Spin-orbit split two-dimensional electron gas with tunable Rashba and Fermi energy

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We demonstrate that it is possible to tune the Rashba energy, introduced by a strong spin-orbit splitting, and the Fermi energy in a two-dimensional electron gas by a controlled change of stoichiometry in an artificial surface alloy. In the $Bi_xPb_{1-x}/Ag(111)$ surface alloy, the spin-orbit interaction maintains a dramatic influence on the band dispersion for arbitrary Bi concentration x, as is shown by angle-resolved photoelectron spectroscopy. The Rashba energy E_R and the Fermi energy E_F can be tuned to achieve values larger than one for the ratio E_R/E_F, which opens up the possibility for observing phenomena, such as corrections to the Fermi liquid or a superconducting state. Relativistic first-principles calculations explain the experimental findings.

In electron systems that lack inversion symmetry the spin degeneracy is lifted by the spin-orbit (SO) interaction even without the presence of magnetic fields. This Rashba-Bychkov effect has been found in different two-dimensional electron gases.[1–9] Spin selection rules apply and the density of states features a singularity, which alter electronic interactions in the Fermi liquid[10] and even strongly enhance the transition temperature T_C into a superconducting state.[11] The strength of the SO splitting—the Rashba energy E_R—introduces an energy scale influencing the electronic structure and competing against other energy scales, such as the Fermi energy E_F. However, in most of the known systems up to now, the Rashba energy is a perturbative correction, which leaves most of the proposed changes experimentally undetectable. Here we show that it is possible to tune the Rashba energy and Fermi energy to become comparable in size by controlling the stoichiometry in the SO-split mixed surface alloy $Bi_xPb_{1-x}/Ag(111)$. In this way the Rashba-Bychkov type of SO splitting is no longer a small correction to the band structure. Consequently, a number of phenomena, such as a superconducting state or corrections to the Fermi liquid, will become experimentally observable.

Recently, a class of materials has been identified, in which surface alloying of heavy elements in light-element substrates produces a two-dimensional electronic structure with a giant SO splitting.[12,13] These materials have made it possible to locally detect the SO splitting in the differential conductance measured by scanning tunneling spectroscopy due to a characteristic singularity in the local density of states.[14] Therefore, the strong increase in the Rashba energy for these systems opens up opportunities to learn more about this mechanism, especially if the Rashba energy can be tuned and becomes comparable to the Fermi energy. Although it is difficult to change both quantities independently, for practical purposes it is sufficient to tune the E_R/E_F ratio, a characteristic quantity in a SO split 2DEG. Starting from the pure surface alloys Pb/Ag(111) ($E_R=67$ meV) and Bi/Ag(111) ($E_R=195$ meV), a homogeneous $Bi_xPb_{1-x}/Ag(111)$ mixed

surface alloy can be formed for arbitrary x.[15] For $0<x<1$, a well-defined two-dimensional band structure with a continuous evolution of the SO splitting is observed by means of angle-resolved photoelectron spectroscopy (ARPES). In addition, a continuous shift of the bands in energy occurs. As a result, the ratio between Rashba energy E_R and Fermi energy E_F can be tuned. The experimental findings are fully supported by first-principles electronic-structure calculations which provide further details not directly accessible to experiment.

$Bi_xPb_{1-x}/Ag(111)$ alloys were prepared by first cleaning the Ag(111) surface in ultrahigh vacuum by successive sputtering and annealing cycles. Subsequently, Bi and Pb atoms were codeposited by *in situ* evaporation. The total amount corresponded to $1/3$ of a monolayer, and the relative atomic concentrations were determined by the photoemission intensities of the respective $5d$ core levels. The $(\sqrt{3}\times\sqrt{3})R30°$ superstructure of the surface alloy was verified by low energy electron diffraction, indicating structural long-range order.

