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Spin-orbit splitting of the Shockley state in the Ag/Au(111) interface

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We have studied the modification of Au(111) surface state parameters with Ag deposition. We unambiguously evidence a continuous decrease in the spin-orbit splitting of the two surface state subbands upon increasing Ag coverage. An annealing leads to the formation of a chemically disordered Ag-Au alloy. This alloy formation is accompanied by an increase in the spin-orbit splitting. We established a quantitative correlation between the amplitude of this splitting and the relative amount of Au and Ag atoms probed by the surface state wave function proving the atomic character of the spin-orbit splitting. Control of the Ag-Au interface allows a continuous fine tuning of surface state properties; in particular, the *k*-dependent spin polarization.

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The (111) surfaces of noble metals that present a *sp* surface state (Shockley state) close to the L point of the Brillouin zone,[1] have been extensively studied by angle-resolved photoelectron spectroscopy (ARPES) in the last two decades.[2,3] This electronic state is a paradigm of two-dimensional electronic systems, and it has been used to study fundamental interactions such as electron-electron or electron-phonon interactions in solids.[4,5] Recently, the effect of spin-orbit interaction on the Shockley state has been evidenced.[6,7] In Au(111), this interaction yields a splitting of the Shockley band and the formation of two spin-polarized subbands.[8,9] A similar behavior is observed on the *d*-derived surface state in Li/W(110).[10,11] This splitting is, in principle, forbidden in centrosymmetric solids due to combined time reversal and inversion symmetries.[12,13] As an example, it appears in noncentrosymmetric semiconductors with blende structure such as GaAs,[14] but not in centrosymmetric semiconductors with diamond structure such as Ge.[15] The Au structure is centrosymmetric, but there is a breakdown of the inversion symmetry due the surface potential. However, it was shown that this surface potential cannot explain quantitatively the magnitude of the splitting, and it was suggested that atomic spin-orbit interaction plays an important role.[16] This atomic origin explains the large splitting observed on the surface state of Au (heavy metal and large spin-orbit interaction), whereas a vanishing one is observed in the case of Ag.[17] In this paper, we will show that this splitting can be continuously tuned by controlling the Ag/Au interface. Its evolution with Ag film thickness and with annealing leads us to the conclusion that the key parameter is the amount of Au atoms probed by the evanescent surface state. This result demonstrates that the spin-orbit coupling on the Shockley state has essentially an atomic origin.

The measurements were carried out in a UHV setup composed of a molecular-beam epitaxy chamber for the elaboration and characterization of the surfaces and a photoemission chamber with a high resolution Scienta SES 200 analyzer ($\Delta E < 5$ meV and $\Delta\theta < 0.5°$). Ag ultrathin films were prepared by molecular-beam epitaxy from a Knudsen cell [rate $\simeq 0.5$ monolayer (ML)/mn] on a Au(111) substrate with a miscut better than 0.1°. The sample was characterized by low energy electron diffraction and Auger electron spectroscopy. The substrate deposition temperature was 300 K to get a sharp Ag/Au(111) interface and a layer by layer growth, as actually claimed in the literature.[18–20] However, an alloying is observed with increasing temperature. All the ARPES measurements have been carried out at $T = 80$ K with He I ($h\nu = 21.22$ eV) or Ar I ($h\nu = 11.83$ eV) excitation energies. The measurement temperature has been chosen in order to minimize contamination and to avoid interdiffusion.

