Experimental and Theoretical Evidence of a Highly Ordered Two-Dimensional Sn/Ag Alloy on Si(111)

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The existence of a highly ordered, two-dimensional, Sn/Ag alloy on Si(111) is reported in this study. We present detailed atomic and electronic structures of the one atomic layer thick alloy, exhibiting a 2×2 periodicity. The electronic structure is metallic due to a free-electron-like surface band dispersing across the Fermi level. By electron doping, the electronic structure can be converted into a semiconducting state. A rotated Sn trimer constitutes the key structural element that could be identified by a detailed analysis of constant energy contours derived from the free-electron-like band.

Atomically thin, two-dimensional (2D), materials may exhibit unique properties not observed in three-dimensions. Graphene is currently the prime example of such a 2D material [1]. In case of metallic elements, the ultimate, one monolayer, 2D structure is unstable and it has to be supported by a substrate like, e.g., one monolayer of Pb on Si(111) [2]. It is of great interest to investigate such 2D structures beyond the case of a single atomic species. Presently, very little is known about ordered 2D multi component alloys, which represent a novel class of 2D materials. Taking into consideration the large number of combinations of atomic species, the number of potentially interesting ordered alloys could be quite large. However, only a few examples of ordered alloys on silicon substrates have been reported in the literature, i.e., Pb/Sn [3], Bi/Sb [4], Au/Cu [5], and Au/Pb [6,7]. The 2D character of these binary alloys was just briefly discussed in Refs. [4–7]. Further, the techniques used in these experimental studies were not sufficient to derive conclusive atomic models or to determine electronic structures. In an effort to make detailed determinations of the atomic and electronic structures of possible ordered binary alloys, we have discovered that Sn and Ag form an exceptionally well defined alloy on Si(111).

In this paper we report experimental evidence, supported by theory, which clearly establishes the Sn/Ag/Si(111)2×2 surface as a 2D, one layer thick, ordered Sn/Ag binary alloy. The atomic structure of the Sn/Ag layer, which is in registry with the substrate, exhibits a characteristic structural element, i.e., a rotated Sn trimer. This 2D binary alloy can be viewed as a nearly close packed layer containing both Sn and Ag atoms in an ordered arrangement. The presence of rotated Sn trimers found compelling support from rotated constant energy contours obtained by angle resolved photoelectron spectroscopy (ARPES). Electronically, the 2D alloy shows a metallic character due to a steep free-electron-like dispersion that crosses the Fermi level (E_F). Doping the 2D alloy results in a semiconducting character.

In order to prepare the 2×2 Sn/Ag structure on Si(111) a specific protocol has to be followed. The first step is a preparation of a Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface by deposition of 1.2 ML (1 ML is 7.84 atoms per nm^2) of Ag, at a rate of 0.3 ML per minute, on a clean Si(111)-(7×7) substrate kept at about 600 °C. At this temperature, Ag atoms desorb and that is why more than the nominal amount of Ag (1 ML) is needed [8]. In this way, the qualitatively best surface is achieved with the least number of defects, e.g., islands, domains or domain walls. The final step in the preparation of the 2×2 structure is a deposition of 0.75 ML of Sn on the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface kept at room temperature including subsequent annealing at 450 °C for 2 minutes.

ARPES experiments were performed using synchrotron radiation at beam line I4 at MAX-lab, Sweden. The data were collected using a Phoibos 100 analyzer with a 2D detector (Specs). The total energy resolution of the ARPES data presented in this paper was about 65 meV and the angular resolution was 0.3°. Scanning tunneling microscopy (STM) experiments were performed in a UHV system at Linköping University equipped with a variable-temperature scanning tunneling microscope (VT-STM, Omicron).

Structural and electronic properties of various atomic models of the 2D Sn/Ag surface alloy were investigated by density functional theory (DFT) as implemented in the WIEN2K package [9]. For this purpose, a Si slab was built with various periodic arrangements of Sn and Ag atoms on top of the Si double layer that terminated the Si slab. All slabs had inversion symmetry, a lateral size corresponding to the 2×2 unit cell and a vertical dimension of 5.5 nm. On both sides of the slab there was a 1.0 nm wide vacuum gap. Calculations of the atomic models were carried out with five k points in the irreducible Brillouin zone and an energy cutoff of 81 eV. All atoms in the surface layer (Sn and Ag atoms) and two Si layers closest to the surface were relaxed until the force components for each atom were within 0.04 eV/Å. Simulated STM images were generated

from local density of states according to the Tersoff-Hamann approach [10].

