Influence of the reconstruction in Ag/Cu(111) on the surface electronic structure: Quantitative analysis of the induced band gap

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In this work we present high-resolution angle resolved ultraviolet photoelectron spectroscopy on the system Ag/Cu(111). For 1 ML Ag one obtains the well-known quasicommensurate triangular reconstruction for which we observe the opening of a band gap in the Shockley state at a parallel momentum of $k_{\|} \approx 0.151$ Å^{-1} as a consequence of a Bragg reflection at the new zone boundaries of the supercell. The position of the zone boundaries in k space corresponds to a hexagonal supercell with an extension of 9.4 times the interatomic distance of the Cu(111) surface. We present a quantitative analysis of the position and width of the band gap and discuss the modified shape of the Shockley-state Fermi surface. The reduced surface Brillouin zone can also be observed for the 2 ML system. Here the Shockley state is shifted further towards the Fermi level and, consequently, the gap lies in the region of the unoccupied electronic states clearly above the Fermi level. Our results are in contradiction to previous studies.

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I. INTRODUCTION

In nanostructured films, there appears a strong influence of the surface structure on the electronic states in the valence band region. The reduced dimension can lead to completely new physical properties, such as, e.g., Luttinger-liquid behavior in one-dimensional atomic chains,[1] whereas in two-dimensional films Fermi-liquid behavior is observed.[2] One of the most important model systems for two-dimensional electronic states is the Shockley state on metal systems.[3] Shockley states appear in the band gaps of the projected bulk states and can be observed on various metal surfaces, such as, e.g., the (111)-faces of noble metals.[4] They are confined to the top-most atomic layers of the crystal and consequently form a two-dimensional electronic system. The in-plane band dispersion $E_B(k_{\|})$ of the Shockley states can be well approximated by a parabola, representing a nearly free-electron behavior. However, a detailed analysis of line shape and band dispersion on the meV scale displays the influence of many-body interactions as electron-electron and electron-phonon scattering.[5–7] Moreover, because Shockley states are localized near the surface, they are very sensitive to surface modifications, both to the lateral structure[8] and to the interaction with a coverage.[9] Even the weak interaction with a physisorbed rare-gas layer can significantly modify the binding energy of the Shockley state of the substrate.[10–13]

A very interesting system in this context is Ag/Cu(111) that shows a highly ordered and abrupt interface. Ag/Cu(111) is a particularly attractive model to study nucleation, layer-growth processes and surface reconstruction.[14–16] In fact, the silver adatoms are very mobile on the Cu surface, thus they can diffuse at room temperature over long distances and are able to form perfectly ordered islands, usually growing laterally from the step edges of the substrate. Because the surface energy of Ag and the stress energy at the interface are lower than the Cu substrate energy, the Ag film grows layer by layer for the two first monolayers (Stranski-Krastanov growth mode).[17] The surface of the Ag monolayer displays a (9×9) reconstruction resulting from the large lattice mismatch between Cu and Ag (about 13%; $a_{\mathrm{Cu}}=3.614$ Å, $a_{\mathrm{Ag}}=4.085$ Å). At low preparation temperatures the Ag monolayer forms an unstrained hexagonal moiré structure defined as a modulation resulting from the superposition of the Ag and the Cu lattice.[17] Several Ag atoms are in energetically unfavorable on-top positions leading to strongly stressed Cu regions in the substrate. Prepared at room temperature, the surface presents a triangular corrugation induced by the formation of misfit dislocation loops in the underlying Cu(111) plane. This mechanism is associated with the shift of single substrate atoms from fcc to hcp sites, as it was also demonstrated for the related system Au/Ni(111).[18] The Shockley states of the moiré and the triangular structure of the Ag/Cu(111) monolayer system have different binding energies[19] (approximately 300 and 240 meV, respectively) and can be used to distinguish the two structures by spectroscopy.

Quantum molecular dynamics simulations show[14,15] that the reconstruction of the top substrate layers occurs by introduction of a few Cu vacancies collapsing in a partial loop. The triangular superstructure corresponds to a relaxed layer with quasicommensurate patterns. By photoemission spectroscopy (PES) and scanning tunneling microscopy (STM) measurements, an irreversible transition from the instable moiré structure to the stable triangular structure has been found.[20] Furthermore, the influence of the in-plane atomic structure on the binding energy of the Shockley state has been also investigated in detail.[19] As observed also in other intermetallic overlayer systems[21,22] the Shockley state shifts with increasing number of monolayers towards the Fermi level, with binding energies specific for the individual monolayer or multilayer system.

