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Electronic and atomic structures of the Ag induced $\sqrt{3}\times\sqrt{3}$ superstructure on Ge(111)

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Abstract

The Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ surface together with Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ constitute a set of surfaces that is ideally suited for fundamental studies related to low dimensional physics. We here focus on the atomic and electronic structures of the two-dimensional $\sqrt{3}\times\sqrt{3}$ superstructure induced by Ag on Ge(111), a surface that is significantly less studied than the Si counterpart. Extensive information on the surface band structure obtained by angle resolved photoelectron spectroscopy (ARPES) is presented, complemented by atomic information from scanning tunneling microscopy (STM). The results reveal new findings that are important for the understanding of the Ag induced $\sqrt{3}\times\sqrt{3}$ structure, acting as a prototype for semiconductor/metal interfaces. i) We have identified a new occupied surface band near the $\bar{M}$ - point of the $\sqrt{3}\times\sqrt{3}$ surface Brillouin zone. ii) The Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ surface exhibits a partially occupied surface band, S_1 , with a parabolic-like shape at $\bar{\Gamma}$. At low temperature (≈ 100 K) this band splits into two bands, S_{1U} and S_{1D} . The identification of two bands is significantly different from the case of Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ for which just one band has been reported. Besides these specific results, our extensive ARPES study reveals four surface bands at room temperature (RT), while five surface bands were identified at ≈ 100 K (LT). Room temperature empty state STM images show, depending on the tunneling bias, both honeycomb and hexagonal periodicities which are consistent with the honeycomb chained trimer and the in-equivalent trimer models, respectively.

Keywords: Ge(111), Ag, monolayer, atomic structure, electronic band structure, free electron like band, STM, LEED, and ARPES.

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1. Introduction

Semiconductor surfaces with metallic adsorbates exhibit well-ordered two-dimensional (2D) structures that are fundamentally important since various physical phenomena can be observed which contain rich science. Phase transitions, metal-insulator and metal-semiconductor transitions, charge density waves, and domain wall structures are examples of subjects that have been studied [1-10]. In addition, these systems provide an ideal 2D platform for the study of surface electronic and atomic structures. Silver (Ag) and gold (Au) are examples of metallic adsorbates that can induce several 2D structures [11,12]. Especially Ag on elemental semiconductor surfaces, such as Si(111), has been used as a prototype element to modify the atomic and electronic properties [8,11-16]. These investigations have been concentrated to one monolayer (ML) of Ag on Si(111), i.e., the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ superstructure [13-33] covering quite many properties of the surface, such as, atomic and electronic structures, surface conductivity, Fermi surfaces, electron group velocity, substrate band bending and the Hall effect, among others [13-33]. The Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface shows an increased conductivity upon exposure to a tiny amount of noble or alkali metals [13,14,26,27,34]. The four point probe technique has been introduced to measure the conductivity and resistivity on such surfaces [15,35-37]. A similar $\sqrt{3} \times \sqrt{3}$ superstructure is formed by 1 ML of Ag on Ge(111) [7,38-42]. The atomic structure of this surface is believed to be described by the honeycomb chained trimer (HCT) and/or the in-equivalent trimer (IET) model as for the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface [41,42]. Surprisingly, the electronic structure of Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ has not yet been studied in detail and just a few references [7,39,40] give some information about the surface bands and then just along one symmetry line of the $\sqrt{3} \times \sqrt{3}$ surface Brillouin zone (SBZ). Therefore, it is worth to explore the electronic structure of Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ in detail, at both RT and LT.

In the present study, Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ surfaces were formed after initial depositions of two different amounts of Ag, i.e., 0.9 and 1.1 monolayer (ML), onto the clean Ge(111)c(2×8) surface. These two preparations facilitated a study of the influence of extra Ag atoms on the surface band structure. This is particularly important when it comes to a partially occupied surface band, S_1 , also observed for Ag/Si(111) $\sqrt{3} \times \sqrt{3}$. Detailed surface band dispersions are

