for the QW peaks in the spectrum. Therefore, a correct thickness calibration for the annealed Ag/Cu(111) probably requires complementary STM studies.

#### 4 Summary

The bifurcation of epitaxial ultra-thin Ag films grown on Cu(111) into two distinct film thicknesses after annealing at 450 K is identified by means of angle-resolved photoemission spectroscopy. The silver surface prepared in this manner exhibits areas of 2 ML thickness as well as thicker areas characterized by well-defined Lorentzian-shaped quantum well states. The photoemission spectra show that both films are uniform and atomically flat and dominate the entire surface morphology. Furthermore, we were able to accurately determine the thickness dependence of the binding energy for the Shockley surface state at 300 K for films up to 5 ML thick. In comparison to calculations from [9], this result confirms that, for silver film thicker than 2 ML, the energy of the Shockley surface state is barely affected by the lattice relaxation of the Cu substrate caused by the mismatch in the lattice constant between silver and copper.

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<sup>1</sup> We would like to note that a bifurcation of the silver film after annealing has not been reported by Chiang et al. [12]. The improved energy resolution as well as  $k_{\parallel}$ -resolution in the present study may at least partly account for this discrepancy to our work

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