In a recent Letter[23] Schiller *et al.* observed the back folding of the Shockley state and could measure the energy position of the lower edge of the band gap, which opens close to the Fermi level. Back-folding effects have been observed by photoemission for various systems, such as stepped

surfaces,[24–27] surface reconstructions,[28] and commensurate overlayers.[12] Although they were not able to determine the position of the upper gap edge, they extracted a gap width of $\Delta_G = 86 \pm 10$ meV and a $\bar{\Gamma}$-$\bar{M}$ distance of 0.15 Å^{-1}. From these results they concluded, that the observed (9.5×9.5) superstructure represents a charge density wave (CDW) state with a characteristic temperature of $T_{\mathrm{CDW}} = 295$ K.

In the present paper we present angle-resolved photoemission in the VUV range (ARUPS) on one and two Ag monolayers on Cu(111) with both high energy and angular resolution. We demonstrate in detail the influence of the quasicommensurate triangular superstructure on the Shockley state. The 1 ML system shows an opening of a band gap at the zone boundary of the reconstructed surface Brillouin zone (RSBZ). From a quantitative analysis of the $k_{\|}$ and the energy positions of this gap we determine the exact periodicity of the superstructure and the strength of the responsible electronic potential V_G. Furthermore, we discuss the shape of the Fermi surface as observed in the Fermi surface maps. Although for the 2 ML system, the band gap could not be observed in the photoemission data, the back folding can unambiguously be observed by the existence of replicas of the Fermi surface and band dispersion in the neighboring surface Brillouin zones.

II. EXPERIMENTAL DETAILS

The measurements were performed in a UHV setup composed of a molecular beam epitaxy (MBE) chamber for sample preparation and the spectrometer chamber for the ARUPS measurements. Before the Ag deposition, the Cu(111) substrate was prepared by repeated sputter-annealing cycles, using Ar^+ at a voltage in the range of 1.5–3 kV and an annealing temperature of approximately 800 K. The quality of the substrate was checked by x-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED).

The Ag atoms were evaporated from an electron-beam heated crucible with a deposition rate of about 0.5 ML/min. The substrate was kept at 200 K during the deposition, and slightly annealed at 100 °C for about 10 min afterwards. The amount of deposited Ag was checked by measuring the *d*-band intensities and the development of the surface state bands in the ARUPS data.[29] The second monolayer was grown subsequently on the first monolayer by an additional deposition and annealing cycle, in the same way as described above.

The ARUPS measurements have been performed with a high-resolution photoelectron analyzer SES 200 in combination with a monochromatized VUV lamp (GAMMADATA) for the photoexcitation. The energy resolution for HeI_α ($h\nu = 21.23$ eV), consisting of contributions from the finite linewidth of the light source and the analyzer resolution, was approximately 3 meV. The angular resolution was 0.3°.[30] All photoemission data were recorded at about 40 K, at which the measured surface state linewidth is already close to its minimum. At lower temperatures, the surface deteriorates significantly faster.[5,29] The angle resolved mode of the analyzer allows a parallel detection of a range of approximately ±6°, which covers the whole occupied part of the nearly parabolic dispersion of the Shockley state on Cu(111). The contour maps for constant energy, in particular the Fermi surface maps (FSMs), were obtained by subsequent measurements of data sets at different tilt angles (rotational degree of freedom perpendicular to the slit direction of the analyzer). After a series of five measurements with increasing tilt angle, the sample was "refreshed" by annealing for a few minutes at 100 °C.

For the determination of the exact position of the gap in the Shockley state band, it is very important to measure the photoemission spectra precisely at the high-symmetry points. A slight rotation of the sample off the high-symmetry direction ($\bar{\Gamma}$-$\bar{M}$ in our case, see Fig. 3) leads to a significant shift of the gap position towards the Fermi level.

