

New Mechanism for Spin-Orbit Splitting of Conduction States in Surface Alloys*

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We present Angle-Resolved Photoelectron Spectroscopy (ARPES) data on spin-orbit split states in two XAg₂ surface alloys grown on an Ag(111) substrate, and of the Si(111)-AgBiAg₂ trilayer system. We briefly discuss the origin of the unusually large energy and momentum splitting, and the possibility of tuning by surface engineering the spin polarization at the Fermi level.

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I. INTRODUCTION

The spin degeneracy of the electronic states in a solid is lifted by the spin-orbit (SO) interaction when electrons are subject to an electric potential lacking inversion symmetry. It is namely the case for a two-dimensional electron gas at a surface, or at an heterogeneous interface. In Rashba's free-electron model [1] the SO interaction enters the non-relativistic Schrödinger equation as an additional term in the Hamiltonian :

$$H_{SO} = \alpha_R \cdot \vec{\sigma}(\vec{k} \times \vec{e}_z) \quad (1)$$

\vec{k} is the electron wavevector, $\vec{\sigma}$ the vector of Pauli matrices and α_R the so-called Rashba parameter which is determined by the potential gradient ($\vec{\nabla}V$) in the out-of-plane direction (z). This Hamiltonian term splits the free electron parabola in two branches, with dispersion :

$$E^\pm(k) = \frac{\hbar^2 k_{\parallel}^2}{2m^*} \pm \alpha_R k_{\parallel} \quad (2)$$

as is illustrated in fig. 1 for an effective mass $m^* < 0$. The k -splitting between the two branches is $2\Delta k_{\parallel} = 2m^*\alpha_R/\hbar^2$, and the energy difference between the top of the band and the crossing point of the two branches defines the Rashba energy $E_R = \hbar^2 \Delta k_{\parallel}^2 / 2m^*$. $\vec{\nabla}V$ is often assumed – but need not be, see below – to be perpendicular to the 2D (xy) plane. In this case, for each branch the

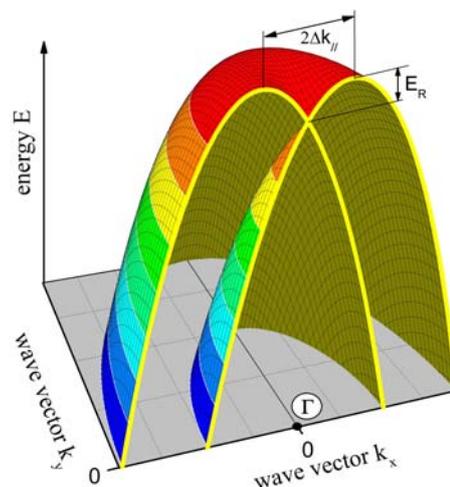


FIG. 1: Energy dispersion for the 2D Rashba model.

spin polarization lies in the plane, and is perpendicular to \vec{k} [2].

Rashba's original work was motivated by magneto-transport in semiconductor heterojunctions, but SO split states were first directly observed by angle-resolved photoemission (ARPES) on the Au(111) surface [3]. More recent spectroscopic work has also been focused on metal surfaces [2, 4–8]. The SO splitting of the Shockley surface states of Au(111) is much larger than in the previously studied semiconductor systems and, remarkably, orders of magnitude larger than estimates based on Eq. (2). This reveals the limitations of a simple free-electron approach, which ignores the strong electric field of the ions. A more realistic tight-binding model shows that the size of the effect depends on the product of the surface potential gradient and the atomic SO parameter [9]. Due

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to the latter term, the splitting is larger in high-Z metals. ARPES data on disordered Ag/Au(111) alloys indeed shows that α_R varies according to the amount of heavy (light) atoms probed by the surface state wavefunction [5]. At clean metal surfaces, e.g. Au(111), the atomic term dominates, and the main role of the surface potential is to induce the necessary asymmetry of the electron's wavefunction at the ionic cores [10].

The surprising recent observation of very large SO splittings in metallic surface alloys containing heavy elements has opened up new lines of research [11, 12]. These monolayer systems are obtained by the selective ordered substitution of atoms of a metallic substrate with atoms of the heavy element. The new experimental results require alternative scenarios which take into account the large atomic SO parameter of the heavy element but also the important role of an in-plane component of $\vec{\nabla}V$. Here we present ARPES data for two ordered XAg₂ alloys (X=Pb, Bi) grown at the Ag(111) surface, and for a Si-Ag-(BiAg₂) trilayer system. These results outline the spectral features of these artificial materials, and some perspectives for future investigations.