The experimental band structures for selected Bi concentrations were measured by ARPES near $\bar{\Gamma}$ ($\mathbf{k}=0$; Fig. 1). For the pure alloys Pb/Ag(111) [$x=0$, (a)] and Bi/Ag(111) [$x=1$, (e)], one finds the SO split p_z-type surface states, reported elsewhere.[12,13] The splitting shows up as a shift of the (almost) parabolic bands by a momentum offset k_0 to positive and negative wave numbers. Additional features are clearly visible in Fig. 1 for $x>0.5$, and outlined by arrows. They belong to a second set of higher-lying SO split bands with mostly p_{xy} character, observed for both the Pb/Ag(111) and the Bi/Ag(111) surface alloys.[12,13]

The striking feature for intermediate concentrations [Figs. 1(b)–1(d)] is that the surface bands continuously evolve between the pure cases, (a) and (e). More specifically, one finds a gradual increase of the splitting k_0 and the band maximum shifts from the unoccupied states (Pb/Ag; $E>0$) into the occupied states (Bi/Ag; $E<0$). The latter is attributed to the different valence configuration of Pb (s^2p^2) and Bi (s^2p^3).
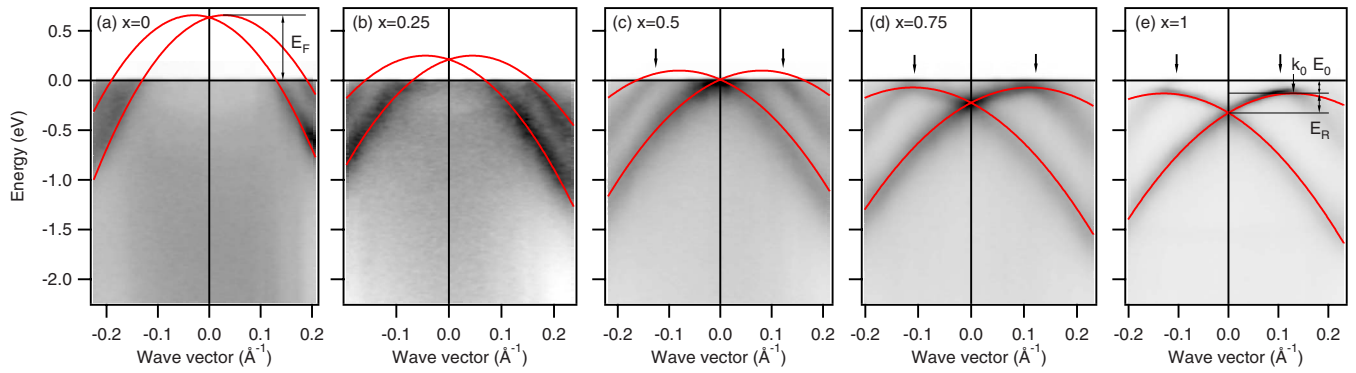
FIG. 1. (Color online) Experimental band structures of $Bi_xPb_{1-x}/Ag(111)$ surface alloys for x as indicated. The photoemission intensity is depicted as linear gray scale, with dark corresponding to high intensity, versus energy E and wave vector $\boldsymbol{k}$ along $\overline{K}\,\overline{\Gamma}\,\overline{K}$. Data are taken at 21.2 eV (HeI). Red (dark gray) lines represent parabolic fits to the surface-state bands. The Fermi energy of the holes is indicated in (a). The spin-orbit splitting k_0, the Rashba energy E_R as well as the energy offset E_0 are defined in (e).

Further, the mixed alloys show a larger linewidth than the pure alloys, and there is no evidence for a superposition of the band structures of the stoichiometric alloys (which would indicate the presence of Pb and Bi domains). Both findings indicate chemical disorder, i.e., a substitutional binary alloy.