The 2×2 structure, which covers the entire surface, is well defined as evidenced by the sharp spots in the low energy electron diffraction (LEED) pattern shown in Fig. 1(a). Information about the morphology of the surface was obtained by STM. The large scale (400×400 nm^2) STM image in Fig. 1(b) shows large terraces of the 2×2 alloy with some irregular domain boundaries. A zoom in on the terraces reveals the detailed structure of the 2×2 periodicity. Figs. 1(c) and 1(d) show a 2.4×2.4 nm^2 area of the 2×2 structure imaged at 50 K using a sample bias of -1 V and $+1$ V, respectively. The filled state image in Fig. 1(c) looks very different to the empty state image in Fig. 1(d). Three small protrusions per 2×2 unit cell, forming a trimer, are observed in the filled state image, while the unit cell in the empty state image is dominated by one prominent protrusion.

ARPES reveals a free-electron-like surface band structure following the 2×2 periodicity. Figure 2(a) shows the experimental dispersion relation along the $\bar{\Gamma}_2$-$\bar{K}$-$\bar{M}$-$\bar{\Gamma}_2'$ path of the 2×2 surface Brillouin zone (SBZ) [outlined in Fig. 2(b)]. This specific path was chosen since the projected bulk band gap is deeper outside the inner 2×2 SBZ, facilitating an easier determination of the surface

band dispersion. The surface band, S, has an upward dispersion from 1.2 eV below E_F at the $\bar{\Gamma}$ point and it is metallic as evidenced by the dispersion across E_F before reaching the $\bar{K}$ point. At the $\bar{M}$ point, S has a binding energy of 0.55 eV.

In order to figure out the shape of the metallic band above E_F, in the vicinity of the $\bar{K}$ point, we have doped the surface with alkali metals (K and Cs) in order to fill the band with electrons. The electron donation can also be realized by adding extra Ag atoms which will be diffusing on the surface [11]. A complete filling of the band was achieved which resulted in a downward energy shift of 0.1 eV. The shape of the band near the $\bar{K}$ point is rounded-off when completely filled and the bandwidth could be determined to ≈ 1.3 eV.

From the experimental band dispersions along the high symmetry lines, one would conclude that there is only one free-electron-like band below E_F. However, when moving away from high symmetry lines, two metallic bands appear that are separated in energy and momentum space, as will be explained further. Figure 2(b) shows constant energy contours at 0.4 eV below E_F mapped on the 2×2 SBZ. As an intriguing result, Fig. 2(b) clearly reveals the presence of two differently rotated, triangular shaped, contours surrounding every $\bar{K}$ point. These two contours are highlighted by triangular figures with rounded-off corners around one of the $\bar{K}$ points (solid and dashed white lines). The separation of the bands in momentum space also implies a separation of the bands along the energy axis. Consequently, two bands can be observed when probing $k_{\parallel}$-space off the high symmetry directions. Along the high symmetry lines only one dispersive feature is observed due to the fact that the two bands overlap.

FIG. 1. (a) LEED pattern (30 eV) exhibiting very sharp 2×2 spots indicating a high degree of order. (b) STM image of a 400×400 nm^2 area showing the morphology of the 2×2 surface. (c) and (d) Detailed STM images obtained at 50 K from a 2.4×2.4 nm^2 area. The filled state image in (c) was recorded at a sample bias of -1.0 V while the empty state image in (d) was recorded at $+1.0$ V. Both images (c) and (d) were recorded in constant current mode with a tunneling current of 100 pA. A 2×2 unit cell has been included in images (c) and (d) as a guide to the eye. Note the strong reversal of the appearance of the images. The filled state image, (c), shows three bright protrusions in the upper left half of the unit cell, while the empty state image, (d), only shows one bright protrusion in the opposite half of the unit cell.