II. EXPERIMENTAL RESULTS

The deposition of 1/3 of a monolayer (ML) of Pb on a clean Ag(111) surface, followed by a mild annealing, yields a reconstructed ($\sqrt{3} \times \sqrt{3}$)R30° surface, where Pb atoms replace every third atom of the substrate. We have studied this PbAg₂ surface alloy by a combination of ARPES and density functional (DFT) electronic structure calculations [11]. The experimental band structure is presented in Fig. 2(a) as an ARPES intensity map for the $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ high symmetry directions. It exhibits a prominent SO split and downward dispersing feature centered at $\bar{\Gamma}$. A DFT calculation assigns it to a band of sp_z character which results from the hybridization between the Pb p and the Ag sp states. The two branches of this split band cross the Fermi level (E_F) at $\pm 0.14\text{\AA}^{-1}$ and $\pm 0.19\text{\AA}^{-1}$. A closer inspection reveals also a second set of weaker split bands of p_{xy} character crossing E_F at slightly larger wavevectors. The DFT bands correctly reproduce the experimental dispersion, but of course the splitting is only captured by relativistic calculations [13, 14]. Following the Rashba-Bychkov scenario we have fitted the sp_z branches by two identical parabolas symmetrically offset with respect to $\bar{\Gamma}$. We found a best fit for an effective mass $m^* = -0.15m_e$ and the top of the band at 0.6eV. This yields $\alpha_R = 1.5 \text{ eV}\cdot\text{\AA}$ and $\Delta k_{\parallel} = 0.03\text{\AA}^{-1}$. These values are significantly larger than the corresponding $\alpha_R = 0.33 \text{ eV}\cdot\text{\AA}$ and $\Delta k_{\parallel} = 0.012\text{\AA}^{-1}$ for the SO split surface states of the clean Au(111) surface.

ARPES results for the isostructural BiAg₂ surface alloy are presented in Fig. 2(b) [12, 13]. Again, the dispersion is dominated by the sp_z band which is even more broadly split around $\bar{\Gamma}$. The weaker p_{xy} features are barely visible with the contrast of the intensity map of Fig. 2. Due to the additional 6 p electron in Bi, the band is now fully occupied, and its maximum is 0.13 eV below E_F . The whole surface band structure is shifted to lower energy with respect to the Pb-Ag case, consistent with a

rigid-band picture. A similar parabolic fitting yields the parameters of the Rashba model: $\alpha_R = 3.05\text{eV}\cdot\text{\AA}$ and $\Delta k_{\parallel} = 0.13\text{\AA}^{-1}$. The Rashba energy $E_R = 0.20 \text{ eV}$ is two orders of magnitude larger than for Au(111).

The band splitting of the Bi/Ag(111) surface alloy is the largest Rashba-like splitting observed in a 2D system. Again, the free-electron model, which we used above as a qualitative guideline, cannot justify the size of the effect. The simple inclusion of the large atomic SO parameter of Bi in a *virtual crystal* scenario, proposed e.g. for the disordered Ag/Au(111) alloy [5], is also not satisfactory. In fact, the splitting observed on the alloy is larger than for either of its constituents [6]. On the other hand, there are indications that the structural anisotropy within the surface layer is an important element determining the electronic structure of the alloy. This is clearly illustrated by the deviation from a parabolic dispersion of the bands of Fig. 2. Figure 3 (a)-(d) shows, for the BiAg₂ case, constant energy cuts performed at four representative binding energies between 100 meV and 900 meV around $\bar{\Gamma}$ through the measured ARPES bands. The intensity of the constant energy contours is strongest for the p_z band, but contours of the p_{xy} bands are also visible, as schematically indicated in panel (e). All curves are centered at the $\bar{\Gamma}$ point. In particular, panel (c) corresponds to the crossing point of the two spin-split p_z branches, and one of the contours collapses into a point at $\bar{\Gamma}$. Contrary to the free-electron model of Fig. 1, the shapes of the contours are circular only for small values of the wavevector k . They evolve towards a hexagonal shape for larger k values, thus demonstrating the influence of the hexagonal lattice.