To quantitatively verify the change in SO splitting and to separate it from band structure effects, such as a changing effective mass $m^\star$, the above results are analyzed by means of the Rashba-Bychkov (RB) model for an isotropic 2DEG. In the nearly free electron model the dispersion for the SO split bands (RB model) can be written as

$$E(\boldsymbol{k}) = \frac{\hbar^2}{2m^\star}(|\boldsymbol{k}| \pm k_0)^2 + E_0, \qquad (1)$$

where E_0 is an energy offset, k_0 is the momentum offset, and $m^\star$ is the effective mass. The Rashba parameter α_R, which is the coupling constant in the Hamiltonian (see, e.g., Ref. [12]), can be determined from the splitting k_0 and from the effective mass $m^\star$: $\alpha_R = \hbar^2 k_0/m^\star$. The Rashba energy E_R is defined as $E_R = \hbar^2 k_0^2/2m^\star$.

In this model, α_R accounts for contributions from both the atomic SO and from the potential gradient perpendicular to the surface.[16] However, the giant splitting in $Bi/Ag(111)$ is explained by an additional SO contribution from the in-plane potential gradient.[12,17] The latter, showing up in an anisotropic 2DEG, is important for large $|\boldsymbol{k}|$. Considering small $|\boldsymbol{k}|$ here, we interpret our results within the above model, being aware of its limitations. Thus, α_R is viewed as effective and comprises all three (the atomic and two kinds of surface-potential) SO contributions.

The parameters in the model were determined by fitting parabolae to the experimental bands [red (dark gray) lines in Fig. 1] as well as to further data sets (not shown). In particular, k_0, $m^\star$, and E_0 depend almost linearly on x (Fig. 2). The Rashba parameter α_R (d), derived from k_0 and $m^\star$, increases by about a factor of 2 upon changing x from 0 (Pb/Ag) to 1 (Bi/Ag). This directly proves that the SO splitting can be continuously tuned in a substantial range by surface alloying. This striking result cannot be explained by contributions from the atomic SO interaction because these are very simi-

lar for Pb ($Z=82$) and Bi ($Z=83$).[18] Consequently, the effect should be attributed to the potential gradient at the surface. The latter depends on the surface geometry, especially on the relaxation of Bi and Pb. To elucidate these issues, first-principles electronic-structure calculations were performed.

The surface relaxation was determined using the Vienna Ab initio Simulation Package (VASP), well-known for providing precise total energies and forces.[19] Both Pb and Bi atoms relax outward by 18% and 16% of the bulk interlayer spacing, respectively, with respect to the positions of the adjacent Ag atoms. In-plane displacements of these Ag atoms are negligibly small ($<1\%$). The structural parameters serve as input for first-principles multiple-scattering calculations (Korringa-Kohn-Rostoker method, KKR) which already proved their suitability for relativistic electronic-structure computations for surfaces,[20] in particular for $Bi/Ag(111)$.[12]
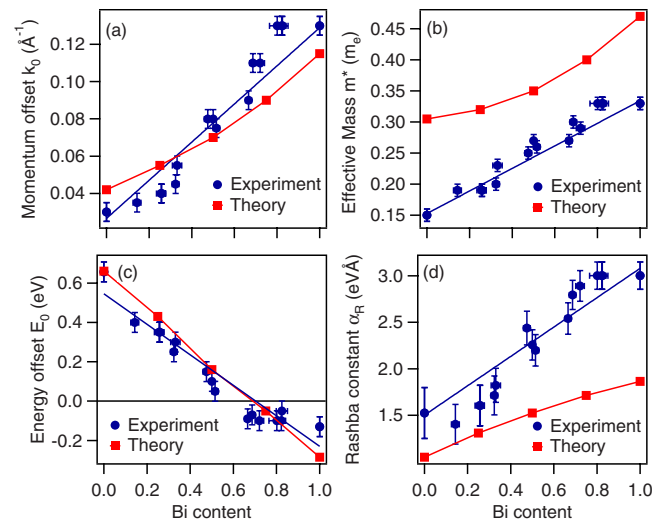