FIG. 2. (a) Dispersion relation of the surface state S obtained at a photon energy of 52 eV along the $\bar{\Gamma}_2$-$\bar{K}$-$\bar{M}$-$\bar{\Gamma}_2'$ path of the 2×2 SBZ as outlined in (b). The surface band has a free-electron-like shape with a binding energy of 1.2 eV at the $\bar{\Gamma}$ point. Along $\bar{\Gamma}$-$\bar{K}$, the band disperses across the Fermi level before reaching the $\bar{K}$ point, which implies that the surface is metallic. (b) Constant energy contours obtained at 0.4 eV below the Fermi level. The image reveals two triangular shaped contours with rounded-off corners around every $\bar{K}$ point. The shape of the differently rotated contours is illustrated around one $\bar{K}$ point by the white solid and dashed lines. Each contour corresponds to one metallic band. Along the $\bar{\Gamma}_2$-$\bar{K}$-$\bar{M}$-$\bar{\Gamma}_2'$ path, these two bands are degenerate resulting in a single dispersion, S, as in (a).

A model of the Sn/Ag 2D alloy was constructed based on the information from STM images and according to the amounts of Ag and Sn that were evaporated onto the surface. This resulted in the initial model shown in Fig. 3(a) where a 2×2 surface unit cell is indicated by the parallelogram. The three Sn atoms (gray), labeled 1, 2 and 3, form a trimer that corresponds to the three protrusions in the unit cell as shown by the filled state STM image in Fig. 1(c). The four Ag atoms (black), labeled 4, 5, 6 and 7, are positioned in the space available between the Sn trimers. Ag atoms 4, 5 and 6 form another trimer, and the position of the center of this trimer coincides with the position of the bright protrusion in the unit cell of the empty state image of Fig. 1(d). Ag atom number 7 is located at a corner of the unit cell, being surrounded by

three Sn atoms. The Sn/Ag layer is residing on a $Si(111)1 \times 1$ substrate where the Sn atoms are positioned approximately on top of Si atoms and the center of the Sn trimer is located above a second layer Si atom. This initial model was subjected to an energy minimization procedure in order to find the relaxed atomic structure. Figure 3(b) shows the resulting atomic model in which the atom positions have changed toward a more close packed structure. An interesting consequence of the relaxation is that the Sn trimers are now rotated counterclockwise by about 17° from the initial orientation. The three Ag atoms, 4, 5, and 6, also changed their lateral positions which resulted in a change of the Ag trimer orientation by 21° while Ag atom number 7 did not move. After the relaxation, the Sn/Ag layer is not perfectly coplanar. The Ag trimer, positioned 246 pm above the Si substrate layer, is 22 pm lower than the Sn trimer. Ag atom number 7, which occupies the outermost position is located 62 pm higher than the Sn trimer. The in plane distance between the Sn atoms of the trimers is 312 pm and between Ag atoms in the Ag trimers the distance is 299 pm. The centers of adjacent Sn and Ag trimers are separated by 460 pm.

Results from the band structure calculation of the relaxed structure are shown in Fig. 3(c) along the high symmetry path $\bar{\Gamma}$-$\bar{K}$-$\bar{M}$-$\bar{\Gamma}$ of the 2×2 SBZ. In this figure, the size of a circle corresponds to the strength of the surface character summed over all orbitals at a particular $k_\parallel$ value. In the occupied part of the calculated band structure there is just one surface state in the band gap, labeled Σ, with s and p character from Sn atoms and d contribution from Ag atoms. Although less clear, the band can be traced in the surface resonance region resulting in a bandwidth of 1.2 eV, which is close to the ≈ 1.3 eV obtained experimentally. The calculation positions the Fermi level such that the maximum of the metallic band at the $\bar{K}$ point is about 0.5 eV above E_F, which is higher than the 0.1 eV value found experimentally. This difference can be related to the effect of doping by some extra Ag atoms and/or the difficulty of the calculations to reproduce band positions accurately. The calculated band structure in Fig. 3(c) has been shifted downward by 0.4 eV to match the absolute position of the experimental surface band S. It is quite encouraging to note how extremely well the calculated band Σ reproduces both the qualitative and quantitative features of the experimental surface band, S. Both the general, free-electron-like, shape and the bandwidth, come out correctly. Also the experimental observation of unoccupied states near $\bar{K}$- points is predicted since the Fermi level cuts the top of the band near these symmetry points.

Calculated constant energy contours at 0.4 eV below E_F, corresponding to the metallic band in Fig. 3(c), are shown in Fig. 3(d). The band produces only one contour around every $\bar{K}$ point of the SBZ. Note however, that the shape of the contour is the same as that found experimentally, see Fig. 2(b), and that the calculated contour is rotated as well.