The effect of the lattice on the SO splitting has been explored for a 2D free electron model with SO interaction, enhanced by an additional hexagonal in-plane potential showing structural inversion asymmetry (i.e. $V(r) \neq V(-r)$), to mimic the conditions experienced by the electrons within the surface alloys. It was found that the SO splitting can be drastically enhanced when both normal and in-plane crystal asymmetries coexist [15]. An in-plane asymmetry is also present on the Au(111) surface – and in general at the (111) surface of an *fcc* lattice due to the stacking sequence of the planes [15] – but it is smaller since only one atomic species is present at the surface. Moreover, the effect of the in-plane asymmetry is larger in the XAg₂ alloys [15] with respect to the (111) noble metal surfaces, because the electronic states of the former are more tightly confined within the surface layer. Moreover, an in-plane potential gradient induces an out-of-plane rotation of the spin polarization. This has been indeed verified by recent spin-resolved ARPES measurements [16].

A close-up of the split bands near $\bar{\Gamma}$ (Fig. 4) gives a further indication that the atomic potential of the high-Z element cannot be the only origin of the giant SO splitting. While the atomic SO parameter is only about 25% bigger in Bi [17], Δk_{\parallel} is almost four times bigger for BiAg₂ and the Rashba parameter α_R is more than double. This is actually consistent with the idea of an in-plane gradient. For both alloys the sp_z band has some p_{xy} character mixed in by hybridization, and the latter is more than twice as large for BiAg₂. Since the p_{xy} component is more sensitive to the in-plane potential gradient, this

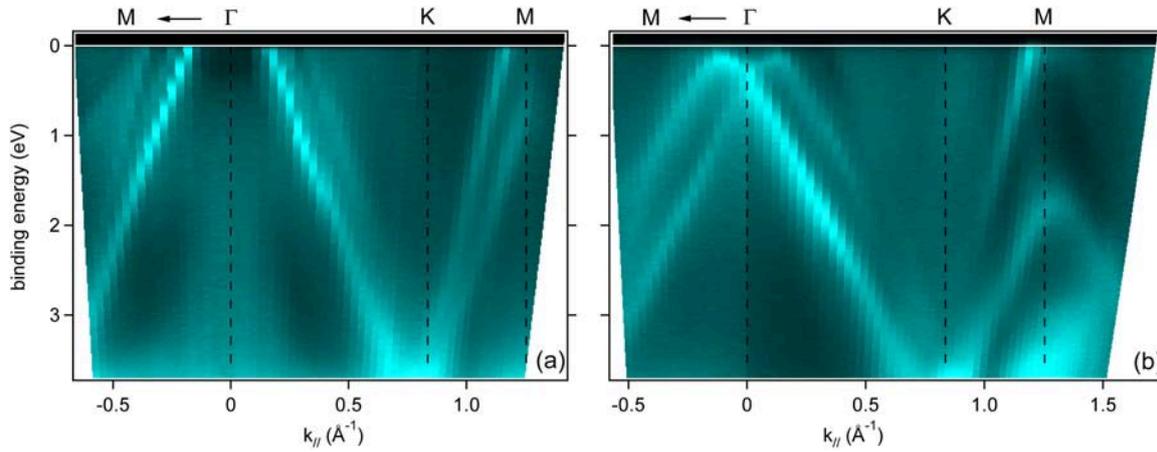


FIG. 2: ARPES intensity maps ($h\nu=21.2$ eV) for the Pb/Ag(111) (a) and Bi/Ag(111) (b) surface alloys along the $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ high symmetry directions. In Bi/Ag(111) the whole band structure is rigidly shifted to lower energy and the maximum of the sp_z band is below the Fermi level. In both cases, the intense strongly dispersing feature crossing the Fermi level near \bar{M} is the bulk s conduction band of Ag.

