RAPID COMMUNICATIONS

PHYSICAL REVIEW B **78**, 161408(R) (2008)

Importance of surface states on the adsorption properties of noble metal surfaces

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(Received 28 August 2008; published 30 October 2008)

The Shockley-type surface state on noble metal (111) surfaces can be used as a sensitive probe for different surface modifications, adsorption processes, and interactions between adsorbate and substrate. On the model systems of Cu and Au(111) surfaces covered with noninteger monolayers of Ag we demonstrate that angle-resolved photoelectron spectroscopy is able to identify the growing positions of adsorbates by the investigation of the Shockley state. Vice versa, we discuss in a simple model to what extent the surface states themselves influence the adsorption process and determine the favored surface for physisorbed closed-shell systems.

DOI: 10.1103/PhysRevB.78.161408 PACS number(s): 73.20.At, 68.43.−h, 79.60.Dp

The influence of metallic surface states on the surface structure properties and adsorption processes is intensively discussed in literature.[1–7] In spite of their minor contribution to the total electronic structure in comparison to bulk states surface states can play a crucial role in many physical phenomena. This has been impressively demonstrated by calculations based on density-functional theory for the surface lattice relaxation of Al(100) (Ref. 5) and Be($10\bar{1}0$).[6] A further interesting example is the superlattice formation of Ce atoms on Ag(111) at low temperatures due to the interaction of the adsorbate with Shockley-state electrons.[7] Moreover one speculates about the importance of surface states on the bonding of physisorbed atoms and molecules and on catalytic processes.[1–4]

Two-dimensional electronic states are formed on the (111) surface of the noble metals Cu, Ag, and Au due to the broken lattice invariance at the interface between the vacuum and the crystal. These Shockley-type surface states are partially occupied and show a nearly perfect parabolic dispersion[8,9] with a band mass m^* giving, by definition, the two-dimensional density of states (DOS). Due to their strong localization at the surface, Shockley states represent a sensitive probe for surface modifications, e.g., by Ag deposition[10–15] or by weakly interacting rare-gas adsorbates.[16–20] In both cases, an energy shift of the surface state to lower binding energies has been observed. While the former can be explained by surface-potential changes, the latter has been discussed in detail in terms of a Pauli-repulsive interaction between the rare-gas atoms and the noble metal surface.[1,2]

In this Rapid Communication we demonstrate to what extent Shockley states of noble metals are of importance for the adsorption behavior and determine in particular the favored surfaces for physisorbed Xe atoms. We carried out angle-resolved photoelectron spectroscopic (ARPES) investigations on Cu and Au(111) surfaces modified by noninteger Ag monolayer (ML) coverages in a low-pressure Xe atmosphere. Hence, a single experiment covers the investigation of two different surfaces [here N and $(N-1)$ atomic Ag layers][15] at exactly the same experimental conditions, e.g., sample temperature and Xe pressure. Such noninteger heterosurface systems are appropriate models for investigating quantum size effects and determining preferred and inhibited adsorption positions for Xe, turning out to be a probe for the *local* density of states (LDOS). Whereas by the means of the established method of photoemission on adsorbed xenon (PAX) the Xe 5p electrons are investigated[21–23] we quantify the modification of the Shockley states[18,24] and propose a simple model explaining the experimental observations. We give evidence of the important role of surface states in the adsorption of rare gases on noble metal surfaces indicating its considerable influence on more complex surface processes.