presented along the $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ and $\bar{\Gamma}-\bar{K}-\bar{M}$ high symmetry lines of the $\sqrt{3}\times\sqrt{3}$ SBZ obtained at room temperature (RT) and at ≈ 100 K (LT) for both the 0.9 and 1.1 ML Ag cases. Four surface bands were found in the room temperature (RT) data, while five surface bands were identified at ≈ 100 K (LT). Of these bands, the three completely occupied ones do not change with temperature or Ag amount. Interestingly, one of these bands has not been reported before. The existence of the band is verified for the two Ag amounts, the two temperatures, and for the three photon energies used in this study. Another new result is related to the behavior of the partially occupied S_1 band at $\bar{\Gamma}$. At low temperature (≈ 100 K) this band splits into two bands, S_{1U} and S_{1D} . The identification of two bands is significantly different from the case of Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ for which just one band has been reported. The S_1 , S_{1U} and S_{1D} , bands are discussed based on both RT and LT data for the two Ag coverages. Atomic structure information from the Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ surface was obtained by STM. Depending on the tip to sample bias, the STM images were in agreement with the HCT or the IET model [41,42].

2. Experimental details

All electronic structure studies were performed at beamline I4 located at the MAX-III storage ring of the MAX-lab synchrotron radiation facility in Lund, Sweden. The photoemission data presented in this paper were obtained at photon energies of 21.2, 30, and 40 eV. The major part of the photoemission data was obtained at 30 eV with a total energy resolution of ≈ 20 meV, and an angular resolution of $\pm 0.3^\circ$. There are two UHV chambers at the experimental station, one for surface preparation equipped with a sputter gun, quartz crystal thickness monitor, residual gas analyzer, low energy electron diffraction (LEED) optics, and an Ag evaporator, while the second chamber is equipped with a LEED optics and a SPECS Phoibos 100 electron analyzer with a 2D detector. The chambers had base pressures of less than 1.0×10^{-10} Torr, while during the Ag evaporation the pressure in the preparation chamber was $< 4.0\times 10^{-10}$ Torr. The substrate was cut from an n-type Ge(111) wafer doped with Sb, with a resistivity in the range 7-10 Ωcm at room temperature. The Ge(111) substrate was degreased *ex-situ* using acetone and isopropanol and cleaned *in-situ* by multiple Ar^+ -ion sputtering (1 keV) and annealing (730 $^\circ\text{C}$) cycles in order to produce a well-ordered Ge(111)c(2 $\times$ 8) surface as verified by LEED. A quartz crystal thickness monitor was used to establish the Ag evaporation rate, i.e., 0.4 ML/min in our case.

Surfaces were prepared by evaporating two different amounts of Ag, i.e., 0.9 and 1.1 ML (1 ML is defined as the density of atoms on the unreconstructed Ge(111) surface, i.e., 7.2×10^{14} atoms/cm²), in order to facilitate an investigation of the effect of additional Ag atoms. Subsequent post annealing of the surfaces up to 330 °C for a few minutes, resulted in well-ordered Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ superstructures in both cases. The preparation based on 1.1 ML of Ag ensures that the $\sqrt{3} \times \sqrt{3}$ superstructure is fully developed, i.e., there are no signs of c(2×8) or 4×4 domains in LEED patterns or STM images. However, there are extra Ag atoms freely moving on the surface at room temperature on the surface prepared this way. The number of these Ag atoms can be reduced by annealing, but it is hard to completely remove them as reported in earlier studies [7,23]. The surface with 0.9 ML of Ag was prepared in order to significantly reduce the number of extra Ag atoms. As a consequence of the less than optimal amount of Ag, the surface showed 4×4 diffraction spots and streaks in LEED. As expected, the dominating $\sqrt{3} \times \sqrt{3}$ areas had a lower number of additional Ag atoms which had a significant effect on the electronic structure.

An investigation of the surface atomic structure was performed in a separate UHV chamber equipped with a LEED optics, a sputter gun, an Ag evaporator, a quartz crystal thickness monitor, and an Omicron variable-temperature scanning tunneling microscope (VT-STM), situated at Linköping University, Sweden. The VT-STM uses an electrochemically etched W-tip cleaned in-situ by electron beam heating. The surface preparation methods were the same as those described above for the two Ag coverages (0.9 and 1.1 ML). All STM measurements were performed at room temperature in the constant current mode (100 pA).