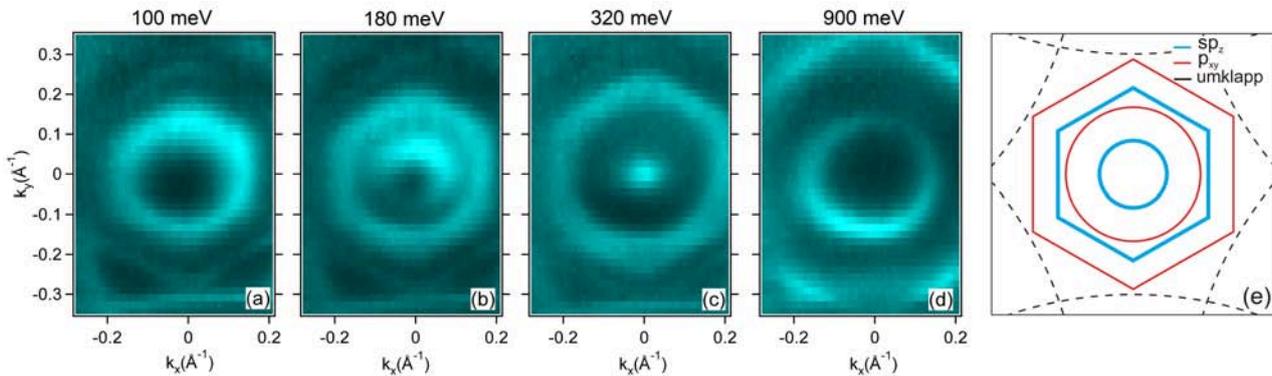


FIG. 3: (a)-(d) Constant energy contours for the BiAg₂ alloy. k_x and k_y correspond to the $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ directions, respectively; (e) schematics of the band contours for case (b). The hexagons are turned 30° with respect to the surface Brillouin zone. The dashed lines are umklapps of the bulk Ag $5s$ band.

argument gives a qualitative justification of the large difference. This is quantitatively confirmed by first principle calculations [13]. It was also pointed out that the different outward relaxation of the Pb and Bi atoms controls the hybridization between the p_{xy} and sp_z states, and therefore influences the size of the SO splitting [14].

The density of states (DOS) of the split bands is considerably affected by the SO interaction in a region of width E_R between the top of the band and the crossing point of the two branches. The DOS switches from a constant value, characteristic of a parabolic 2D band, to a $1/\sqrt{E}$ behavior typical of 1D systems, with a singularity at the band maximum. The latter was actually detected by scanning tunneling spectroscopy (STS) for both Bi/Ag(111) and Pb/Ag(111) as an asymmetric peak in the dI/dV spectrum [18]. Effective interactions are expected to be strongly renormalized when the Fermi level lies in this range, and even enhanced superconductivity has been predicted [19]. The rigid band behavior of the BiAg₂ and PbAg₂ alloys suggest a route to attain this regime. Tuning of the Fermi level position, and of the SO splitting, can actually be achieved in a mixed Bi _{x} Pb _{$1-x$} /Ag(111) surface alloy, for $0.5 < x < 0.56$ [13]. ARPES data confirm the gradual enhancement of the k splitting $\Delta k_{||}$ and

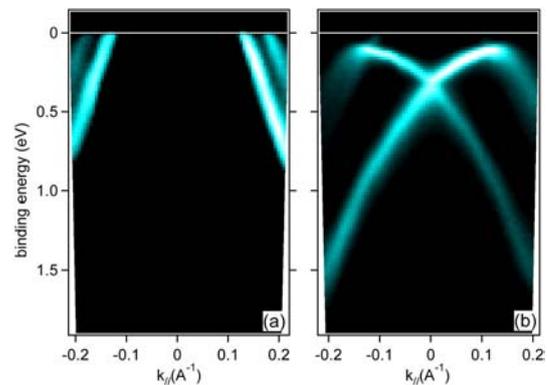


FIG. 4: Close-up of the band dispersion near $\bar{\Gamma}$ for the BiAg₂ (a) and PbAg₂ (b) surface alloys

of the Rashba parameter α_R with increasing Bi concentration between the two extreme compositions.