The ARPES experiments have been performed under UHV conditions (base pressure of 5×10^{-11} mbar) on a GammaData Scienta R4000 spectrometer equipped with a monochromatized He discharge lamp. The analyzer allows us to measure an angular range of up to ±15° with a resolution of ≈0.3° in a single experiment, which is sufficient to display the complete dispersion $E_B(k_\parallel)$ of the occupied surface state. The total-energy resolution amounts to $\lesssim 5$ meV. The substrates have been prepared by standard sputtering and annealing cycles as described elsewhere[9] until the surface-state linewidth at normal emission reached the minimum values at maximum binding energies. The quality of the sample surfaces has been checked by core-level spectroscopy and low-energy electron diffraction. For the Ag deposition we used a Knudsen cell, controlled by a quartz microbalance. The (111) oriented Cu and Au substrates were cooled down to $T<250$ K during Ag deposition to prevent alloy formation and subsequently annealed at room temperature to restore the surface order. On both substrates one observes a nearly perfect layer-by-layer growth of the Ag films up to 2 ML on Cu(111) (Ref. 25) and even at larger coverages on Au(111).[14,26] Therefore we were able to prepare noninteger coverages of Ag on Cu and Au(111) with both clean and 1 ML Ag covered regions or 1 and 2 ML thick Ag islands, respectively. For the investigation of the rare-gas adsorption these surfaces were cooled down to $T\leq 60$ K and exposed to a Xe pressure of $p_{\mathrm{Xe}}\approx 5\times10^{-8}$ mbar at the measurement position. All presented ARPES experiments were performed at this constant sample temperature low enough to adsorb a single Xe monolayer but still sufficiently high to guarantee a large mobility of the Xe atoms.[18]

The photoemission data on 0.6 ML Ag/Cu(111) (see Fig. 1, top left) show a superposition of the surface states of clean

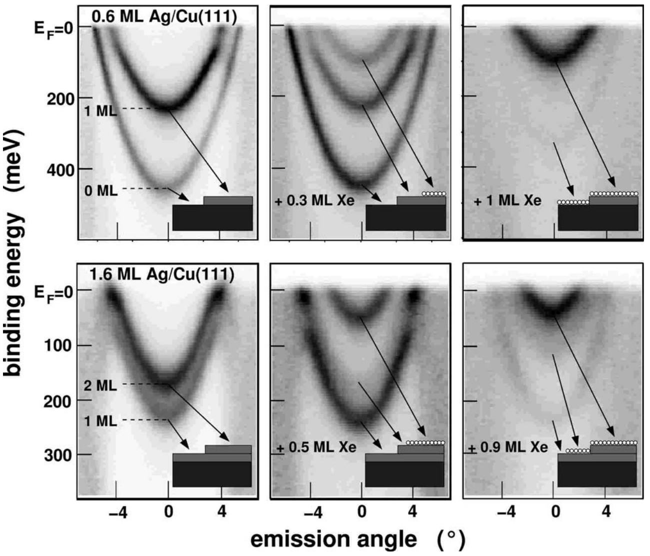

FIG. 1. Surface-state bands of 0.6 ML Ag/Cu(111) (top) and 1.6 ML Ag/Cu(111) (bottom) at $T=40$ K. The evolution of photoemission intensity of the surface states and the formation of new states with increasing Xe deposition (from left to right) indicate the favored adsorption position of Xe monolayer islands. (Top): Xe prefers regions with 1 ML Ag rather than the clean substrate. (Bottom): Xe prefers regions with 2 ML Ag rather than regions with a 1 ML thick Ag film.

substrate regions and Ag covered areas with almost the same band mass m^* and separated in energy by about 220 meV.[24] The slight deviation of the parabolic dispersion at large emission angles for 1 ML Ag/Cu(111) is due to a 9×9 surface reconstruction inducing a small band gap at the reduced surface Brillouin-zone boundary.[12,13] The microscopic origin of this superstructure can be neglected in the present context, provided that it can be assigned to a reproducible surface-state dispersion from which all relevant model parameters can be determined. Figure 1 (bottom left) shows the photoemission results of a 1.6 ML thick Ag film on Cu(111). These data also show two different surface-state bands (at $E_B=230$ and 170 meV maximum binding energies) which are attributed to surface regions with 1 and 2 ML thick Ag coverages, respectively.

This can be analogously observed for Ag on Au(111). After deposition of 0.6 ML Ag on Au(111) the photoemission data show both the surface states of clean Au and of the 1 ML Ag/Au(111)—separated in energy by about 155 meV—due to the monolayer island growth (see Fig. 2, top left). The characteristic Rashba splitting of both states is discernible, slightly smaller for 1 ML Ag/Au(111) than for clean Au(111) whereas the band mass m^* is significantly larger.[14] In addition, the photoemission results on 1.5 ML Ag/Au(111) are presented in Fig. 2 (bottom left) showing the surface states of the first and the second Ag monolayer.