III. RESULTS AND DISCUSSION

The Ag/Cu(111) system has already been studied intensively by photoemission exploring the Shockley states modification at low coverage[17,19,20,31,32] and the quantum well states at thick layers.[33] As previously reported[20,23] and also observed for other systems,[11,22] one can observe in the photoemission data for submonolayer coverages a superposition of two independent Shockley-state bands (not shown here), one at higher binding energies with a band minimum at $E_B^0 = 435$ meV, corresponding to clean Cu(111) surface areas, and the second one with $E_B^0 = 241$ meV, associated with Ag islands with the thickness of 1 ML.[20] With our method of surface preparation, the mobility of the Ag atoms at the surface is high enough to form closed and well ordered islands where the Shockley state exists. With increasing Ag coverage, the intensity of contribution from the Ag islands increases until the whole substrate surface is covered by one closed Ag monolayer.

A. 1 ML Ag on Cu(111)

At 1 ML we get only one Shockley state band as displayed in Fig. 1. The photoemission intensity is given on a grey scale versus the binding energy E_B and the parallel momentum $k_{\|}$. The orientation of the sample was chosen to have the parallel momentum along the $\bar{\Gamma}$-$\bar{M}$ direction of the surface Brillouin zone (SBZ). The photoemission intensity $I(E_B, k_{\|})$ shows clearly an abrupt decrease around $k_{\|} \approx \pm 0.15$ Å^{-1} and restores close to the Fermi level. As already interpreted by Schiller *et al.*,[23] this intensity variation is caused by the opening of a band gap, resulting from the presence of the superstructure in the 1 ML system. Note that by the evaporation at room temperature, what has led to a triangular superstructure in previous investigations,[19,20] we observe the same phenomenon, however, it was not possible to perform a reliable quantitative analysis on these data because of the higher concentration of defects in these films. It was demonstrated that in this case well ordered monolayers can be produced by a weak annealing after the deposition.[34]

To understand the observed effect one has to start with the properties of the Shockley state of the clean Cu(111) surface. The Shockley state on Cu(111)—and also on Ag(111) and

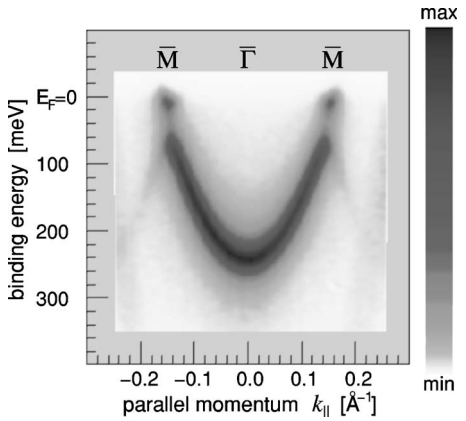

FIG. 1. Photoemission data on Cu(111) covered with 1 ML of Ag measured with HeI$_\alpha$ at T=40 K. The photoemission intensity $I(E_B,k_\parallel)$ is given on a grey scale (high intensities appear dark) versus the binding energy E_B and the parallel momentum $k_\parallel$ along the $\bar{\Gamma}$-$\bar{M}$ direction in the first Brillouin zone (see Fig. 4).

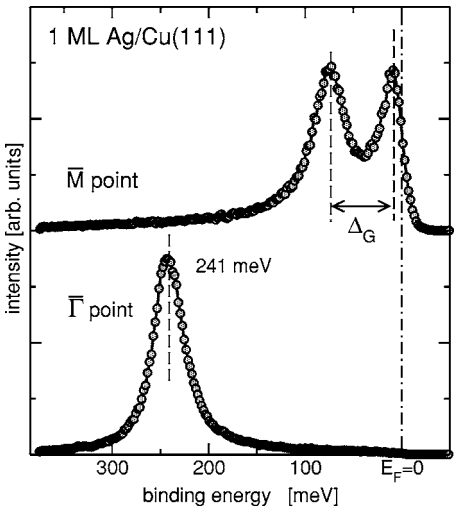

FIG. 2. Photoemission spectra [energy dispersion curves (EDCs)] at normal emission ($\bar{\Gamma}$) and at $k_\parallel$=0.151 Å^{-1} ($\bar{M}$). The maximum binding energy amounts to E_B^0=241±2 meV. The gap size at the $\bar{M}$ point is Δ_G=69±2 meV centered at 39±2 meV (from least squares fits of the band dispersion).