The above results demonstrate that a *giant* SO splitting can be achieved by the manipulation of metallic surfaces or interfaces. On the other hand, the emerging field of spintronics is based on the exploitation of spin-orbit effects in semiconductors. The challenge, in view of pos-

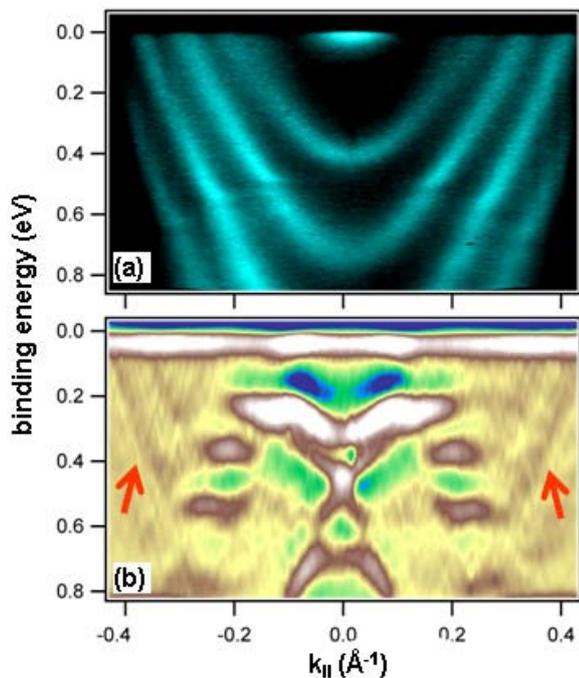


FIG. 5: (a) raw ARPES data around $\bar{\Gamma}$ at 55K evidences QWS originating from the confinement of the bulk sp bands for an Ag thin films of 16ML. (b) second derivative of the ARPES intensity around $\bar{\Gamma}$ for an alloy-covered sample at 55K. White and blue indicate the maxima and minima of photoemission intensity. The two arrows indicate the remaining signature of the QWS which hybridize with the p_{xy} and sp_z bands.

sible applications, is to develop stable interfaces between silicon and materials exhibiting large spin-orbit splitting, and to control the electronic states and their spin polarization near E_F . The latter determine the electron and spin transport through interfaces and nanostructures. Experiments on thin layers of Bi on Si(111) have been already carried out and evidenced a SO splitting of the surface states similar to the Bi(001) surface [8, 20]. However, they failed to highlight any modification induced by the silicon substrate.

Very recent experiments suggest a different approach to transfer the giant SO splitting of the Bi/Ag(111) onto a silicon substrate. Specifically, we propose a trilayer system composed of a Si(111) substrate, an Ag buffer layer of variable thickness (d), and a BiAg₂ surface alloy grown on top [21]. We have found that the electronic properties of the surface alloy grown on a thick Ag film are identical to those of the alloy formed on a Ag(111) single crystal. Namely, the spin-split branches are offset from $\bar{\Gamma}$ by $\Delta k_{||} = \pm 0.13 \text{\AA}^{-1}$. This demonstrates that the electronic properties of the alloy are not affected by the Ag/Si interface for thicknesses larger than a few ML, verifying the

theoretical calculations which predict that the BiAg₂ surface states are strongly localized in the surface layer [12].

For thin Ag buffer layers of a few MLs, quantum confinement of the Ag bulk sp -states leads to quantized wavevectors along the surface normal and to discrete energy levels [22]. These so-called quantum-well states (QWS) exhibit free-electron parabolic dispersion perpendicular to the surface normal. Their number and energy position can be tuned by varying the Ag film thickness (Fig. 5 (a)). After the formation of the BiAg₂ alloy on a thin Ag buffer, both the ARPES results and the first-principles calculations show a significant interaction between the spin-split surface states and the QWS. Hybridization band gaps are found at the intersection of the QWS with both branches of the spin-split sp_z and p_{xy} alloy states (Fig. 5 (b)). The spin polarization is predicted to be especially large and of opposite sign on the two sides of the gaps. The number, energy position and width of the spin-gaps can be easily tuned by modifying the buffer thickness d , making it possible to tailor the electronic structure and spin polarization near the Fermi level. The above findings suggest that the transport properties of the trilayer system can be drastically modified by varying the thickness of the Ag buffer layer, making it potentially interesting for future spintronic applications.

III. SUMMARY

Recent results have shown that unexpectedly large values of SO splitting can be achieved in artificial alloy systems fabricated at the interface with metal substrates, but also in more complex trilayer structures on a silicon substrate. The splitting and spin polarization at the Fermi level can be tuned by acting on parameters like the atomic number Z , the stoichiometry and the buffer layer thickness. This new concept opens the way to a promising new branch of materials engineering for future spintronics applications. The present results show that a combination of high resolution ARPES and of first-principle calculations may clarify still unexplored aspects of the physics of these new artificial systems.

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