The gradual modification of the Cu(111) and Au(111) surface states by Ag deposition was already studied in detail by scanning tunneling spectroscopy and ARPES and discussed in terms of potential changes in the surface region.[11,14] The prepared substrate surfaces with regions of 0 and 1 ML thick Ag films on the one hand, as well as 1 and 2 ML thick films on the other, and their respective surface states allow the determination of the favored surface for the rare-gas physisorption. The photoemission experiments on Xe adsorption on Ag/Cu(111) are shown in Fig. 1. For the system 0.6 ML Ag/Cu(111) one clearly observes the evolution of the surface states with increasing Xe deposition. The state at low binding energies, linked to 1 ML Ag/Cu(111), loses intensity and a new state at even lower binding energy appears (shifted by $\Delta E_B=135$ meV).[18,19] The surface state connected to clean Cu(111) remains unchanged. Only after further Xe deposition the state of the pristine surface shifts by $\Delta E_B=125$ meV. This indicates immediately that the Xe atoms favor the adsorption on the 1 ML Ag film, where they form closed islands themselves, while the clean Cu(111) surface regions primarily remain uncovered. Figure 1 (bottom) represents the ARPES results on Xe deposition on 1.6 ML Ag/Cu(111) with surface regions of 1 and 2 ML thick Ag films. As before, the surface state at lower binding energy—here connected to 2 ML Ag films—shifts about $\Delta E_B=120$ meV while the state of the 1 ML Ag film remains unchanged. Only a further Xe coverage affects the binding energy of the 1 ML Ag/Cu(111) surface state ($\Delta E_B=125$ meV). Therefore one can conclude that the Xe-island formation on 2 ML Ag films is favored. A comparison of the adsorption energy of a single Xe atom on clean Ag(111) and on clean Cu(111) (Ref. 27) gives $E_{\mathrm{ad}}^{\mathrm{Ag(111)}}=211\pm15\ \mathrm{meV}>183\pm10\ \mathrm{meV}=E_{\mathrm{ad}}^{\mathrm{Cu(111)}}$, explaining the preferred Xe-island nucleation on Ag in agreement with the results above. Nevertheless not only the chemical character of the topmost layer of the surfaces determines the adsorption behavior. There must also be a non-negligible influence of subjacent atomic layers due to the observed Ag-film thickness dependence.

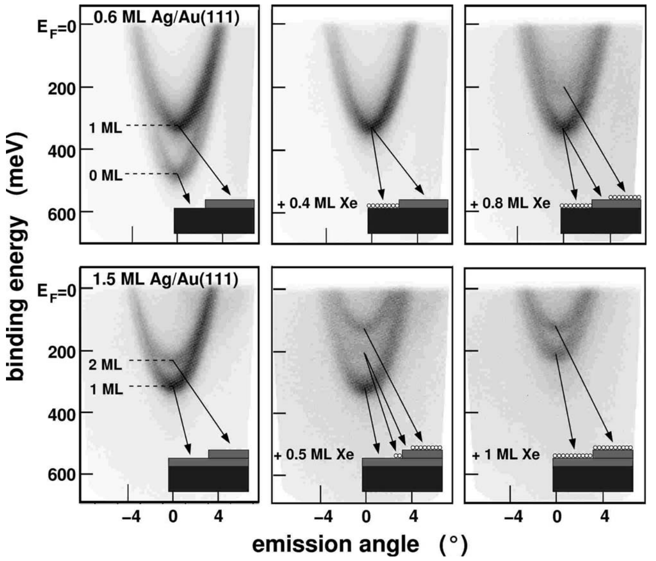

FIG. 2. Analogously to Fig. 1 for Xe/Ag/Au(111) at $T=60$ K. (Top): Xe prefers regions of the clean substrate rather than regions with 1 ML Ag. (Bottom): Xe prefers regions with 2 ML Ag rather than regions with a 1 ML thick Ag film.

