Large spin splitting of metallic surface-state bands at adsorbate-modified gold/silicon surfaces

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Finding appropriate systems with a large spin splitting of metallic surface-state band which can be fabricated on silicon using routine technique is an essential step in combining Rashba-effect based spintronics with silicon technology. We have found that originally poor structural and electronic properties of the Au/Si(111)3×3 surface can be substantially improved by adsorbing small amounts of suitable species (e.g., Tl, In, Na, Cs). The resultant surfaces exhibit a highly-ordered atomic structure and spin-split metallic surface-state band with a momentum splitting of up to 0.052 Å−1 and an energy splitting of up to 190 meV at the Fermi level. The family of adsorbate-modified Au/Si(111)3×3 surfaces, on the one hand, is thought to be a fascinating playground for exploring spin-splitting effects in the metal monolayers on a semiconductor and, on the other hand, expands greatly the list of material systems prospective for spintronics applications.

Generation of spin-polarized electrons on the basis of Rashba spin splitting in the two-dimensional electron-gas systems on semiconductors is considered to be an essential step in developing semiconductor spintronics applications. To reach the goal, three requirements have to be satisfied as follows. First, spin splitting should be large enough to allow operations of the device at room temperature. Second, the surface-state band has to be metallic to allow significant spin transport. Third, the substrate should be a semiconductor as a large bulk current in metallic substrate would sweep off the surface spin signal. In addition, due to device application reasons it is highly desirable that the substrate would be a silicon, the most widely used semiconductor material. The last demand is that the structure could be easily fabricated using routine technique, e.g., molecular beam epitaxy.

The last decade has been marked by the step-by-step progress in this direction. The surface Rashba effect was first found on the metal surfaces like Au(111)2–3 and Bi(111)4–5 and a giant spin splitting was detected on Bi-covered Ag(111)6. The latter finding indicates that a large spin splitting is possible (and even enhances) when only a monolayer of a heavy element is placed on a surface of a light element. This discovery stimulated expanding the search area to semiconductor surfaces such as Si and Ge covered by heavy-metal monolayers. Large Rashba splitting has been found on Bi/Si(111)6–10, Bi/Ge(111)11, Ti/Si(111)12,13, and Pt/Si(110)14 surfaces but it occurs in the non-metallic surface-state bands. The first metal/semiconductor reconstruction with a spin splitting of metallic surface-state band found was the Pb/Ge(111)3×3 followed by the Au/Ge(111)3×3 reconstruction. As indicated in Ref. 15, the spin-splitting effect does not depend on any peculiar property of Ge, hence it seems possible to realize a similar electronic structure on a Si surface. In this respect, the Au/Si(111)3×3 reconstruction is thought to be a promising candidate as its atomic arrangement (described by the conjugated
honeycomb chained-trimer (CHCT) model\(^\text{20,21}\) (see Fig. 1e) is similar to that of the Au/Ge(111)\(\sqrt{3} \times \sqrt{3}\) and a strong Rashba-type spin-orbit splitting in it has already been predicted theoretically\(^1\). Substantial Rashba effect observed for self-assembled Au nanowires on vicinal Si surfaces\(^\text{24,25}\) also supports the suggested prospects of the Au/Si material systems. However, the structural and electronic properties of Au/Si(111)\(\sqrt{3} \times \sqrt{3}\) surface are actually poor due to a presence of random domain walls. Fortunately, the breakthrough way was found to improve the surface, namely, adding small amount of In eliminates completely domain walls\(^26\) and enhances metallic surface band filling\(^27\). It has been recognized that after the transformation the basic CHCT structure of the original Au/Si(111)\(\sqrt{3} \times \sqrt{3}\) surface is preserved, while the indium adsorbate forms a 2D gas of adatoms on \(\text{Si}(111)\).

