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Broken symmetry induced band splitting in the $\text{Ag}_2\text{Ge}$ surface alloy on $\text{Ag}(111)$

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We report a study of the atomic and electronic structures of the ordered $\text{Ag}_2\text{Ge}$ surface alloy containing $\frac{1}{3}$ monolayer of Ge. Low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and angle-resolved photoelectron spectroscopy (ARPES) data reveal a symmetry breaking of the expected $\sqrt{3} \times \sqrt{3}$ periodicity, which is established for other $\text{Ag}_2M$ alloys ($M = \text{Bi}, \text{Sb}, \text{Pb}$, and $\text{Sn}$). The deviation from a simple $\sqrt{3} \times \sqrt{3}$ structure manifests itself as a splitting of diffraction spots in LEED, as a striped structure with a $6 \times 6$ periodicity including a distortion of the local hexagonal structure in STM, and as a complex surface band structure in ARPES that is quite different from those of the other $\text{Ag}_2M$ alloys. These results are interesting in view of the differences in the atomic and electronic structures exhibited by different group IV elements interacting with $\text{Ag}(111)$. Pb and Sn form $\sqrt{3} \times \sqrt{3}$ surface alloys on $\text{Ag}(111)$, of which $\text{Ag}_2\text{Pb}$ shows a surface band structure with a clear spin-orbit split. Si and C form silicene and graphene structures, respectively, with linear band dispersions and the formation of Dirac cones as reported for graphene. The finding that $\text{Ag}_2\text{Ge}$ deviates from the ideal $(\sqrt{3} \times \sqrt{3})R30^\circ$ $\text{Ag}_2\text{Sn}$ and $\text{Ag}_2\text{Pb}$ surface alloys makes Ge an interesting “link” between the heavy group IV elements (Sn, Pb) and the light group IV elements (Si, C).

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I. INTRODUCTION

Surface alloys present unique chemical and physical properties that are not observed in the bulk. For instance, Rashba-Bychkov- (RB) type spin splits [1] have been observed on several two-dimensional (2D) ordered surface alloys. In particular, $\text{Ag}(111)$ has turned out to be an important substrate on which well-ordered surface alloys can be formed with a variety of elements. The $\text{Ag}_2M$ type of 2D surface alloys, where $M$ represents Sn, Sb, Pb, or Bi, have been in the focus of recent studies. All of these show a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure where $\frac{1}{3}$ monolayer (ML) of the Ag surface atoms is replaced by an $M$ element. In the case of Bi, a giant RB split was reported in the surface band structure of the 2D alloy [2]. The RB split is expected to decrease with decreasing atomic number, and in the case of Sn, no split could be observed [3]. Apart from studies of surface alloys, $\text{Ag}(111)$ has a central role as a substrate in the formation of graphene (C) [4] and silicene (Si) [5,6]. Ge is similar to the lighter group IV elements, C and Si, in the sense that it crystallizes in the diamond structure with an $sp^3$ hybridization of the valence electrons. Possible 2D structures of Ge have been investigated theoretically, and it is predicted that Ge can form a stable graphenelike structure (germanene) [7]. However, so far, to our knowledge, there are no published experimental reports on a successful formation of this novel 2D material. On the other hand, $\frac{1}{3}$ ML of Ge deposited on $\text{Ag}(111)$ has been reported to form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction, as observed by reflection high-energy electron diffraction (RHEED) [8] and low-energy electron diffraction (LEED) [9], but there are no clear atomically resolved topographical results on this surface [9,10].