To support this assumption we present photoemission results on the Xe growth on Ag films on another substrate, namely, Au(111). Remarkably, we see a significant Ag-film thickness dependence of the Xe adsorption behavior, al-

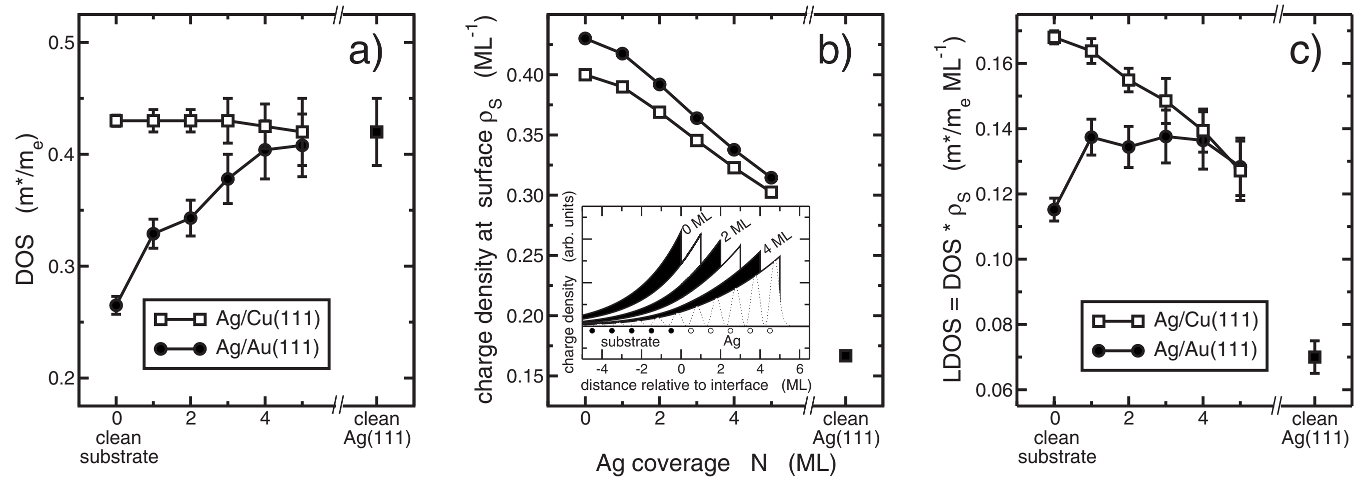

FIG. 3. Evolution of the DOS (E_F) (a) of the Shockley state of Ag/Cu(111) (□) and Ag/Au(111) (●) and their charge density ρ_S (b) as a function of the Ag-film thickness N. The values for clean Ag(111) are added. The inset in (b) shows the modeled charge-density distribution of Ag/Au(111). (c) The product of ρ_S and DOS (E_F) is a measure for the local density of the surface state (LDOS). Whereas the LDOS of Ag/Cu(111) decreases continuously with the Ag-film thickness, the LDOS of Ag/Au(111) shows a maximum at $N=1$ ML.

though the adsorption energy of Xe on clean Ag(111) $(E_{\mathrm{ad}}^{\mathrm{Ag}(111)}=211$ meV) is comparable to that on clean Au(111) $(E_{\mathrm{ad}}^{\mathrm{Au}(111)}=214$ meV).[27] The characteristic $(22\times\sqrt{3})$ herringbone reconstruction of the Au surface extends to the first few Ag layers[14] and hence is negligible for the direct comparison on Xe adsorption on 0–2 ML Ag/Au(111). Figure 2 (top) shows the data of 0.5 ML Ag/Au(111) and its evolution during Xe deposition. First of all, one observes a disappearing of the surface state of clean Au(111). As before, a new state $(\Delta E_B=135$ meV) appears at binding energies close to the 1 ML Ag/Au(111) surface state. Only a further Xe deposition induces a shift of the 1 ML Ag/Au(111) state to lower binding energies $(\Delta E_B=110$ meV). Therefore we conclude that the monolayer island formation of Xe atoms is preferred on clean and not on 1 ML Ag regions. However, one has to consider the results on Xe growth on 1.5 ML Ag/Au(111) shown in Fig. 2 (bottom). Here, one clearly observes that at the beginning of Xe deposition the surface state of 2 ML Ag films shifts by $\Delta E_B=110$ meV toward the Fermi level before the state linked to 1 ML Ag also becomes influenced $(\Delta E_B=105$ meV). This indicates a preferred Xe-island growth on the thicker Ag film rather than on areas with only 1 ML Ag. Therefore we conclude that a Xe-island formation on 1 ML Ag/Au(111) is inhibited in comparison to an adsorption on clean or 2 ML Ag covered Au(111) surface regions. This means that the behavior of the Xe growth does not change monotonously with the Ag layer thickness.