In the present study, we have revealed that the above effect is not a peculiar feature of only In, but is a common trait for a set of adsorbate species (e.g., Na, Cs, and Tl). Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) observations have shown that adsorption of each above mentioned species onto the Au/Si(111)\(\sqrt{3} \times \sqrt{3}\) produces a homogeneous well-ordered surface. In addition, angle-resolved photoelectron spectroscopy (ARPES) and spin-resolved ARPES data as well as first-principles calculations clearly demonstrate occurrence of the well-defined metallic surface-state band with a large spin splitting. Thus, finding such a family of adsorbate-modified Au/Si(111) systems (having the same \(\sqrt{3} \times \sqrt{3}\) reconstruction) paves a way to combine Rashba-effect based spintronics with a silicon technology.

Results

Figure 1a illustrates structural and electronic properties of the pristine Au/Si(111)\(\sqrt{3} \times \sqrt{3}\) surfaces. One can see that the main characteristic structural feature of the surface is a disordered meandering domain-wall network\(^29\). Such a surface displays the \(\sqrt{3} \times \sqrt{3}\) LEED pattern with cloudlike diffraction streaks in between \(\sqrt{3}\) spots\(^27,28\). As for its electronic properties, the surface is known to be metallic\(^29\), but its metallicity is not strongly expressed: the surface-state spectral features are smeared due to the domain walls and electron filling of the metallic \(S_1\) surface band is rather low, \(\sim 0.1\) electrons per unit cell\(^7\). In the ARPES spectra, the \(S_1\) band is invisible in the first surface Brillouin zone (SBZ) (Fig. 1a) and its faint traces can be detected only in the higher SBZs\(^27\).

Adding 0.15 ± 0.05 ML of Tl, In, Na or Cs atoms to this surface produces strong effect on its structure, namely, the domain walls disappear and homogeneous well-ordered surface forms (Fig. 1b–d, upper panel). Consequently, a sharp \(\sqrt{3} \times \sqrt{3}\) LEED pattern without any other features develops (not shown). STM observations reveal that the adsorbed species are present at the surface as adatoms which are mobile at room temperature but can be frozen at fixed positions by cooling the sample down to \(\sim 100\) K (except for Cs atoms which motion is frozen only at \(\sim 30\) K).

ARPES observations demonstrate that upon adding adsorbates (Fig. 1b–d, lower panel) all spectral features of the initial Au/Si(111)\(\sqrt{3} \times \sqrt{3}\) surface are preserved but become noticeably sharp due to removal of domain walls. All bands are shifted towards the higher binding energy and the well-defined metallic \(S_1\) surface state band develops (being clearly seen even in the first SBZ). Electron filling of the \(S_1\) band increases three to seven times (up to \(\sim 0.3–0.7\) electrons per unit cell). Next important feature is that the metallic \(S_1\) surface state is split. The splitting being modest along the \(\Gamma-K\) direction becomes substantial along the \(\Gamma-M\) direction (Fig. 2a).

To reveal a spin-split character of the metallic surface states, we have performed the spin-resolved ARPES measurement on Tl-adsorbed system. Figure 2b shows the spin-resolved energy distribution curves of \(S_1^h\) and \(S_1^l\) subbands at \(K_{\|} = 0.30\) \(\text{Å}^{-1}\) (here and below we refer inner and outer subbands as \(S_1^h\) and \(S_1^l\), respectively). This result clearly shows that the \(S_1\) state is spin-split and the spin orientations are opposite in \(A\) and \(B\) subbands.

Figure 3 summarizes the results for various adsorbate species. All spectra have a qualitatively similar appearance but the splitting value varies. Momentum splitting at the Fermi level \(\Delta K_{\|}\) ranges from \(\sim 0.018\) \(\text{Å}^{-1}\) obtained for Cs to that of \(\sim 0.052\) \(\text{Å}^{-1}\) for Tl. Consequently, energy splitting \(\Delta E_p\) changes in the range from

![Figure 1](image_url)