Very recently, a paper was published presenting an experimental study of the surface band structure of $\text{Ge}/\text{Ag}(111)(\sqrt{3} \times \sqrt{3})R30^\circ$ [8]. The surface band structure was reported to be similar to those of the $\text{Ag}_2M$ surface alloys mentioned above. The similarities were clearest when comparing to $\text{Sn}/\text{Ag}(111)(\sqrt{3} \times \sqrt{3})R30^\circ$. In the $\text{Sn}/\text{Ag}$ case, it was not possible to observe any RB split, and since Ge is an even lighter element, one would not expect such a split in the Ge/Ag data, which is confirmed in Ref. [8]. However, as reported in that study, the Ge/Ag surface alloy shows an unexpected surface band split at the $\bar{M}$ points along the $\bar{K}\bar{M}$ line of the $\sqrt{3} \times \sqrt{3}$ surface Brillouin zone (SBZ). The observation of split bands at the $\bar{M}$ points clearly indicates that the Ge/Ag alloy differs substantially from the other group IV alloys ($\text{Pb}/\text{Ag}$ [11] and $\text{Sn}/\text{Ag}$ [3]; as well as from the alloys induced by Bi [2] or Sb [12]). As was concluded in Ref. [8], “...it remains an open question distinguishing Ge from other similar systems as, for example, Sn-$\text{Ag}(111)$ surface alloy.” The deviation of the Ge/Ag system from the ideal $(\sqrt{3} \times \sqrt{3})$ surface alloys formed by Sn and Pb makes it interesting as a “link” to the silicene/graphene forming lighter group IV elements.

In this paper, we report LEED and scanning tunneling microscopy (STM) data showing that the atomic structure of the Ge/Ag surface alloy, formed by $\frac{1}{3}$ ML of Ge, deviates from the atomic structure of Pb and Sn surface alloys. An unexpected long-range (“$\sqrt{3} \times 6\sqrt{3}$”) modulation was observed resulting in a striped appearance of the surface. Also, the electronic structure obtained by angle-resolved photoelectron spectroscopy (ARPES) in this study differs substantially from the results of the Pb/Ag and Sn/Ag cases. The most striking difference is the presence of multiple constant energy contours, suggesting the existence of rotated structural elements within the surface alloy.

II. EXPERIMENTAL DETAILS

Samples were prepared in situ in two separate ultrahigh vacuum (UHV) systems, i.e. one with LEED and STM and one with LEED and ARPES. Scanning tunneling microscopy images were recorded at room temperature using an Omicron variable temperature STM at Linköping University.
FIG. 1. (Color online) (a) LEED pattern (56 eV) of the Ge/Ag(111)(√3 × √3)R30° surface alloy exhibiting slightly blurred spots. The inset shows the existence of satellite spots around 1 × 1 spots which leads to a fuzzy appearance. (b) LEED pattern (25 eV) revealing the details of the diffraction pattern near √3 positions. The inset shows that the “√3” spots consist of six spots forming a triangle. Note that there is no spot at the exact √3 position which corresponds to the center of the triangle. The fine structure of the LEED pattern indicates a high-order periodicity. The gray scale of both insets is inverted, and the contrast is enhanced. (c) Ge 3d core-level spectrum obtained at a photon energy of 80 eV in normal emission. The dots are the experimental data and the fitting curve is the sum of SC1, SC2 components, and a Shirley background. The spectrum is dominated by an exceptionally narrow spin-orbit split component (SC1). The broadening at the base is due to a metallic tail and shifted Ge 3d emission fitted by a single component. Fitting parameters: Spin-orbit split: 0.546 eV, Branching ratio: 0.665, Gaussian widths: 105 and 332 meV, respectively, Lorentzian width: 144 meV. The asymmetry parameter of the Doniach-Šunjić line profile is 0.055, and the energy difference between the two components is 0.17 eV.

Angle-resolved photoelectron spectroscopy data were obtained at the MAX-lab synchrotron radiation facility using the end station of the I4 beam line. The data were acquired at room temperature by a Phoibos 100 analyzer from Specs with a two-dimensional detector. The energy and angular resolutions were 50 meV and 0.3°, respectively. Angle-integrated Ge 3d core-level spectra were also measured in order to further characterize the surface alloy. The Ag(111) crystal was cleaned by repeated cycles of sputtering by Ar⁺ ions (1 keV) and annealing at approximately 400°C until a sharp (1 × 1) LEED pattern was obtained. Atomically resolved STM images, as well as the presence of a sharp Shockley-type surface state in ARPES, confirmed a high quality of the Ag(111) surface. Here, ⅓ ML of Ge was deposited on the substrate at room temperature from a tungsten filament source. The deposition rate was monitored by a quartz crystal microbalance both immediately before and immediately after the deposition. A (“√3 × √3”)R30° LEED pattern was observed without annealing. Post annealing of the sample at 200°C resulted in more well-defined LEED spots. Quotation marks are used throughout the paper to indicate that