As an explanation for these observations, we propose a simple model which regards the surface density of states at the Fermi level E_F. The total DOS (E_F) is composed of both bulk and surface states. In the following discussion the contribution of bulklike states can be neglected since no influence of thin Ag-film deposition on the bulk electronic structure at E_F is observed. Just at more than 7 and 5 ML Ag on Au (Ref. 26) and Cu(111),[25] respectively, adsorbate induced quantum-well states contribute to the total DOS (E_F). Due to the quasi-free-two-dimensional surface states the effective band mass m^* is a measure for the DOS (E_F), as given in Fig. 3(a) for various Ag-film thicknesses on Cu and Au(111), respectively. In the particular case of the 9×9 reconstructed Ag/Cu(111) the deviation from the free-electron behavior was considered by an appropriate fit of the band dispersion.[13] To consider the surface-state localization we calculated the charge density at the surface ρ_S [see Fig. 3(b)] according to the penetration depth and the evolution of the binding energy with increasing Ag coverage as carried out by Hsieh and Chiang.[10] The inset of Fig. 3(b) displays the envelope of the charge density as a function of Ag-film thickness. The product of the DOS (E_F) and surface charge density is therefore a measure for the local DOS (E_F) which is shown in Fig. 3(c) as a function of Ag coverage. One can clearly observe a monotonous decay for Ag/Cu(111) with increasing Ag-film thickness N. Due to the fact that physisorbed rare gases avoid areas with a strong repulsive potential, meaning a large LDOS,[4,28] this explains the preference for Xe-island formation on the surface of the thickest available Ag film for a given heterosystem. In the case of Ag/Au(111) the LDOS (E_F) exhibits a small distinct local maximum at $N=1$ ML Ag coverage. This corresponds to the inhibited Xe monolayer growth on the 1 ML thick Ag film in favor of a Xe monolayer island formation on clean or 2 ML Ag/Au(111) surface areas. The adsorption behavior on the basis of the proposed model is also supported by ARPES on thicker Ag films. However, since the energy separation between the Nth and the $(N+1)$th surface state decreases with increasing Ag coverage in combination with the reduced signal-to-noise ratio and an enhanced state broadening after Xe deposition an accurate determination of the preferred surface is hindered.

Our results are of importance for chemisorptive interactions between surfaces and adsorbates, as well as, e.g., in organic monolayer films, where the surface state shows a huge energy shift.[29,30] First findings on weakly bound 3,4,9,10-perylene-tetracarboxylic dianhydride molecules (PTCDA) on Ag/Au(111) are in accordance with the discussed LDOS dependence. In that case, contrary to physisorbates, the preferred adsorption site is determined by a large LDOS.[31]

In conclusion we investigated noninteger Ag ML covered heterosurfaces of Cu and Au(111) for the analysis of preferred surfaces for Xe adsorption by angle-resolved photoelectron spectroscopy. We determined a significant dependence of the adsorption properties on the Ag-film thickness without, however, disguising the influence of the substrate. The observed behavior can be explained by a simple model exclusively considering the DOS and the localization of the modified Shockley states. These results give strong evidence for the non-negligible or even dominant influence of surface states on adsorption behavior. Therefore, surface states must be considered particularly in the analysis of physisorption, chemisorption, and even catalytic properties. The Shockley states show usually large changes although the local energy differences, e.g., for different adsorption sites[28] are very small. Therefore, the investigation of surface states in adsorbate and thin-film systems represents an important tool for the understanding of electronic properties and interactions at interfaces. We hope that this work stimulates further theoretical investigations beyond our simplified model, which, of course, neglects certain structural aspects.

This work was supported by the Deutsche Forschungsgemeinschaft (Grant No. Re 1469/4-4) and the BMBF (Grant No. 05KS7WW1).

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