Au(111)[5]—behaves as a nearly free electron (NFE) state in two dimensions. The $k_\parallel$ range where the Shockley state is occupied—and therewith is accessible by ARUPS—is centered at the $\bar{\Gamma}$ point and lies far away from the zone boundaries of the surface Brillouin zone (SBZ). Therefore, the dispersion and the Fermi surface is isotropic within the experimental certainty, or with other words the dispersion has cylindrical symmetry. For the Ag(111) surface, for example, the $\bar{M}$ point, as the point on the zone boundary closest to $\bar{\Gamma}$, lies at about $k_\parallel(\bar{\Gamma}\text{-}\bar{M})\approx 1.26$ Å^{-1}, which is a factor of 16 larger than the Shockley state Fermi vector $k_F \approx 0.08$ Å^{-1}. For clean Cu(111) one gets approximately a factor of 6.[5] Since in the NFE model the influence of the lattice periodicity becomes significant only close to the zone boundaries, we can usually not observe by ARUPS a deviation from the parabolic dispersion of the Shockley states on clean and unreconstructed noble metal surfaces.

In reconstructed surfaces or for overlayers with a commensurate or quasicommensurate superstructure, the size of the surface Brillouin zone can be significantly reduced. In the case for clean Au(111), for example, there exists the peculiar herringbone pattern due to a $22\times\sqrt{3}$ reconstruction of the top-most Au layer, or 1 ML Xe on Cu(111) which forms a commensurate $\sqrt{3}\times\sqrt{3}$ superstructure. The influence of the reduced surface Brillouin zone can immediately be observed in the photoemission data[12,28] by the appearance of replicas of the Shockley state around the new $\bar{\Gamma}$ points and the appearance of band gaps at the RSBZ boundaries. This effect is usually called "back folding."

In the case of 1 ML Ag on Cu(111), the superlattice of the triangular reconstruction corresponds to a factor of approximately nine times the Cu(111) surface lattice parameter. Thus the $k_\parallel$ vector from the $\bar{\Gamma}$ point to each point at the zone boundary of the reconstructed SBZ (RSBZ) is approximately nine times smaller than the original SBZ. From an analysis of the dispersion in Fig. 1 we obtain distance for $\bar{\Gamma}$-$\bar{M}$ of about 0.151±0.005 Å^{-1}. This is slightly smaller than the Shockley-state Fermi vector of the shifted Ag(111) Shockley state on the monolayer system ($k_F\approx 0.163$ Å^{-1}), a fact that has significant consequences for the shape of the Fermi surface.

In Fig. 2, we present the energy distribution curves (EDCs) at the normal emission and at the $\bar{M}$ point with a parallel momentum $k_\parallel$=0.151 Å^{-1}, equivalent with vertical cuts through the intensity distribution in Fig. 1 at the band minimum and the gap range, respectively. At normal emission, the Shockley state appears as one single line with a maximum position of E_B^0=241 meV and a full width at half maximum of 37 meV. The values for clean Cu(111) under the same experimental conditions are 435 and 23 meV, respectively.[5] Whereas the shift of the Shockley state is an intrinsic property of the monolayer system, the larger linewidth for the monolayer system is a result of the increased number of defects in the modified surface (also leading to an increased background intensity, clearly visibly by the existence of a Fermi edge in these spectra).

In the EDC of the gap range in Fig. 2, one can observe two spectral features representing the lower and the upper edge of the band gap at $\bar{M}$. The distance between the two peaks is close to the value of the gap size Δ_G=69±2 meV which we extract more precisely by a least squares fit of the dispersion above and below the gap, considering the influence of the Fermi distribution for energies close to E_F.[35] From these fits we can also extract the distance from the $\bar{\Gamma}$ point to the $\bar{M}$ point of the RSBZ. With 0.151±0.005 Å^{-1} we obtain a value which is in agreement with the literature.[23] From this value one can calculate the size of the superlattice by

$$x = \frac{\sqrt{\frac{8}{3}}\pi/a_{\mathrm{Cu}}}{|k_{\parallel}(\bar{\mathrm{M}}) - k_{\parallel}(\bar{\Gamma})|}, \tag{1}$$

with the lattice constant a_{Cu} of FCC copper at the respective temperature and x being the ratio between the period length of the triangular structure and the atomic distance at the Cu(111) surface. From this formula we obtain from the photoemission data an estimated value of $x=9.4\pm0.1$, with a rather large incertainty compared to other experimental methods. However, these results are in good agreement with the theory. The calculations of the favorable relaxed atomic structure of a complete monolayer of Ag on Cu(111) surface by extended tight-binding quenched molecular dynamics simulation (ETBQMD) demonstrates that the lowest adsorption energy is obtained for a pseudoepitaxy superstructure $p(n\times n)$ with $n=10$. Scanning tunneling microscopy (STM) and surface x-ray scattering[34] (SXRD) measurements give a reconstruction constant which is slightly different.