3. Results and discussion

3.1. Atomic structure

In Fig. 1, we present LEED and STM results from the two Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ surfaces prepared by depositing 0.9 and 1.1 ML of Ag, respectively. With an Ag coverage of 0.9 ML the LEED pattern shows streaks and 4×4 diffraction spots (Fig. 1(a)), while the 1.1 ML preparation

exhibits only well-defined $\sqrt{3}\times\sqrt{3}$ diffraction spots (Fig. 1(b)). The large scale ($150\times150\text{ nm}^2$) empty state STM images in Figs. 1(c) and 1(d) present the 0.9 and 1.1 ML cases, respectively. Fig. 1(c) shows small patches of the 4×4 structure (indicated by arrows) on a surface that is dominated by the $\sqrt{3}\times\sqrt{3}$ periodicity. In the 1.1 ML case, Fig. 1(d), there is no trace of any other structure than $\sqrt{3}\times\sqrt{3}$.

Fig. 1 (a) LEED pattern of the $\sqrt{3}\times\sqrt{3}$ surface prepared by 0.9 ML of Ag. Besides $\sqrt{3}\times\sqrt{3}$, there are streaks and additional 4×4 spots. (b) In the case of 1.1 ML of Ag the LEED pattern only exhibits $\sqrt{3}\times\sqrt{3}$ diffraction spots. The LEED patterns in (a) and (b) were obtained at an electron energy of 40 eV. (c) and (d) Large scale ($150\times150\text{ nm}^2$) empty state STM images obtained at RT from the 0.9 and 1.1 ML surfaces, respectively. The images were recorded in constant current mode (100 pA) at a bias of 1.5 V in (c) and 2.0 V in (d).

Figures 2(a) and 2(b) show small scale ($\approx 6.4\times 6.4\text{ nm}^2$) empty state images obtained at a sample bias of 0.3 and 1.0 V, respectively. At the 0.3 V bias the image shows an apparent honeycomb structure while at 1.0 V the image has a strong hexagonal appearance. The honeycomb pattern has been explained by the honeycomb-chained-trimer (HCT) model (Fig. 2(c)) which was considered to describe the atomic structures of Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ and Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ at RT for a long time [18,38,41]. The positions of the bright protrusions observed by STM, forming the honeycomb pattern, correspond to the centers of Ag trimers,

while the dark center of a honeycomb corresponds to the center of a Si or Ge trimer, respectively. Later, another model, the in-equivalent trimer (IET) model (Fig. 2(d)), was proposed for the Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ surface to explain the hexagonal structure observed by STM at low temperature [19-21,32]. Due to the two trimers being in-equivalent one becomes brighter than the other in the STM image resulting in a hexagonal pattern as that of Fig. 2(b). Recently, the same type of model has been suggested for the Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ surface as well [42].

Fig. 2 (a) and (b) Small scale ($\approx 6.4 \times 6.4 \text{ nm}^2$) empty state STM images obtained at RT at a bias of 0.3 and 1.0 V, respectively. A $\sqrt{3}\times\sqrt{3}$ unit cell is indicated in (a) and (b). (c) and (d) HCT and IET models of the Ag induced $\sqrt{3}\times\sqrt{3}$ superstructure. The HCT model in (c) is consistent with the honeycomb structure observed in (a), while the IET model in (d) accounts for the hexagonal pattern in (b).

3.2. Electronic structure

3.2.1. Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$: 1.1 ML Ag case

The electronic structure of the Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ surface was studied by ARPES, using linearly polarized synchrotron light at a photon energy of 30 eV. The measurements were performed both at RT and at $\approx 100 \text{ K}$ (LT). In Fig. 3, a detailed electronic band structure of the $\sqrt{3}\times\sqrt{3}$ surface is presented for the 1.1 ML Ag case. Figure 3(a) shows the 1×1 and $\sqrt{3}\times\sqrt{3}$ SBZs

and highlights high symmetry directions. Figs. 3(b)–3(e) show experimental band structures along the high symmetry directions $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ and $\bar{\Gamma}-\bar{K}-\bar{M}$ of the $\sqrt{3}\times\sqrt{3}$ SBZ at both RT and LT. The figures show a representation of the second derivative along the energy axis of the original photoemission intensity data collected by the 2D detector of the electron analyzer. The representation of photoemission data using the second derivative is useful in order to make also weak but well-defined features visible. In this way all bands can be visualized in the same figure.