**Figure 1 | Adsorbate-induced transformations in structural and electronic properties of Au/Si(111).** STM images and ARPES spectra taken in the first \(\sqrt{3} \times \sqrt{3}\) surface Brillouin zone (SBZ) along the \(\Gamma-\text{M}\) direction from (a) pristine Au/Si(111)\(\sqrt{3} \times \sqrt{3}\) surface and the same surface after adsorption of 0.15 ± 0.05 ML of (b) Tl, (c) In, and (d) Na. Scale of the STM images is 250 × 250 \(\text{Å}^2\), that of the insets is 50 × 50 \(\text{Å}^2\). Note that ARPES data are confined to the interior of SBZ as exact position of the \(\text{M}\) point is at 0.546 \(\text{Å}^{-1}\). (e) Atomic arrangement (CHCT model) of the Au/Si(111)\(\sqrt{3} \times \sqrt{3}\) surface consisting of Au trimers (shown by orange circles) and Si trimers (shown by blue circles) residing on Si(111) bilayer (shown by black circles) and sketch of reciprocal space geometry with boundaries of the first \(\sqrt{3} \times \sqrt{3}\) SBZ given by black lines (dashed hexagon depicts the 1 × 1 SBZ). The high symmetry points are marked by circles.
$100 \text{ meV}$ to $190 \text{ meV}$. From the graph shown in Fig. 3b one can conclude that the splitting value is essentially controlled by position of the Fermi level, i.e., by the electron filling of the $S^1$ band. The concept is illustrated in Fig. 3c where the experimental dots from Fig. 3b are superposed on the $S^1_A$ and $S^1_B$ dispersion curves of the calculated band structure. One can see that by choosing appropriate adsorbate species the Fermi level position can be tuned within the range of $350 \text{ meV}$ (shown by the pink shaded area in Fig. 3c). Position of Fermi level also varies slightly depending on concentration of a given adsorbate.

Figure 4a shows the ARPES Fermi surface of the TI-adsorbed Au/Si(111)$\sqrt{3} \times \sqrt{3}$ surface determined with spin-unpolarized ARPES. Data are confined to the interior of SBZ as exact positions of the $M$ and $K$ points are at $0.546 \text{ Å}^{-1}$ and $0.630 \text{ Å}^{-1}$, respectively. (b) Spin-resolved ARPES spectra taken for the same surface at a fixed $k_{\parallel} = 0.30 \text{ Å}^{-1}$ in the $\Gamma-M$ direction.

Figure 3a shows the ARPES Fermi surface of the TI-adsorbed Au/Si(111)$\sqrt{3} \times \sqrt{3}$ surfaces. One can clearly see the two Fermi contours of which the outer (corresponding to the $S^1$ band) has an almost circular shape while the inner (corresponding to the $S^1$ band) has a shape of a smoothed hexagon. As the hexagon corners lies at the $\Gamma-K$ directions, these are the directions of the minimal splitting, while the greatest splitting is at the hexagon sides (i.e., along the $\Gamma-M$ directions). One can see that the calculated constant energy contours (Fig. 4b) properly reproduce all the principal features of the experimentally derived Fermi surface map. The only small deviation that can be noticed is the discrepancy between the calculated and experimental splitting along the $\Gamma-K$ direction where theory yields slightly underestimated value (Fig. 4c).

Figure 4b also shows the clockwise and counterclockwise spin helicity for the inner and outer contours, respectively, with abrupt change of the sign for out-of-plane spin component at the $\Gamma-K$ direction.

Figure 2 | Splitting of dispersion curves measured by ARPES and spin-resolved ARPES. (a) Band structure along the $\overline{M}-\Gamma-K$ of the TI-adsorbed Au/Si(111)$\sqrt{3} \times \sqrt{3}$ surface determined with spin-unpolarized ARPES. Data are confined to the interior of SBZ as exact positions of the $M$ and $K$ points are at $0.546 \text{ Å}^{-1}$ and $0.630 \text{ Å}^{-1}$, respectively. (b) Spin-resolved ARPES spectra taken for the same surface at a fixed $k_{\parallel} = 0.30 \text{ Å}^{-1}$ in the $\Gamma-M$ direction.