The details of the atomic corrugation obtained by STM demonstrate the presence of two or three kinds of triangles; a large one with 6 atoms protuding in the center, a medium sized one with three atoms in the center, and small triangle with only one center atom.[31] The distance between two neighboring triangles with large and medium size is equal to nine times the nearest neighbor distance of fcc Ag $d_{\mathrm{Ag—Ag}}=a_{\mathrm{Ag}}/\sqrt{2}$ while it is only eight times $d_{\mathrm{Ag—Ag}}$ between two neighboring small triangles. SXRD which is sensitive to both Cu and Ag lattices shows the presence of two superstructures, namely, 9×9 and 10×10 relatively to the Cu substrate.[34] We attribute the noninteger superlattice parameter (9.4 ± 0.1) resulting from our ARUPS investigation to the coexistence of the two or three different triangular sites (thus, different distances between the triangular structures), as it was observed already by STM.

The surface state appears much more intense in the first SBZ than in the adjacent ones. Therefore, the grey-scale plot in Fig. 1 does not clearly display the dispersion of the Shockley states left and right from the one centered at normal emission. To get rid of this intensity effect one can take the derivative of the intensity distribution or simply rescale the intensity to amplify the low-intensity range. Another possibility is to tilt the sample out of the normal emission direction. With a tilt angle of approximately 7°, the parallel angle detection of the analyzer gives a cut through two adjacent second RSBZ, including the two $\bar{\Gamma}$ points and the $\bar{M}$ point in between (see Fig. 3). Figure 4 shows the photoemission data along this line. Due to identical experimental symmetry, the two parabolas appear with the same intensity. Although the crossing of the two Shockley-state bands is obvious, the intensity change in the gap range is much less pronounced than at the zone boundary of the first RSBZ. However, the energy position and the distance of the crossing point from the $\bar{\Gamma}$ points confirms the results of the quantitative analysis described above (see the 2 ML system).

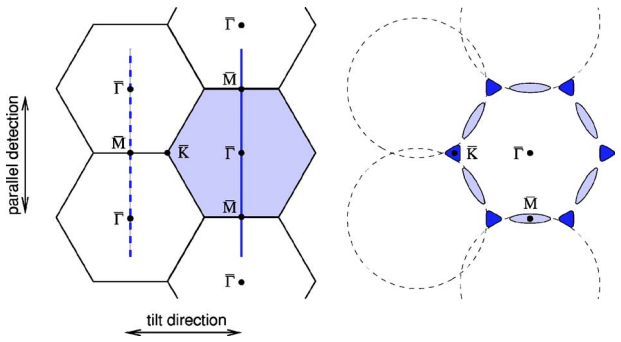

FIG. 3. (Color online) The left panel displays the position of the high symmetry points of the reconstructed surface Brillouin zone (RSBZ) and the measured $k_{\parallel}$ range of the data in Figs. 1–6; the first RSBZ is shaded. The right panel shows the Fermi surface of the Shockley state as a result of the Ag supercell.

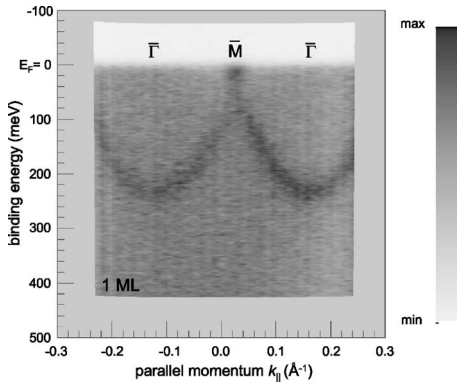

FIG. 4. Back-folding of the 1 ML system, measured along $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ in the second reconstructed Brillouin zone (dotted line in the left panel of Fig. 3). The intensity of the two surface state bands is identical but the gap appears less clear than in the first RSBZ.