Four bands are observed at RT, labeled S_1 – S_4 , that follow the $\sqrt{3}\times\sqrt{3}$ periodicity, all within 1.4 eV below the Fermi level. The S_1 band is observed around $\bar{\Gamma}$ - points along the $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ high symmetry line (except for normal emission), while it does not show at any $\bar{\Gamma}$ - point along $\bar{\Gamma}-\bar{K}-\bar{M}$, see Figs. 3(b) and 3(c). S_1 is a quite steep band with a shape deviating slightly from a free electron like parabola with an energy minimum of ≈ 0.6 eV below E_F at RT. A similar band has also been observed for the Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ surface [17,30]. The energy minimum is related to the number of electrons occupying the band, which can be altered by doping the surface with a tiny amount of monovalent atoms, as in the case of Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ [29,30]. At LT, two new bands, S_{1U} and S_{1D} appeared within 0.3 eV below E_F , while some weak traces of the S_1 band remained. In contrast to the S_1 band, S_{1U} and S_{1D} are visible at every $\bar{\Gamma}$ - point, see Figs. 3(d) and 3(e). The behavior of the S_1 , S_{1U} and S_{1D} bands at 0.9 ML of Ag will be discussed in the next section while a detailed discussion of their behavior at RT and LT will be presented for the two Ag coverages at the end of this electronic structure section.

Fig. 3 (a) 1×1 and $\sqrt{3} \times \sqrt{3}$ surface Brillouin zones with high symmetry directions. (b) and (c) ARPES results obtained at room temperature (RT) along the high symmetry directions $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ and $\bar{\Gamma}-\bar{K}-\bar{M}$ of the $\sqrt{3} \times \sqrt{3}$ SBZ, respectively. (d) and (e) ARPES results along the high symmetry directions obtained at ≈ 100 K (LT). The amount of evaporated Ag was 1.1 ML. The black curves in (b) – (e) represent the edge of projected bulk bands.

Another band, S_2 , is located at 0.6 eV below E_F at the $\bar{M}$ -points and shows a small downward dispersion toward $\bar{K}$ in the limited $k_{\parallel}$ -range where it is observed, see Figs. 3(c) and 3(e). Toward $\bar{\Gamma}$, the S_2 band shows a downward dispersion of about 0.6 eV. There are, however, kinks in the experimental curves that make the identification somewhat uncertain, see Figs. 3(b) and 3(d). These kinks are also clear in the original photoemission data. Close to S_2 , there is an additional band, S_3 , observed along $\bar{\Gamma}-\bar{K}-\bar{M}$. It has an energy of 0.8 eV below E_F at $\bar{M}$ and it disperses to an energy minimum of -1.0 eV at $\bar{K}$, see Figs. 3(c) and 3(e). S_2 and S_3 show similar

dispersions around $\bar{M}$ but are separated in energy by ≈ 0.2 eV, as evident from Fig. 3(e). Further, it is interesting to note that S_3 is not observed along $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$. The presence of these two bands are in contrast to the results for $\text{Ag/Si(111)}\sqrt{3}\times\sqrt{3}$ where only one band is observed in the corresponding energy and $k_{\parallel}$ range [17]. For this reason, we have given quite much attention to the S_2 and S_3 bands and checked them with different photon energies at LT, i.e., 21.2, 30 and 40 eV as shown in Fig. 4. These data confirm the presence and dispersion of S_2 as shown in Fig. 3. Furthermore, the absence of S_3 along $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ is a common observation for all three photon energies (not included here). In the data obtained at 21.2 eV the dispersion of the S_2 band can be followed all the way from $\bar{M}$ to $\bar{K}$ showing a constant separation with respect to S_3 , see Figs. 4(a) and 4(d). At 40 eV, the S_2 band has strong appearance around the $\bar{M}$ -point, see Figs. 4(c) and 4(f). We conclude that there is an additional band in the case of $\text{Ag/Ge(111)}\sqrt{3}\times\sqrt{3}$ that has not been observed for $\text{Ag/Si(111)}\sqrt{3}\times\sqrt{3}$. The observation of two bands shows some resemblance with the surface band structure of $\text{Ag/Si(111)}\sqrt{21}\times\sqrt{21}$ reported in Ref. 8. The single band observed for the $\text{Ag/Si(111)}\sqrt{3}\times\sqrt{3}$ surface, with a dispersion similar to those of the S_2 and S_3 bands in Figs. 3(c) and 3(e), is split into two bands on the $\sqrt{21}\times\sqrt{21}$ surface. The separation was ≈ 0.2 eV, which is similar to what we find for the split between S_2 and S_3 . The occurrence of two bands was associated with a partial occupation of the Ag trimer sites by additional Ag atoms. In the case of $\text{Ag/Si(111)}\sqrt{21}\times\sqrt{21}$, the occupied sites form the periodicity of the reconstructed surface. Even though the Ag/Ge(111) surface presented in this study has a $\sqrt{3}\times\sqrt{3}$ periodicity, the two bands, S_2 and S_3 , might have a similar origin as for the $\sqrt{21}\times\sqrt{21}$ periodicity on Si(111). In the case of Ge, there is a stronger tendency for the extra Ag atoms to occupy the Ag trimer sites since a $\sqrt{39}\times\sqrt{39}$ structure forms already at RT, while the $\sqrt{21}\times\sqrt{21}$ counterpart in the case of Si forms at lower temperature [7,8]. In Ref. 7, it was reported that RT LEED patterns from the $\text{Ag/Ge(111)}\sqrt{3}\times\sqrt{3}$ surface always showed some weak ring-like structure indicating an additional periodicity with a lattice constant larger than that of $\sqrt{39}\times\sqrt{39}$. Irrespective of the actual periodicity, the ring-like LEED pattern indicates the presence of Ag atoms on some of the Ag trimers at RT which may be the reason for the appearance of the two bands, S_2 and S_3 , instead of just one as expected for an intrinsic $\sqrt{3}\times\sqrt{3}$ surface.