Figure 3 | Effect of adsorbate species. (a) Fragments of the ARPES spectra taken in the $\Gamma-M$ direction near the Fermi level of the TI-, In-, Na-, and Cs-adsorbed Au/Si(111)$\sqrt{3} \times \sqrt{3}$ surfaces. (b) Momentum splitting at the Fermi level $\Delta k_{\parallel}$ plotted as a function of the Fermi wave vector $k_{\parallel}$ for $S^1_A$ and $S^1_B$ bands measured for various species (as indicated in the graph). (c) Calculated band structure along the $\overline{M}-\Gamma-K$ with the experimental dots from (b) superposed on the $S^1_A$ and $S^1_B$ dispersion curves. Surface state bands are shown by filled yellow circles, shaded region indicates projected bulk bands. Range of the varied Fermi level position is indicated by the pink shaded area.
directions, which is intrinsic feature of the Rashba-split surface states at hexagonal surfaces. The detailed spin texture is illustrated in Fig. 4d. Figure 4d (upper panel) shows the azimuthal dependencies of in-plane components in the tangential and normal directions to the $S_A^1$ and $S_B^1$ Fermi contours. One can see that tangential components for both bands demonstrate a very similar behavior with sharp maxima in the $\Gamma$-$C_2$ and wide minima around the $\Gamma$-$M$ directions. The normal component (a signature of the Dresselhaus term) is small for the inner $S_A^1$ band but it becomes noticeable for the outer $S_B^1$ band and demonstrates an undulating behavior. Maximal deviation of the in-plane spin component from a purely tangential is about $-3^\circ$ and $-16^\circ$ for the $S_A^1$ and $S_B^1$ subbands, respectively. For both bands, the out-of-plane $z$ component (Fig. 4d, lower panel) remains almost constant in the wide area near the $\Gamma$-$M$ directions and abruptly changes its sign going through zero while crossing the $\Gamma$-$K$ directions. As a result, spin has a fully in-plane alignment there. The calculations have also revealed that changing the Fermi level position affects the spin texture of the $S_1$ band. Upon the downward shift of the Fermi level from its highest position, corresponding to Tl-adsorbed surface to its lowest position obtained on Cs-modified Au/Si(111) surface (see pink stripe in Fig. 3c) the maximal deviation of the in-plane spin component from a purely tangential increases up to about $-24^\circ$ for the $S_B^1$ subband while that for the $S_A^1$ subband remains about $-3^\circ$. At the same time this shift of the Fermi level leads to decreasing maximal out-of-plane spin tilt angle from about $68(63)^\circ$ to $64(53)^\circ$ for the outer(inner) subband.

**Discussion**

Our results show that chemically very different species, alkali metals, Na and Cs, and heavy group-III metals, In and Tl, when being adsorbed onto the Au/Si(111) surface, affect its structural and electronic properties in a very similar way, namely, eliminate domain walls and donate electrons to the metallic $S_1$ surface state band. DFT calculations for In-adsorbed surface showed that removal of domain walls is due to a stress-relieving effect produced by In adsorption. However, origin of this effect was not disclosed.
Typically, surface lattice stress changes when foreign atoms become incorporated directly into the lattice and the greater the size difference between the host and foreign atoms the greater the stress. This typical scenario is apparently not held for the present case where foreign adatoms are not incorporated into the lattice and their atomic size does not play a decisive role. As an alternative, we suggest that adsorbates can affect the surface lattice stress by donating electrons to the substrate surface layer. As a result, the top layer possesses a non-compensated charge which means adding a Coulomb repulsion term into the interactions between surface atoms, hence changing the surface stress.

We have found a number of adsorbate species (Ti, In, Na, and Cs) which make the Au/Si(111) √3 × √3 surface suitable for observing significant spin-orbit splitting. We believe that the list of such adsorbates can be extended (at least, at the expense of the left alkali metals). The main requirements for candidate species seem to be as follows. First, they are metals that could easily donate a sufficient amount of electrons to the surface state band. This could be attained with species like monovalent alkali metals with high electropositivity and/or species having several valent electrons, as Group-III metals. In this respect, it is worth noting the very recent finding that extra Au or Ge atoms produce a similar doping effect on Au/Ge(111)√3 × √3 surface, extending further the list of possible candidate species. Second, they have to preserve the original Au trimer structure (which is believed to be responsible for the spin-splitting effect) or, in other words, they should not form 2D alloys with Au on Si(111) surface. For example, in contrast to In and Ti, the other group-III metals, Al and Ga, are not suitable, as they form binary reconstructions with Au, (Au,Al)/Si(111)√3 × √3(12). (Au,Al)/Si(111)2 × 21, and (Au,Ga)/Si(111)√3 × √3(3).