B. Fermi surface maps and equipotential lines

Figure 5 shows a grey-scale plot of the photoemission intensity $I(E_B=\mathrm{const},\boldsymbol{k}_{\parallel})$ at three different binding energies as a function of the parallel momentum $\boldsymbol{k}_{\parallel}=(k_x,k_y)$. The vertical axis labeled k_y is the horizontal k axis in the plots of the band dispersion in Figs. 1, 4, and 6. The horizontal axis (k_x) represents the tilt angle, perpendicular to the analyzer slit direction. The plot at the left side, measured at $E_B=E_F$ gives the Fermi surface map (FSM), the middle and the right data

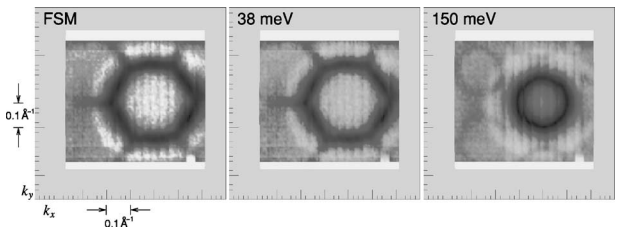

FIG. 5. Contours of the photoemission intensity $I(\boldsymbol{k}_{\parallel})$ at constant binding energies; high intensities appear dark. Left: Fermi surface map (FSM) at $E_B=E_F=0$ meV, middle: $E_B=38$ meV, right: $E_B=150$ meV. The plots are a result of subsequent measurements with different tilt angles (see Fig. 3).

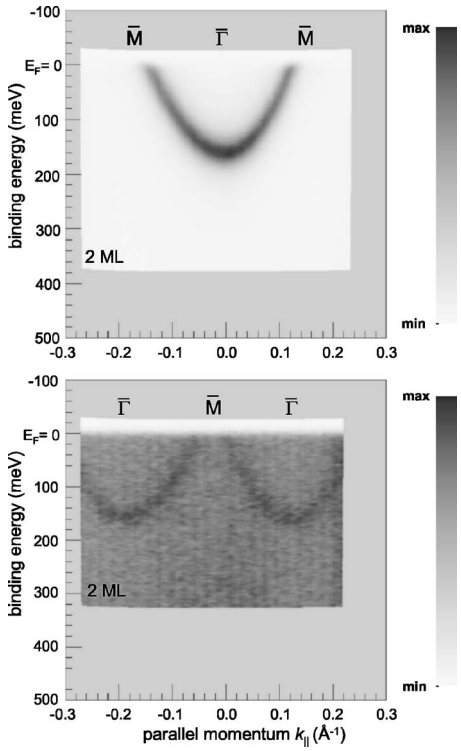

FIG. 6. Photoemission data of the 2 ML system, measured in the first (upper panel) and second RSBZ (lower panel) along $\bar{\Gamma}$-$\bar{M}$. In comparison to the 1 ML system, the Shockley state is shifted further towards E_F, the lower gap edge lies in the unoccupied energy range at approximately 38 meV above E_F.

set were taken at E_B=38 and 150 meV, respectively. Analogous to the intensity maps in Figs. 1 and 6 the intensity of the surface states is highest in the first SBZ around normal emission. Here also the projected bulk band gap (i.e., the neck of the bulk Fermi surface or the L gap) appears as a bright circular area centered at $\bar{\Gamma}$. Clearly visible is the sixfold symmetry of the intensity distribution in the FSM, whereas energy contours (equipotential lines) of the occupied part of the Shockley state on clean Cu(111) are nearly perfect circles.[5]

The reduced size of the SBZ leads near the zone boundaries to an overlap of the—originally circular—Fermi surfaces (indicated by dashed lines in Fig. 3, right panel), which results in a reorganization of the Fermi surface as composed of two different features. As sketched in Fig. 3, there is a narrow ellipse around the $\bar{M}$ point, resulting from an electron pocket of the states above the band gap. In addition, there appear small triangular hole pockets at the $\bar{K}$ points where the gap lies completely above the Fermi level. Due to the finite experimental resolution, in particular the angular resolution (0.3° is equivalent with approximately 0.01 $Å^{-1}$), the border lines of the small Fermi surfaces can not be resolved in the given data set. However, the variation of the intensity along the RSBZ boundaries is obvious, caused by the ellipses at the $\bar{M}$ points and the triangles at $\bar{K}$ where the intensity is higher, and in between the gap range with lower intensity, according to the sketch in Fig. 3.