Fig. 4 (a)–(c) Gray scale images of the S_2 , S_3 and S_4 bands obtained at LT, for photon energies of 21.2, 30 and 40 eV, respectively. The amount of evaporated Ag was 1.1 ML. (d)–(f) show the second derivative along the energy axes of the original photoemission data in (a)–(c). The black curves in (d)–(f) represent the edge of projected bulk bands. The bands show dispersion along the $\bar{K}_1 - \bar{M}_1 - \bar{K}_2$ line of the $\sqrt{3} \times \sqrt{3}$ SBZ, see Fig. 3(a).

In the $\bar{\Gamma} - \bar{K} - \bar{M}$ direction, a fourth band, S_4 , has a local maximum of ≈ -1.2 eV at $\bar{M}$ and disperses downward and overlaps with S_3 at the $\bar{K}$ -point. The bands seem to be degenerate at the $\bar{K}$ -points since no clear evidence of a gap between the two bands was observed, a result that has also been reported experimentally for the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface [17,33]. For this surface, these bands are degenerate at the $\bar{K}$ -point when the atomic structure follows the HCT model as predicted by first principles calculations [19]. According to another experimental observation, the bands are split with a 0.22 ± 0.07 eV gap [25] while calculations predicted a gap of 0.15 eV, when the IET model is followed [19]. However, a more recent calculation predicted a very tiny gap of 0.04 eV [45] which is quite small compared to what is reported in Ref. 19. The obvious difference in energy gap was due to different exchange-correlation functions used in these calculations [19,45]. In the present study, we have carefully looked at this important issue for Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ surface, but could not detect any clear gap neither at RT nor at LT. However, if the expected gap between these bands is as small as that calculated in Ref. 45 for the Si case, it

would not be resolved in the photoemission data. In addition, there is no clear evidence of a gap between these bands at the $\bar{K}$ - point as verified by the other photon energies, see Fig. 4. Therefore, we conclude that there is no clear experimental evidence of a gap for Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ surface. Furthermore, the S_4 band can also be observed between 1.1 – 1.4 eV below E_F along $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ where it has energy maxima (– 1.1 eV) at $\bar{\Gamma}$ -points and minima (– 1.4 eV) between $\bar{\Gamma}$ and $\bar{M}$, while at the $\bar{M}$ -points the band has an energy (– 1.2 eV) similar to that in the $\bar{\Gamma} - \bar{K} - \bar{M}$ direction, see Figs. 3(b) and 3(d).