The photoemission spectra as a function of energy and momentum of the Shockley surface state of Au(111) substrate, a 0.5 ML, and a 1 ML Ag film, are reported in Fig. 1. The Au(111) spectrum exhibits a Shockley band whose energy at the center of the surface Brillouin zone ($\overline{\Gamma}$ point) is

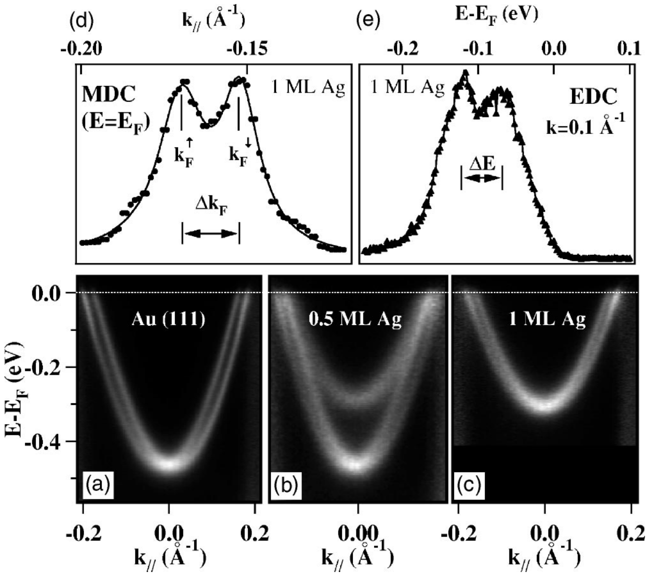

FIG. 1. ARPES intensity as a function of wave vector and energy for the Au(111) substrate (a), a 0.5 ML Ag film (b), and a 1 ML Ag film on Au(111) (c). Momentum distribution curves at E_F (d) and energy distribution curve at $k = 0.1$ Å^{-1} (e) for the 1 ML Ag film.

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$E_0=E(\overline{\Gamma})-E_F=-475$ meV, in good agreement with published data.[7] This band is split by spin-orbit interaction into two spin-polarized subbands. Due to the nearly free-electron-like character of the Shockley state, its Fermi surface is composed of two concentric circles in the first Brillouin zone.[7] The dispersion relations of these subbands can be written as

$$E(\vec{k}_{\parallel}) = \frac{\hbar^2 k_{\parallel}^2}{2m^*} \pm \alpha_R k_{\parallel}, \tag{1}$$

where the Rasbha coefficient (α_R) measures the magnitude of the spin-orbit interactions $H_{S.O}=\alpha_R(\vec{e}_z\times\vec{p})\ \vec{\sigma}$ (Ref. 21) and m^* is the electron effective mass. From a fitting procedure of the two dispersive subbands by parabolas, a value of $2\alpha_R^{Au}=0.66\pm0.08$ Å eV can be estimated. This corresponds to a difference in Fermi momentum of the two subbands $\Delta k_F=|k_F^{\uparrow}-k_F^{\downarrow}|=0.023\pm0.003$ Å^{-1}, as defined on the momentum distribution curves (MCD's) in Fig. 1(d), in perfect agreement with the previous published value.[17]

Similar spin-orbit split bands are also observed in the Ag/Au(111) system. This is illustrated in Figs. 1(b) and 1(c), where we report the respective photoemission intensities for 0.5 and 1 ML Ag films deposited on Au(111). For the 1 ML Ag film, the Shockley state at the $\overline{\Gamma}$ point is found to be shifted by 170 meV toward the Fermi energy ($E_0=-305$ meV). This latter value can be understood as the surface state energy of Au(111) perturbed by a modified potential in the last layer due to Ag atoms. The various electronic parameters are also affected by the modification of the potential. Firstly, we observe a significant increase in the electron effective mass from 0.26 m_0 for the bare substrate to 0.33 m_0 for the 1 ML film. Secondly, the value of the splitting measured by the momentum separation (Δk_F) between the two subbands at E_F is reduced by about 20% with respect to pure Au(111) surface. However, due to the very different effective mass, the energy between the two subbands at a given momentum [Fig. 1(d)] is significantly reduced (about 40%) with respect to Au(111). An interesting behavior is observed in the spectra of submonolayer films ($0<\theta<1$ ML). The normal emission spectra exhibit two spectral features at $E_0=-475$ meV and $E_0=-305$ meV, as shown in Fig. 1(b) for $\theta=0.5$ ML. Upon increasing the Ag coverage, a balance of intensity of these two series of dispersive bands is observed. Such a behavior was previously observed in similar systems like Ag/Cu(111).[22,23] The two structures can be interpreted by surface states confined in the noncovered Au terraces ($E_0=-475$ meV) and in the Ag islands ($E_0=-305$ meV).[23,24] The Ag thickness dependence follows an exponential behavior, as already reported.[20]