FIG. 2. (Color online) (a) Overview filled-state STM image of a 130 × 130 nm² area showing a striped structure of the surface. Three domains, differing by a 120° angle, are present. The contrast of the image is enhanced by local-derivative treatment. (b) Atomically resolved filled state STM image of a 26 × 26 nm² area. (c) Fast Fourier transform (FFT) of the image in (b). The large hexagon shows the “√3” contribution to the FFT. There is a clear split into several “spots”, which is in good agreement with Fig. 1(a). The small inner hexagon corresponds to a ∼6√3 periodicity. (d) Atomically resolved filled state STM image of a 2.4 × 12.8 nm² area showing the striped structure within one domain. The 6√3 periodicity is indicated by a parallelogram. All three STM images were recorded at room temperature in the constant current mode with a tunneling current of 300 pA and a sample bias of −50 mV.
FIG. 3. (Color online) Valence band dispersions obtained using a photon energy of 27 eV. The bands were mapped along three lines in the $\sqrt{3} \times \sqrt{3}$ SBZs as illustrated by the inset. The $\bar{K}$-$\bar{K}$ panel shows two surface bands, $S_1$ and $S_2$, which cross $E_F$. There are also some very weak bands between the two $S_1$ branches. The $\bar{K}$-$\bar{M}$ panel shows emission from the bulk $Ag \, sp$ band (B) and $S_{2+}$ and $S_{2-}$ label the split of the $S_2$ band. At the $\bar{M}$ point, the $S_{2+}$ and $S_{2-}$ bands are degenerate. The dispersion away from $\bar{M}$ toward $\bar{K}$ is shown in the rightmost panel. The dispersion is parabolic with a seemingly degenerate $S_{2\pm}$ band near $\bar{M}$. However, close to $E_F$, there is a split into two bands.

the surface structure deviates from that of an ideal $\sqrt{3} \times \sqrt{3}$ periodicity. For comparison, ARPES data have been included of surface alloys prepared by depositing 0.36 ML of Sn and $1/3$ ML of Pb, respectively, on Ag(111) kept at 200 °C. The heating was terminated immediately after deposition. An ideal $\sqrt{3} \times \sqrt{3}$ periodicity was verified after this procedure by LEED in each case.

III. RESULTS AND DISCUSSION

A. Atomic structure

Figure 1(a) shows a ("$\sqrt{3} \times \sqrt{3}$")R30° LEED pattern after improvement of the surface quality by annealing at 200°C for 10 min. Compared to the closely related Sn/Ag(111)("$\sqrt{3} \times \sqrt{3}$") surface, the LEED pattern in Fig. 1(a) appears a bit fuzzy. The origin of the fuzziness is revealed in Fig. 1(b), where the details of the diffraction pattern near $\sqrt{3}$ positions are resolved. Instead of a $\sqrt{3}$ diffraction spot, there are six tiny spots forming a triangle, which indicates that the atomic structure deviates from that of a perfect $\sqrt{3} \times \sqrt{3}$ periodicity. The small distances between the spots forming the triangle suggest the presence of a distortion with a long repetition length. A similar triangular LEED pattern has been reported for the so-called Pb/Si(111)(1,3) surface, and the absence of most of the higher-order spots was there explained by a systematic extinction of diffraction [13].