As the list is open, many species are expected to produce a similar effect on the structure and electronic properties of the Au/Si(111)√3 × √3 surface. However, similarity does not mean identity, that makes the family of adsorbate-modified Au/Si(111)√3 × √3 reconstructions to be a promising playground for exploring spin-splitting effects as a function of structural parameters tuned by adsorption of particular species. On the other hand, they represent a wide set of surface systems for the choice of the proper ones for spintronic device applications.

Another degree of freedom for tailoring electronic properties stems from ability to intermix Si and Ge into a desired Si1-xGex layer. Though Si and Ge are akin elements and their √3 × √3-Au reconstructions have the same atomic arrangement, their electronic structures exhibit essential differences. While the Au/Si(111)√3 × √3 surface has a single metallic Si1 band, the Au/Ge(111)√3 × √3 surface in addition to the electronic Si1 band has the hole bands dispersing up to the Fermi level17,18. The spin textures of the Si1 bands for these surfaces are similar but also not identical, namely, contribution of the Dresselhaus terms for the Au/Ge(111)√3 × √3 is substantially greater19. Thus, the variable Au/Si1/Ge1-x(111)√3 × √3 surfaces might be a new interesting object for exploring spin-splitting effects in metal monolayers on semiconductor.

### Methods

#### Sample preparation method.

The STM and ARPES experiments were performed in an ultra-high-vacuum system with a base pressure of ~2 × 10−10 Torr. Atomically-clean Si(111)7 × 7 surfaces were prepared in situ by flashing to 1280°C after the samples were first outgassed at 600°C for several hours. Pristine Au/Si(111)√3 × √3 surfaces were formed by Au deposition onto Si(111)7 × 7 surface held at ~600°C. The adsorbate-modified Au/Si(111) surfaces were prepared by adsorbing 1.85 ± 0.05 ML of a given species, In, Na or Cs, onto the surface held at ~350°C. Due to significant desorption, deposition of Ti was performed at room temperature followed by annealing at ~350°C. Adsorbate deposition was terminated when STM shows domain-wall-free surface and LEED displays a sharp √3 × √3 pattern without any other features.

### STM. STM images were acquired using Omicron variable-temperature STM-XA operating in a constant-current mode. Electrochemically-etched W tips and mechanically cut PtIr tips were used as STM probes after annealing in vacuum.
24. Barke, I., Zheng, F., Rügheimer, T. K. & Himpsel, F. J. Experimental evidence for spin-split bands in a one-dimensional chain structure. Phys. Rev. Lett. 97 (22), 226405–4 (2006).
25. Okuda, T. et al. Large out-of-plane spin polarization in a spin-splitting one-dimensional metallic surface state on Si(557)-Au. Phys. Rev. B 82 (16), 161410–4 (2010).
26. Gruznev, D. V. et al. Si(111) - √3 × √3 - Au phase modified by In adsorption: Stabilization of a homogeneous surface by stress relief. Phys. Rev. B 73 (11), 115335–7 (2006).
27. Kim, J. K. et al. Two-dimensional electron gas formed on the indium-adsorbed Si(111) - √3 × √3 - Au surface. Phys. Rev. B 80 (7), 075312–7 (2009).
28. Nagao, T. et al. Structural phase transitions of Si(111) - √3 × √3 - Au surface. Phys. Rev. B 57 (16), 10100–10109 (1998).
29. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558 (1993).
30. Kresse, G. & joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758 (1999).
31. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
32. Kresse, G. & Lebaca, O. The VASP manual. http://cms.mpi.univie.ac.at/vasp/ vasp/vasp.html. Retrieved April 22, 2013.

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Author contributions

D.V.G. and L.V.B. carried out ARPES and STM under the support of A.A.Y. and A.Y.T. L.V.B., D.U., O.V. and A.F. carried out ARPES and spin-resolved ARPES at BESSY-II with guidance from D.V.V. S.V.E. and E.V.C. carried out the theoretical calculation. D.V.G., A.V.Z. and A.A.S. analyzed the data and wrote the manuscript with input from S.V.E. and E.V.C. and conceived and coordinated the project.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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