In Fig. 2, we focus on the evolution of the MDC at the Fermi energy (E_F). This spectrum corresponds to a cut of the Fermi surface along a radial direction of the Brillouin zone. The solid lines represent an adjustment of the experimental spectra (with two lorentzians with the same width), which allows an estimation of the momentum spin-orbit splitting (Δk_F) at E_F. This figure shows that two contributions are resolved up to 3 ML films, whereas for larger thicknesses, only a broad feature is observed. Nevertheless, the anomalous large width, larger than the experimental resolution, reveals a remaining spin-orbit induced band splitting of the surface state. From the Ag thickness dependence of Δk_F, the evolution of the Rashba coefficient can be obtained: $2\alpha_R$, equal to 0.66 ± 0.08 for Au(111), tends to 0.11 ± 0.08 in the limit of large Ag thickness, in agreement with the value obtained for Ag(111) single crystal $2\alpha_R\approx0.06$.[17]

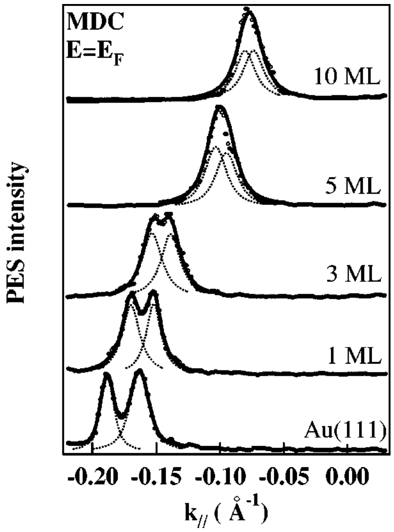

FIG. 2. MDC's taken at $E=E_F$. The dotted lines correspond to an adjustment with two lorentzians, which allows us to estimate the momentum splitting of the two subbands.

Auger spectroscopy indicates interdiffusion with increasing temperature. Figure 3(b) illustrates this alloying effect by showing the temperature dependence of the Au NVV Auger intensity for 1 and 3 ML films. The interfaces have been prepared at 100 K for the 1 ML film and 300 K for the 3 ML film. In both cases, upon increasing temperature, the Auger signal is at first nearly constant (with a slight negative slope) and then exhibits a large increase above a characteristic temperature. The negative slope is likely to be due to a smoothing of the Ag layer. This behavior is especially marked for the 1 ML because a deviation from a perfect layer by layer growth occurs due to the low preparation temperature (100 K). The strong increase in the Au Auger intensity above a characteristic temperature reveals segregation of Au atoms at the surface and the formation of a Ag—Au alloy. This characteristic temperature is thickness dependent since it is about 300 K for the 1 ML film and 450 K for the 3 ML film. The influence of the alloy formation on the electronic properties is evidenced in Fig. 3 by comparing the dispersion of the 3 ML Ag film surface state after an annealing at 510 K [Fig. 3(a)] and after an annealing at 570 K [Fig. 3(b)]. Two effects are clearly evidenced: first, a 200 meV energy shift to lower energy in the 570 K spectrum and second, a correlated increase in the splitting of the two spin-polarized subbands. The values of $E_0=-410$ meV and $2\alpha_R=0.5$ we obtained after the 570 K annealing are close to those observed in a pure Au(111) surface. This result suggests that the surface is essentially composed of Au atoms after such an annealing.