FIG. 2. (Color online) Band-structure parameters extracted from experimental (blue/dark gray circles) and theoretical (red/gray squares) data for various Bi concentrations: (a) spin-orbit splitting k_0, (b) effective mass $m^\star$, (c) energy offset E_0, and (d) Rashba parameter α_R. A straight line has been drawn for the experimental data as a guide to the eye.
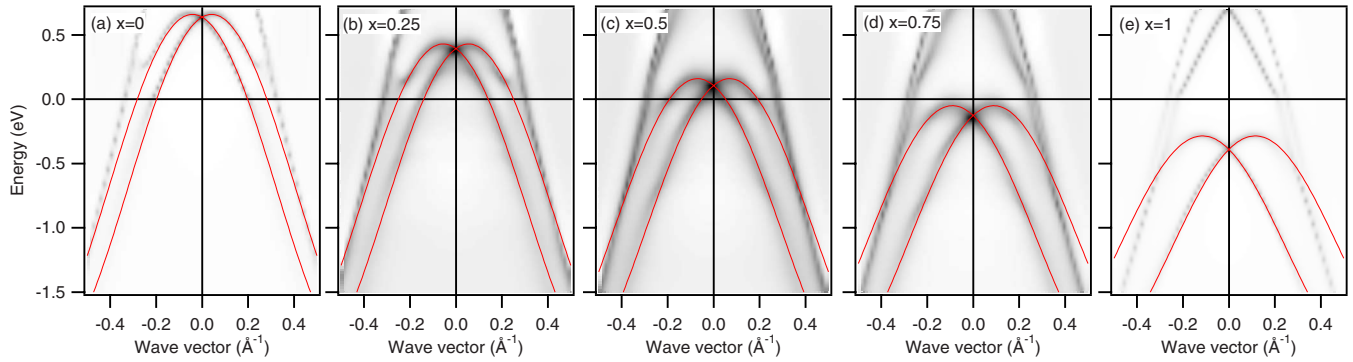
FIG. 3. (Color online) Theoretical band structures of $Bi_xPb_{1-x}/Ag(111)$ for concentrations x as in Fig. 1. The spectral density at the Bi_x/Pb_{1-x} site is depicted as linear gray scale, with dark corresponding to high spectral weight, versus energy E and wave vector $\boldsymbol{k}$ along $\bar{\mathrm{K}}\bar{\Gamma}\bar{\mathrm{K}}$. Red (dark gray) lines represent parabolic fits to the surface-state bands.

Substitutional binary alloys $Bi_xPb_{1-x}/Ag(111)$ are described within the coherent potential approximation (KKR-CPA). The outward relaxation at Bi concentration x was linearly interpolated between $x=0$ and 1.

The spectral densities show well-defined bands, which shift downward in energy with increasing x, while k_0 increases considerably (Fig. 3; note that the range of unoccupied states is accessible, in contrast to ARPES, Fig. 1). For the mixed systems [Figs. 3(b)–3(d)] the bands show an increased width, as is typical for a substitutional alloy. The overall agreement of theory and experiment proves that our theoretical approach captures the essential features of the experiments. As in the experiment, the parameters in the model were obtained by fitting parabolae [red (dark gray) lines in Fig. 3] to the bands lowest in energy (Fig. 2, red squares). In particular, k_0 (a) and E_0 (b) compare well with experiment. The effective mass $m^\star$ is about twice as large as in experiment. As a result, the Rashba parameter α_R is too small. However, the trends (e.g., the slopes) compare well with experiment. In summary, theory fully supports the experimental findings of a tunable SO splitting by surface alloying.