3.2.2. Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$: 0.9 ML Ag case

ARPES results measured at RT and LT using a photon energy of 30 eV, for 0.9 ML of Ag, are shown along the high symmetry directions $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ (Figs. 5(a) and 5(c)) and $\bar{\Gamma} - \bar{K} - \bar{M}$ (Figs. 5(b) and 5(d)). Four bands are observed at RT as for the 1.1 ML case while at LT there are five bands. One of these bands, the free electron like band S_1 , shows an important difference when it comes to the bandwidth. The band is much shallower with an energy minimum of 0.25 eV below E_F instead of ≈ 0.6 eV as observed for the 1.1 ML case. This modification is well known in case of Ag/Si(111) $\sqrt{3} \times \sqrt{3}$, but it is here reported for the first time for the Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ surface. For the 1.1 ML Ag case, there are extra Ag atoms that are freely moving on the surface. The outermost s electrons of these atoms are donated to the S_1 band, resulting in a downward shift. It is interesting to note that the band is visible at all the $\bar{\Gamma}$ - points which is in contrast to the 1.1 ML case. The extra Ag atoms do not have an impact on the other bands ($S_2 - S_4$), as there are no shifts observed here compared to the 1.1 ML case. All bands ($S_2 - S_4$) are reproduced, both at RT and at LT, (cf. Figs. 3 and 5). The band structures of S_2 and S_3 , and those of S_3 and S_4 at the $\bar{K}$ - point confirm the picture from the 1.1 ML case. The shallow S_1 band is replaced by two bands S_{1U} and S_{1D} at LT, in similarity with the changes observed for the 1.1 ML case, see Figs. 5(c) and 5(d). The S_{1U} band is steeper than the S_1 band exhibiting a V-like shape in contrast to the parabolic dispersion at RT. The energy minimum of S_{1U} is close to that of S_1 . Just below the S_{1U} band there is one more band, S_{1D} at ≈ -0.3 eV, which does not show any dispersion in energy. This band was not observed at RT, see Figs. 5(a) and 5(b).

Fig. 5 (a) and (b) ARPES results along the high symmetry directions $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ and $\bar{\Gamma}-\bar{K}-\bar{M}$ of the $\sqrt{3}\times\sqrt{3}$ SBZ obtained with a photon energy of 30 eV at room temperature (RT). (c) and (d) show similar data sets as in (a) and (b) but at LT. The amount of Ag deposited was 0.9 ML.

3.2.3. Characteristics of the metallic band

In this section, a more detailed discussion of the behavior of the free electron like band S_1 , is presented. Three observations are addressed here. One important character of S_1 is the difference in the band width of the occupied part for the two Ag coverages when measured at RT. A second one is the fading out of the S_1 band at LT in the 1.1 ML case, leaving two extra bands that are found at all $\bar{\Gamma}$ - points. The final feature to be discussed is related to the 0.9 ML Ag case where the shape of the band changes from parabolic to non-parabolic at LT.

Figures 6(a) and 6(c) show the RT dispersion of S_1 for the 1.1 ML case, while the corresponding data obtained for 0.9 ML of Ag is displayed in 6(e) and 6(g). For the 1.1 ML case, the band goes as deep as ≈ -0.6 eV and has a shape that is significantly steeper than a free electron parabola, while for 0.9 ML of Ag the band is closer to a parabola with a minimum

energy of 0.25 eV below E_F . The variation in depth of the band is explained by electron doping that occurs when there is a surplus of monovalent atoms on the surface. The behavior of the S_1 band is similar to that of $\text{Ag/Si(111)}\sqrt{3}\times\sqrt{3}$ as reported in Ref. 30, where the binding energy of the band increases as the amount of Au atoms increase on the surface. The shape of the S_1 band in Fig. 6(a) is quite similar to that observed for $\text{Ag/Si(111)}\sqrt{3}\times\sqrt{3}$ with 0.03 ML of Au reported in Ref. 30. The deviation from the parabolic shape was explained in that study by interaction between S_1 and two surface bands with slightly higher binding energies. These bands correspond to three bands, $S_2 - S_4$, in the case of $\text{Ag/Ge(111)}\sqrt{3}\times\sqrt{3}$. The model derived in Ref. 30 to explain the shape of the S_1 dispersion predicts a more parabolic shape when the energy minimum is closer to E_F . This is also what we observe in the case of Ag/Ge(111) , see Fig. 6(e) and 6(g). The second important finding is related to the behavior of the S_1 band at LT (≈ 100 K). At LT, there is just a weak trace of the strong S_1 band observed at RT for 1.1 ML, cf. Figs. 6(a) and 6(b). The electronic structure induced by the extra Ag atoms has transformed into a set of two bands (S_{1U} and S_{1D}) within 0.3 eV from E_F . S_{1U} has a minimum energy at the $\bar{\Gamma}$ -point of ≈ 0.25 eV below E_F , while the S_{1D} band, just below S_{1U} , is located at ≈ -0.3 eV. The dispersion of S_{1D} is rather flat in the immediate vicinity of $\bar{\Gamma}$, and it has a local maximum at that point as indicated by the second derivative displayed in Fig. 6(d). This important behavior of the S_1 band at LT in the present case of $\text{Ag/Ge(111)}\sqrt{3}\times\sqrt{3}$ shows some similarities and differences when compared to the behavior of the S_1 band for $\text{Ag/Si(111)}\sqrt{3}\times\sqrt{3}$ surface [30]. In that case, it splits into two bands when monovalent adatoms (such Au, Ag, and Cs) were deposited at LT [30]. While in the present study for the 1.1 ML Ag case, the band shows a similar split resulting in extra states, but the obvious difference is that the split did not require any further addition of atoms on the surface. In comparison, this behavior suggests that there is a surplus of Ag atoms left on the surface that could not be annealed off entirely. Moreover, extra atoms on the surface at RT can be frozen at particular lattice sites at LT. The resulting perturbation of the $\sqrt{3}\times\sqrt{3}$ potential was used in Ref. 30 to explain the split of the S_1 band into two branches, (Fig. 2 of Ref. 30). The upper branch in the case of $\text{Ag/Si(111)}\sqrt{3}\times\sqrt{3}$ deviated significantly from a parabolic shape with an almost flat lower part. This band seems to correspond to the S_{1D} band but in the case of $\text{Ag/Ge(111)}\sqrt{3}\times\sqrt{3}$ one can also identify another band S_{1U} slightly closer to the Fermi