Core-level spectroscopy is used to obtain information about the inner shell electrons, which in turn can be used to gain information about the atomic structure. Figure 1(c) shows a spectrum of the Ge 3d core-level from the Ge/Ag(111)("$\sqrt{3} \times \sqrt{3}$")R30° surface alloy. The spectrum is dominated by a remarkably narrow spin-orbit split component (SC1), with a Gaussian width of just 105 meV. The base of the spectrum shows some broadening due to a metallic tail and shifted Ge 3d emission. The additional Ge 3d emission is here modeled by one single spin-orbit split component (SC2) shifted by −0.17 eV. Due to the comparatively large Gaussian width of 332 meV, it is difficult to conclude whether this is a single component or the result of several components. The intensity of the SC2 component is sensitive to the exact values of the fitting parameters, and the result is therefore approximate. The crucial point here is that the sharp SC1 component is dominating the spectrum, which implies that most Ge atoms are located at identical positions indicating a well-defined surface structure.

Further information about the atomic structure is obtained by STM. Figure 2(a) shows a large-scale $130 \times 130$ nm² topographic filled-state image after local-derivation treatment, in which a striped structure of the surface is clearly revealed. Stripes are aligned along three different directions, separated by 120°, corresponding to the three domains that are expected. A close-up of a region where the three domains meet is shown in Fig. 2(b). Apart from the height modulation resulting in stripes, there are atomically resolved protrusions forming a hexagonal pattern. The distance between the protrusions and the orientation of the pattern correspond to a "$\sqrt{3}$" periodicity. Based on the size of the unit cell and the amount of Ge deposited, we conclude that the STM image shows the positions of Ge atoms. The striped phase appears as a wavelike modulation resulting in an apparent height difference of ~0.2 Å between the uppermost and lowermost Ge atoms. The height difference does not depend on the magnitude or the sign of bias. Right after deposition of Ge, stripes are present in the form of meandering features. After annealing, they become straight, and the well-ordered striped structure shown in Fig. 2(a) is formed. Through a fast Fourier transform (FFT) of Fig. 2(b), the reciprocal space, shown in Fig. 2(c), is obtained. The map of the Fourier components can be grouped into two hexagonal patterns. The larger hexagon is close to what is expected for a true $\sqrt{3} \times \sqrt{3}$ periodicity. However, in similarity with the LEED pattern in Fig. 1(b), there are several Fourier components around $\sqrt{3}$ positions. The smaller hexagon, formed by the inner Fourier components, corresponds to an approximate $6 \times 3$ periodicity. The existence of the $6 \times 3$ periodicity in LEED could, however, not be confirmed in this study since, even at an electron energy as low as 25 eV, the spots would be hidden behind the electron gun. A detailed STM image obtained from a small area, $2.4 \times 12.8$ nm², is shown in Fig. 2(d), where both the local ("$\sqrt{3} \times \sqrt{3}$") periodicity and the long-range modulation are clearly visible. The periodicity of the striped structure can essentially be described by a unit cell of the form "$\sqrt{3} \times 6 \times 3$", as indicated by the parallelogram in Fig. 2(d). Another deviation from an ideal $\sqrt{3} \times 3$ periodicity can be noticed in Fig. 2(d). The hexagonal structure formed by the protrusions (Ge atoms) appears to be slightly stretched in the valleys compared to the ridges of the stripes. In the well-defined $6 \times 3$ regions, the distances between the Ge atoms in the dark valleys are approximately 10% larger along the $6 \times$ direction than on the bright ridges. Further, the rows of Ge atoms along the $6 \times$ directions appear slightly wiggly. A line
through the three Ge atoms on the ridges makes a small angle with respect to a line through the three Ge atoms in the valleys. This indicates that there might also be a rotational distortion of the alloy layer.

This striped Ge/Ag(111) structure is somewhat similar to recently reported striped structures of Bi/Ag(111) [14,15]. However, the Ge/Ag(111) stripes do not show the coverage dependence reported for the Bi case. Furthermore, the distance between stripes is larger, and the hexagonal pattern is not strongly deformed in the Ge/Ag case, which is in contrast to the rectangular unit cells observed in the Bi/Ag case.