FIG. 3. (a) and (b) Atomic models of the initial and the relaxed 2×2 structure, respectively. The 2×2 unit cell is outlined by the parallelogram. There are three Sn atoms, labeled 1, 2, and 3, and four Ag atoms, labeled 4, 5, 6, and 7, in the unit cell. The relaxation of the atomic structure resulted in a rotation of the Sn trimers (atoms 1, 2, and 3) as well as of the Ag trimers (atoms 4, 5, and 6), leading to the more close packed layer shown in (b). (c) Calculated electronic band structure of the relaxed model. One metallic surface band, Σ, is present in the band gap region that reproduces the dispersion of the experimental band S in Fig. 2(a). (d) Constant energy contours calculated for the relaxed structure in (b) showing one triangular shaped contour around every $\bar{K}$ point. (e) Superposition of the constant energy contours in (d) and those calculated for the enantiomorphous version of the relaxed structure in (b), i.e., a structure where the Sn and Ag trimers are rotated clockwise instead of counterclockwise. Both rotations are equally probably based on the symmetry of model.

FIG. 4. Calculated STM images of the relaxed model in Fig. 3(b). (a) Filled state STM image calculated for the electronic states down to 1.0 eV below the Fermi level. (b) Empty state STM image calculated for the electronic states up to 1.0 eV above the Fermi level. The 2×2 unit cells in (a) and (b) are outlined by parallelograms. The calculated STM images reproduce very accurately the appearances of the experimental STM images in Figs. 1(c) and 1(d).

Furthermore, the rotation angle is the same as that of the Sn trimers. The symmetry of the model provides an explanation to the experimental observation of two differently rotated contours. There exists an equally probable enantiomorphous structure to the one in Fig. 3(b) where the Sn trimers are rotated by the same angle but in the opposite direction. Consequently, one should expect to observe a superposition of two contours, rotated clockwise and counterclockwise, respectively, resulting in the appearance illustrated in Fig. 3(e). This is exactly what is observed experimentally.

For the final verification of the model, we have calculated STM images of the relaxed structure. Simulated filled and empty state images are shown in Figs. 4(a) and 4(b), respectively. There is a very close resemblance between the calculated images and the experimental ones in Figs. 1(c) and 1(d); i.e., the filled state images are dominated by three protrusions in each 2×2 cell while the empty state images just show one bright protrusion per unit cell. It is quite interesting to note that the rotation of the Sn trimers, predicted by the model calculations, is less apparent in the simulated STM image in Fig. 4(a) compared to the atomic model in Fig. 3(b). The lack of obvious rotations of the Sn trimers in the experimental STM image in Fig. 1(c) is conceivable in the light of the small rotation predicted by the simulated filled state STM image, smearing of the image due to thermal vibrations, and instrumental resolution. The experimental band structure on the other hand showed a clear signature of the Sn trimer rotation in terms of the rotated constant energy contours.

In this study, we have shown that Sn and Ag form a well-ordered 2D alloy on Si(111). By comparing experimental results from LEED, STM, and ARPES to the corresponding results from model calculations it was possible to derive a detailed model of the 2D structure. The resulting model consists of 1 ML of Ag and 0.75 ML of Sn arranged periodically, where the most significant structural element is a rotated Sn trimer. The existence of the Sn trimer and the rotation angle could be unambiguously verified by ARPES from the observation of the rotated constant energy

contours. By symmetry, clockwise and counterclockwise rotation is equally probable, resulting in two enantiomorphous structures which are verified by the presence of two sets of constant energy contours experimentally. Electronically, the 2D Sn/Ag alloy is dominated by a steep free-electron-like dispersion, S. Since the band crosses the Fermi level, the alloy is intrinsically metallic. To put the electronic structure in a perspective, it is interesting to compare the dispersion of S to the electronic structure resulting from the π band of graphene. The steep dispersion of S when crossing the Fermi level corresponds to an electron velocity of 7.6×10^5 m/s which is comparable to the value $\approx 1 \times 10^6$ m/s reported for graphene [12,13]. A major difference, though, is that the Dirac point observed for graphene is not part of the electronic structure for the Sn/Ag alloy. This situation allows for an easy tuning of the electronic properties; i.e., the metallic character of the Sn/Ag alloy can be transformed into a semiconducting one by adding extra Ag atoms in order to completely fill the S band.

The highly ordered Sn/Ag/Si(111)2×2 2D alloy represents a novel class of materials that awaits an exploration of their physical properties.

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