The increase of α_R with x is explained by the orbital composition of the surface electronic states, as obtained from theory. For both Pb/Ag(111) and Bi/Ag(111), the lowest-lying bands have a predominantly sp_z character, with some p_xp_y contribution. But the p_xp_y contribution in Bi/Ag is more than twice as large than that in Pb/Ag(111). In-plane orbitals (p_xp_y) are more sensitive to the in-plane potential gradient, which is essential for the giant splitting in Bi/Ag, than perpendicularly oriented orbitals (sp_z). Further, Bi is slightly less relaxed outward than Pb. Consequently, the SO splitting in Bi/Ag(111) is considerably larger than in Pb/Ag(111). Further, in recent first-principles investigations,[21] the enhanced SO splitting is attributed to the relaxation of the Bi and Pb sites. The outward displacement is accompanied by adding a p_{xy} contribution to the otherwise sp_z-like surface state as well as by an increased SO splitting. Therefore, this finding is consistent with the above arguments, although details of the calculations differ significantly.

In many systems, especially 2DEGs in semiconductor heterostructures, E_R is small compared to other energy scales. Hence, SO coupling can be regarded as a perturbation. Sev-

eral theoretical studies are concerned with such a perturbative correction to, e.g., Fermi liquid behavior,[10] electron-phonon coupling,[22] or a possible sign change in the magnetic susceptibility.[23] However, a sizeable Rashba energy is necessary for these effects to be experimentally observable. If E_R cannot be regarded as small, even a superconducting state is predicted.[11] To investigate such effects, tuning of both E_R and E_F is crucial. The $Bi_xPb_{1-x}/Ag(111)$ mixed surface alloy provides unique means for studying the transition from a small to a large SO splitting by variation of the stoichiometry. For the surface states, with their negative effective mass, E_F is measured from the band maximum to the Fermi level of the electrons ($E=0$ eV in Fig. 1). It decreases with x and vanishes at $x \approx 0.56$. Thus, E_R/E_F increases drastically with x (Fig. 4). In particular, $E_R \gtrsim E_F$ for $0.5 < x < 0.56$, i.e., the important range in which the SO splitting cannot be viewed as a small correction to the electronic structure.

In conclusion, we have demonstrated that the spin-orbit splitting along with the chemical potential in a two-dimensional electron gas can be custom tailored by controlling the stoichiometry. For the surface states in the artificial
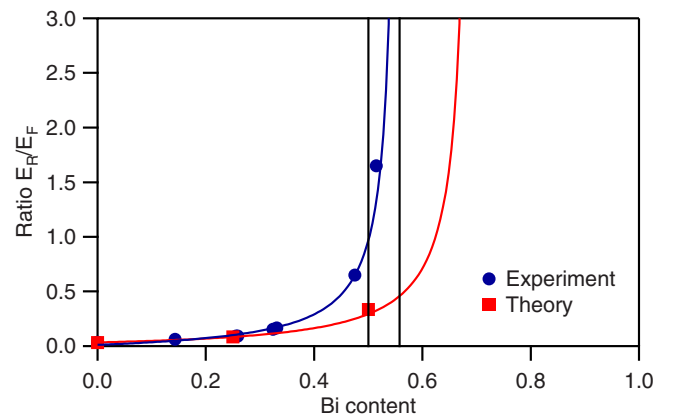

FIG. 4. (Color online) Ratio of Rashba energy E_R and Fermi energy E_F versus Bi concentration x. Dots represent data computed from the parameters in Fig. 2. The line serves as a guide to the eye. Vertical lines at $x=0.5$ and 0.56 indicate the region in which $E_R > E_F$. For $x > 0.56$ the surface band is fully occupied, so that E_F is ill defined for this band (Fig. 1).

surface alloy $Bi_xPb_{1-x}/Ag(111)$, the ratio of Rashba energy E_R and Fermi energy E_F, determined by the Bi concentration x, can be chosen within a wide range, as is shown by angle-resolved photoelectron spectroscopy and first-principles electronic-structure calculations. The $Bi_xPb_{1-x}/Ag(111)$ mixed surface alloy therefore provides an excellent opportunity for future investigations of the intriguing physics of a 2DEG in a regime dominated by the spin-orbit splitting of the electronic states.[24]

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[1] Y. A. Bychkov and E. I. Rashba, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 66 (1984) [JETP Lett. **39**, 78 (1984)].