B. Electronic band structure

The valence band structure of the ½ ML Ge/Ag(111) striped phase was studied by ARPES. Energy dispersions of the surface bands are presented along the $\Gamma \rightarrow \bar{K} \rightarrow \bar{M} \rightarrow \Gamma$ symmetry lines in Fig. 3. The specific parts that were actually measured are highlighted by the red lines in the inset showing three neighboring $\sqrt{3} \times \sqrt{3}$ surface Brillouin zones (SBZs). The surface state dispersions follow basically a $\sqrt{3} \times \sqrt{3}$ SBZ periodicity, and the general shapes are close to those of the corresponding bands reported for other group-IV-induced surface alloys on Ag(111), i.e. Pb/Ag(111)($\sqrt{3} \times \sqrt{3}$) [11]
and Sn/Ag(111)($\sqrt{3} \times \sqrt{3}$) [3]. Close to $\bar{\Gamma}$, there are two steeply dispersing surface bands labeled $S_1$ and $S_2$. The weak intensity of the emission from the $S_2$ band is a consequence of the experimental geometry, something that was also reported for Sn/Ag(111)($\sqrt{3} \times \sqrt{3}$). Both $S_1$ and $S_2$ are metallic bands with unoccupied states close to the $\bar{\Gamma}$ point. The Fermi level ($E_F$) crossings are located at $-0.12$ Å$^{-1}$ and $-0.31$ Å$^{-1}$, respectively, along $\bar{\Gamma}\bar{K}$. It is interesting to note that there are two weak additional bands between the $S_1$ branches. No bands were identified in this region in the Pb/Ag and Sn/Ag cases. Along $\bar{K}\bar{M}$, ARPES shows a strong contribution due to emission from the Ag $sp$ bulk band (B). Except for this bulk contribution, there is an unexpected split ($\delta k_0 \approx 0.11$ Å$^{-1}$) of the $S_2$ band into two bands, $S_{2+}$ and $S_{2-}$. These bands are degenerate at the $\bar{M}$ point. Our results are in agreement with a recent study by Golias et al. [8]. Except for this split, the dispersions of the two bands are close to that of the single $S_2$ band observed for Sn/Ag(111) and Pb/Ag(111). Along $\bar{\Gamma}\bar{M}\bar{\Gamma}$, the ARPES data appears to show a single parabolic band, which would be in accordance with the results for the Sn/Ag and Pb/Ag surface alloys. However, a closer inspection reveals a split into two bands when approaching $E_F$. Such a split was not observed for the Sn and Pb cases.

In order to further characterize the surface band structure of the striped Ge/Ag(111)($\sqrt{3} \times 6/3$) surface, we have investigated constant energy contours at various energies and centered at different symmetry points of the $\sqrt{3} \times \sqrt{3}$ SBZ. The left part of Fig. 4(a) shows constant energy contours at 0.5 eV below $E_F$ centered at the $\bar{\Gamma}$ point of the first SBZ ($k_x,k_y = 0$). There are as many as four outer contours giving rise to an overall flowerlike shape. The inner part consists of two contours. These contours are much more complicated than the results obtained for Sn/Ag and Pb/Ag. In the case of Sn/Ag, shown in Fig. 5(a), there are just two contours, one inner hexagonlike and one outer flowerlike contour corresponding to $S_1$ and $S_2$, respectively. In the case of Pb/Ag, the hexagonlike inner contour is split into two concentric contours as a consequence of a RB type of spin split of the $S_1$ band, and the outer contour is made up of just one band, shown in Fig. 5(b). Hence, Ag$_2$Ge clearly deviates from an ideal $\sqrt{3}$ surface alloy with or without conventional RB type of spin split.