Figure 3(d) shows the annealing temperature dependence of the surface state energy at the $\overline{\Gamma}$ point ($-E_0$) and the

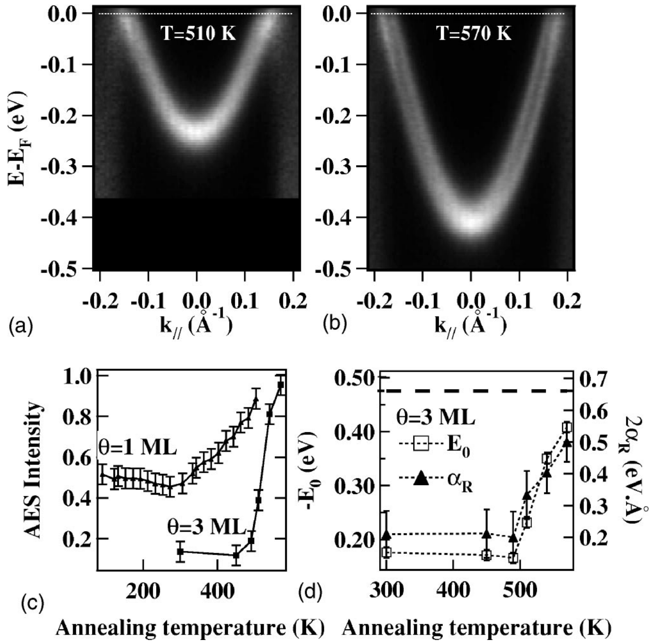

FIG. 3. Photoemission intensity as a function of energy and momentum for a 3 ML film after an annealing at 510 K (a) and at 570 K (b). (c) Annealing temperature dependence of the Au Auger intensity for a 1 and a 3 ML Ag film on Au(111), the spectra have been recorded with a time step of 30 s. (d) Annealing temperature dependence of the surface state energy at the $\overline{\Gamma}$ point and Rashba parameter [the horizontal dashed line represents values for the Au(111)].

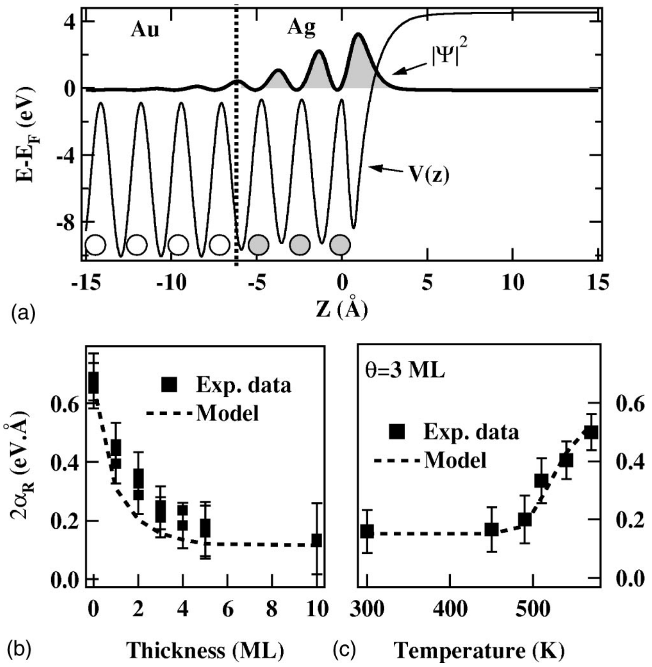

FIG. 4. (a) One-dimensional electronic potential and charge density ($|\Psi|^2$) of the Shockley state for a 3 ML Ag film (the white and gray circles represent the Au and Ag layers, respectively). (b) Experimental and simulated Rashba parameters for room temperature annealed Ag films. (c) Evolution of the Rashba parameter for a 3 ML film as function of annealing temperature.