C. 2 ML Ag on Cu(111)

Increasing the Ag film thickness to 2 ML results in a significant modification of the Shockley state. One should note that for the 2 ML film it was reported that the Shockley state binding energy, measured on a sample prepared in the way described here, is not identical to the binding energy measured on 2 ML systems prepared at low temperatures with subsequent annealing.[20] This means that the structure in the second monolayer is affected by the annealing process and suggests that the dislocation-loop reconstruction, occurring by vacancies induced in the topmost Cu plane, is suppressed if the moiré reconstructed first Ag layer is covered by a second layer. This effect can be avoided by the sequential preparation method described above, which results in a formation of the dislocation loops in the top-most Cu plane.

In Fig. 6, we present the Shockley state dispersion of the 2 ML film along $\bar{M}$-$\bar{\Gamma}$-$\bar{M}$ across the first RSBZ (upper panel) and along $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ across two neighboring second RSBZs as indicated in Fig. 3. In comparison to the 1 ML system, the Shockley state shifts further towards the Fermi level, with the band minimum at a binding energy of $E_B^0 \approx 150$ meV at T=40 K. Due to this shift the Shockley states do not cross the boundaries of the RSBZ below the Fermi level anymore, and consequently, there appears no gap in the photoemission data. A detailed discussion of the binding energies of the Shockley state in dependence on the surface preparation can be found in Ref. 19 (see in particular Fig. 3 therein). From an extrapolation of the parabolic dispersions observed in the two neighboring second RSBZs we estimate the crossing of the Shockley states at the $\bar{M}$ point to 73 meV above the Fermi level. If we assume the same gap width as measured for the 1 ML system (Δ_G=69 meV) we obtain the position of the lower gap edge at ≈38 meV *above* the Fermi level, in contrast to the results by Schiller *et al.*,[23] who found the lower edge close to the Fermi level. It should be noted that their sample temperature during the measurements (T =150 K) was even higher than ours (40 K), resulting in an additional (temperature dependent) shift of the Shockley state towards E_F by about 20 meV.[36]

In addition, the data in the grey scale plots of the Shockley state dispersion in Fig. 6 do not indicate a deviation from the parabolic behavior, neither in the first nor in the second RSBZ. Therefore, we assume that the observation of a lower band edge as published by Schiller *et al.*[23] is an artifact due to the comparatively large experimental broadening of ΔE =30 meV in their data.

The sample temperature during the Ag deposition represents the key parameter for the observation of the gap opening in the Shockley state of the 1 ML system. We find that the preparation at 200 K followed by insufficient or no annealing does not lead to a surface where the gap opening appears. The reason is probably connected with the moiré-triangular transition process.[19] By increasing the temperature and/or the annealing time, the triangular structure becomes more and more dominant, resulting in an improvement of the visibility of the gap in the ARUPS data. From the binding energy of the Shockley state we conclude that the formation of the gap presented and analyzed here is representative for

the quasicommensurate triangular structure, contrary to previous results in the literature.[23]

IV. CONCLUSIONS

Our high-resolution ARUPS data show clearly the backfolding of the Shockley-type surface state on the Cu(111) surface covered with both 1 and 2 ML Ag. In the case of the triangular 1 ML system one can observe a band crossing of the Shockley states from two adjacent reconstructed surface Brillouin zones (RSBZs) below the Fermi level. This induces the development of a Shockley state band gap and a significantly modified Fermi surface. We analyzed quantitatively the gap along the $\bar{\Gamma}$-$\bar{M}$ direction and found a gap width of $\Delta_G = 69 \pm 2$ meV centered at a binding energy of 39 ± 2 meV. An careful analysis of the crossing position along this direction indicates a supercell size of (9.4×9.4) with an accuracy of ± 0.1. The 2 ML system shows in principle the same backfolding. However, the Shockley state is shifted further towards the Fermi level and the band gap can not be observed in the occupied states anymore. Therefore, we estimated the position of the lower band gap edge by an extrapolation of the band dispersion to a binding energy of 38 meV clearly above the Fermi level. Our results are quantitatively different from recently published results in the literature, which showed the first observation of the gap in this system.[23]

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