[2] S. LaShell, B. A. McDougall, and E. Jensen, Phys. Rev. Lett. **77**, 3419 (1996).

[3] E. Rotenberg, J. W. Chung, and S. D. Kevan, Phys. Rev. Lett. **82**, 4066 (1999).

[4] Y. S. Gui, C. R. Becker, N. Dai, J. Liu, Z. J. Qiu, E. G. Novik, M. Schäfer, X. Z. Shu, J. H. Chu, H. Buhmann, and L. W. Molenkamp, Phys. Rev. B **70**, 115328 (2004).

[5] Y. M. Koroteev, G. Bihlmayer, J. E. Gayone, E. V. Chulkov, S. Blügel, P. M. Echenique, and P. Hofmann, Phys. Rev. Lett. **93**, 046403 (2004).

[6] E. Bauer, G. Hilscher, H. Michor, C. Paul, E. W. Scheidt, A. Gribanov, Y. Seropegin, H. Noël, M. Sigrist, and P. Rogl, Phys. Rev. Lett. **92**, 027003 (2004).

[7] K. V. Samokhin, E. S. Zijlstra, and S. K. Bose, Phys. Rev. B **69**, 094514 (2004).

[8] K. Togano, P. Badica, Y. Nakamori, S. Orimo, H. Takeya, and K. Hirata, Phys. Rev. Lett. **93**, 247004 (2004).

[9] H. Q. Yuan, D. F. Agterberg, N. Hayashi, P. Badica, D. Vandervelde, K. Togano, M. Sigrist, and M. B. Salamon, Phys. Rev. Lett. **97**, 017006 (2006).

[10] D. S. Saraga and D. Loss, Phys. Rev. B **72**, 195319 (2005).

[11] E. Cappelluti, C. Grimaldi, and F. Marsiglio, Phys. Rev. Lett. **98**, 167002 (2007).

[12] C. R. Ast, J. Henk, A. Ernst, L. Moreschini, M. C. Falub, D. Pacilé, P. Bruno, K. Kern, and M. Grioni, Phys. Rev. Lett. **98**, 186807 (2007).

[13] D. Pacilé, C. R. Ast, M. Papagno, C. Da Silva, L. Moreschini, M. Falub, A. P. Seitsonen, and M. Grioni, Phys. Rev. B **73**, 245429 (2006).

[14] C. R. Ast, G. Wittich, P. Wahl, R. Vogelgesang, D. Pacilé, M. C. Falub, L. Moreschini, M. Papagno, M. Grioni, and K. Kern, Phys. Rev. B **75**, 201401(R) (2007).

[15] The Rashba energy of a 2DEG, a measure for the strength of the splitting, is the energy difference between the band minimum (for electrons) or band maximum (for holes) and the band crossing at $k=0$.

[16] L. Petersen and P. Hedegård, Surf. Sci. **459**, 49 (2000).

[17] J. Premper, M. Trautmann, J. Henk, and P. Bruno, Phys. Rev. B **76**, 073310 (2007).

[18] Note that this is in contrast to AgAu alloys in which the strength of the SO coupling is attributed to the atomic contribution [$Z(Ag)=47$ and $Z(Au)=79$] (Ref. 24).

[19] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[20] J. Henk, M. Hoesch, J. Osterwalder, A. Ernst, and P. Bruno, J. Phys.: Condens. Matter **16**, 7581 (2004).

[21] G. Bihlmayer, S. Blügel, and E. V. Chulkov, Phys. Rev. B **75**, 195414 (2007).

[22] E. Cappelluti, C. Grimaldi, and F. Marsiglio, Phys. Rev. B **76**, 085334 (2007).

[23] E. I. Rashba, Physica E (Amsterdam) **34**, 31 (2006).

[24] H. Cercellier, C. Didiot, Y. Fagot-Revurat, B. Kierren, L. Moreau, D. Malterre, and F. Reinert, Phys. Rev. B **73**, 195413 (2006).