The constant energy contours, centered at the $\bar{\Gamma}$ point of the second SBZ, give at first an impression of being different from those obtained in the first SBZ. However, the main features are still present in the second SBZ, but with some noticeable differences. The intensity of the curves changes in the $\bar{\Gamma}\bar{M}$ direction in such a way that it results in an overall triangular appearance, as was also reported in Ref. [8]. What is more interesting is the appearance of a fourth contour, which is part of the flowerlike shape. In order to find out the relation between the bands forming the four contours and the $S_{2+}$ and $S_{2-}$ bands observed along $\bar{K}\bar{M}\bar{\Gamma}$, a dataset centered at the $\bar{M}$ point is important. Contours obtained from those data are superimposed on the data of the second SBZ in Fig. 4(a). There is a very nice match between the two datasets where the four contours overlap, as is evident when comparing with the upper left part of the second SBZ. The data including the $\bar{M}$ point are presented as a three-dimensional (3D) plot, i.e. energy as function of ($k_x, k_y$) in Fig. 4(b). Three planes that cut through the 3D data are shown. The front left face of the cube highlights the split of the $S_2$ band into $S_{2-}$ and $S_{2+}$ with a degeneracy at the $\bar{M}$ point (compare with the middle panel of Fig. 3). The top face of the cube shows the constant energy curves as in Fig. 4(a), while the right face shows the dispersions along a line parallel to $\bar{\Gamma}\bar{M}$. This face shows how $S_{2-}$ and $S_{2+}$ each split into two bands (indicated by arrows) labeled $S_{2-}′$, $S_{2+}′$ and $S_{2-}″$, $S_{2+}″$, respectively.

These bands can be followed to the top face of the cube, which results in the labeling that was introduced already in Figs. 3 and 4(a). The constant energy contours generated by the $S_{2+}′$ and $S_{2-}″$ bands in the first SBZ look very much like two flowerlike curves rotated by approximately $\pm 6°$, respectively.
The idea of rotation is supported by the obvious intersection of these curves along \( \bar{\Gamma}K \). The \( S_2' \) and \( S_2'' \) bands are connected with \( S_2 + \) and \( S_2 - \), respectively, as is evident from the right face of Fig. 4(b). This suggests that the band split at the \( M \) point is due to a rotational distortion. However, the structural information from LEED and STM does not confirm the magnitude of the suggested rotation. The appearance of the \( S_2' \) and \( S_2'' \) bands could be regarded as a result of a splitting of \( S_2 + \) and \( S_2 - \), respectively. The \( S_2' \) band appears at lower binding energies compared to \( S_2 + \), while \( S_2'' \) is split off toward higher binding energies relative to \( S_2 - \). Thus, the four contours in the second SBZ could be interpreted as a superposition of two rotated flowerlike contours (\( S_2' + \) and \( S_2' - \)) and two split off contours (\( S_2'' + \) and \( S_2'' - \)). The situation that the outer \( S_2' \) and \( S_2'' \) bands were not observed in the first SBZ may be a cross-section effect due to the change of the incidence angle of the linearly polarized light.

**IV. SUMMARY**

Our combined LEED, STM, and ARPES study of the Ge/Ag(111) surface alloy has revealed new detailed information on the atomic and electronic structure. From these results, it is clear that the atomic structure deviates significantly from the simple \( \sqrt{3} \times \sqrt{3} \) structure reported for the Ag\( _2M \) surface alloys (\( M = Bi, Pb, Sb, \) or Sn). Regarding the electronic structure, Ag\( _2Ge \) shows a complexity not observed on the related Ag\( _2M \) systems, which reflects a difference in the atomic structure. Our main findings are (i) LEED shows a set of diffraction spots centered around the \( \sqrt{3} \) position instead of the expected single diffraction spot at the \( \sqrt{3} \) position. This implies that the structure deviates from a simple \( \sqrt{3} \times \sqrt{3} \) ordering of the Ge atoms. (ii) Scanning tunneling microscopy shows two types of modifications of the \( \sqrt{3} \times \sqrt{3} \) periodicity. The most apparent feature is the striped structure with an apparent height difference of \( \sim 0.2 \) \( \AA \) between ridges and valleys. A closer inspection of the STM images shows a distortion of the Ge hexagons which are stretched by \( \sim 10\% \) in the valleys compared to the hexagons on the ridges. (iii) Apart from the split of the \( S_2 \) band reported in Ref. [8], we report constant energy contours that show a multiplicity of surface bands, which also implies that the Ag\( _2Ge \) surface alloy is electronically and atomically unique. The rotated appearance of the constant energy curves related to \( S_2 \) indicates the presence of rotated structural entities [16]. We conclude that the complex surface band structure, with several split bands, most likely originates from the structural distortions of the alloy layer reported in this study.

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