level. Weak traces of the S_1 band at LT in the 1.1 ML case indicates that there could still be some regions left, where the extra Ag atoms are not frozen into specific positions.

Fig. 6 Gray scale images of the S_1 band in (a) and the S_{1U} and S_{1D} bands in (b) obtained at RT and LT, respectively, for the 1.1 ML Ag case. (c) and (d) show the second derivative along the energy axes of the original photoemission data in (a) and (b). (e)–(h) as (a)–(d) but for the 0.9 ML case. The data were obtained using a photon energy of 30 eV.

The third important feature of the S_1 band is its shape. It is parabolic for 0.9 ML but deviates from a true parabolic shape for the 1.1 ML case at RT, see Fig. 6(a). At LT, for the 0.9 ML case, the dispersion changed to a V-shape while the energy was quite similar, see Figs. 6(e) and 6(f). In addition, a tiny band just below the V-shape is observed at the same energy as the S_{1D} band (≈ -0.3 eV). This band is rather flat and shows almost no dispersion. Furthermore, we consider the S_1 band as a characteristic free electron like band of the $\text{Ag/Ge(111)}\sqrt{3}\times\sqrt{3}$ surface, that should show a shallow dispersion in the case of an ideal $\sqrt{3}\times\sqrt{3}$ surface (i.e., a surface with no extra Ag atoms) while with some extra monovalent atoms, it shifts downward in binding energy.

4. Conclusions

In this study, a detailed investigation of the electronic structure of the $\text{Ag/Ge(111)}\sqrt{3}\times\sqrt{3}$ superstructure at RT and LT has been presented for two different Ag coverages. ARPES data along high symmetry directions show four surface bands (S_1 – S_4) at RT and a total of five bands (S_{1U} , S_{1D} and S_2 – S_4) at LT. Beside the importance of the detailed electronic structure information, we have reported two particularly interesting observations. Firstly, we find two surface bands where only one has been reported for $\text{Ag/Si(111)}\sqrt{3}\times\sqrt{3}$, resulting in the S_2 , S_3 pair with parallel dispersions. Secondly, at LT the S_1 band splits into two bands, S_{1U} and S_{1D} , within 0.3 eV from E_F , irrespective of the amount of extra Ag atoms. Also this second finding is in contrast to results reported for $\text{Ag/Si(111)}\sqrt{3}\times\sqrt{3}$. The discussion about the degeneracy of surface bands at the $\bar{K}$ -point was addressed. Since we cannot find any clear evidence of a gap, we find that the photoemission data do not provide sufficient information when it comes to the discrimination between the HCT and IET models based on the electronic structure at the $\bar{K}$ -point. The appearance of STM images from the $\text{Ag/Ge(111)}\sqrt{3}\times\sqrt{3}$ surface varied with bias voltage. Images consistent with both the HCT and IET models were obtained. The detailed ARPES data along the symmetry lines, provide important input necessary for a decisive comparison with electronic structure calculations of these atomic models.

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