Rashba coefficient for a 3 ML Ag film. Both quantities remain approximately constant for annealing temperatures smaller than 500 K and present a pronounced change above 500 K. Such dependences can be easily interpreted by the formation of a Au-rich alloy at the surface. What we would like to point out is the existence of very well-defined surface state dispersion in spite of the existence of an alloy, i.e., with chemical disorder, at the surface. This robustness of the Shockley surface state was previously observed at the (111) surface of a disordered $Cu_{0.9}Al_{0.1}$ alloy,[25] and is in agreement with theoretical predictions. Although the wave vector is not a good quantum number in chemically disordered alloys, coherent-potential-approximation calculations show that the spectral function exhibits well-defined peaks.[26]

It was proposed that atomic spin-orbit plays an important role in the formation of the two spin-polarized surface state subbands in Au(111).[16] As spin-orbit interactions are larger in Au atoms than in Ag ones, the Rashba parameter in Ag/Au(111) could be proportional to the amount of Au atoms probed by the Shockley state. In the direction normal to the surface, the wave function exhibits an evanescent shape as shown in Fig. 4(a). We have reported the solution of a one-dimensional Schrödinger equation simulating the potential of a 3 ML film according to the surface potential model proposed by Chulkov *et al.*[27] This figure shows that the surface state is mainly confined in the three Ag layers, but also extends slightly into the Au substrate. According to our assumption that the spin-orbit interaction is essentially atomic-like, the effective Rashba parameter can be expressed as the mean value of the parameters of Au(111) (α_R^{Au}) and Ag(111) (α_R^{Ag}) surfaces weighted by the relative amount of Au atoms (p^{Au}) probed by the surface state:

$$\alpha_R = p^{Au}\alpha_R^{Au} + (1 - p^{Au})\alpha_R^{Ag}. \qquad (2)$$

The effect of the increase in the Ag film thickness is a large decrease in p^{Au} probed by the Shockley state. By using Eq. (2) and the calculated wave functions for different film thicknesses, we can estimate the thickness dependence of the effective Rashba (α_R) parameter [dotted line in Fig. 4(b)]. A good agreement is found with experimental results corroborating that the spin-orbit splitting is actually dominated by atomic interaction.

Annealing temperature dependence of the Rashba parameter confirms this interpretation. In order to obtain the p^{Au} values after annealing in the disordered alloys, we have to calculate the relative amount of Au atoms in each layer. This is achieved in the framework of a simple one-dimensional diffusion model.[28] By taking $\nu_0 = 7 \times 10^{16}\ s^{-1}$ for the diffusion rate and $E_A = 1.83$ eV for the energy barrier, we have calculated the concentration profile for 3 ML of Ag on Au(111) corresponding to the experimental conditions (temperature and duration of the annealing). This profile accounts for the Auger intensity dependence of Fig. 3(b). Therefore, from this profile and numerical solutions for the Shockley state, we can estimate the number of Au atoms (p^{Au}) probed by the Shockley wave function and the corresponding Rashba coefficient [Eq. (2)]. With increasing annealing temperature, the amount of Au atoms increases in the top layers leading to an increase in the Rashba term. The good agreement with experimental data demonstrates that the spin-orbit splitting directly reflects the alloy composition close to the surface weighted by the Shockley wave function charge density.

Deposition of noble gases on Au(111) yields an increase in the spin-orbit splitting.[17] A similar increase was also observed on the *d*-derived surface state in Li/W(110) with increasing Li coverage.[10] However, in this system, the evolution of the splitting has been attributed to the modification of the the surface state extension. We take into account this mechanism in Ag/Au(111) by calculating the wave function, but it has a minor influence.

In conclusion, we observed that a continuous decrease in the spin-orbit splitting of the *sp*-derived surface state occurs with deposing Ag on Au(111) substrate. On the contrary, the annealing of the interfaces leads to an increase in the splitting. Both dependences of the spin-orbit splitting can be simply correlated to the amount of Au atoms sampled by the surface state. This behavior confirms the fundamental role of the atomic spin-orbit interaction in the formation of spin-polarized surface state subbands and sheds additional light regarding the possibility of a fine tuning of the splitting.

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