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Metal to semiconductor transition on Ag/Ge(111): Surface electronic structure of the $\sqrt{3}\times\sqrt{3}$, $\sqrt{39}\times\sqrt{39}$, and 6×6 surfaces

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The $\sqrt{3}\times\sqrt{3}$, $\sqrt{39}\times\sqrt{39}$, and 6×6 phases of Ag/Ge(111) have been studied by angle-resolved photoemission and low-energy electron diffraction. The $\sqrt{3}\times\sqrt{3}$ surface, formed at a one-monolayer (ML) Ag coverage, shows a metallic behavior with two partially occupied surface bands resulting from a tiny amount of extra Ag atoms on the surface. The $\sqrt{3}\times\sqrt{3}$ surface transforms into a $\sqrt{39}\times\sqrt{39}$ periodicity, below ~ 250 K, when a small amount of Ag is added to the surface. The presence of the additional Ag atoms leads to an increased filling of two partially occupied surface bands. By depositing ~ 0.2 ML of Ag on the $\sqrt{3}\times\sqrt{3}$ surface, it transforms into a 6×6 periodicity. We observe an interesting transition from the metallic $\sqrt{3}\times\sqrt{3}$ and $\sqrt{39}\times\sqrt{39}$ phases to a semiconducting phase for the 6×6 surface, with a gap of around 0.2 eV with respect to the Fermi level. On the 6×6 surface, the lower band of the partially occupied surface bands is pulled down entirely below the Fermi level while the upper band is missing in the photoemission spectra. These changes result in the observed band gap.

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Metal to semiconductor transitions, which may occur for submonolayer metal coverages on semiconductor surfaces, have attracted both experimental and theoretical interest throughout the years. Most metal to semiconductor transitions that have been studied are temperature-dependent transitions (like the Peierls transition), but it is also very interesting to investigate the physics of coverage-dependent transitions. Reports in the literature indicate that the Ag/Ge(111) system may show such a behavior. At a Ag coverage of one monolayer (ML), the surface shows a $\sqrt{3}\times\sqrt{3}$ periodicity, which changes to a $\sqrt{39}\times\sqrt{39}$ surface for a small amount of additional Ag when the temperature is lowered. Further deposition of Ag onto the $\sqrt{3}\times\sqrt{3}$ surface at room temperature (RT) results in a 6×6 reconstruction. The $\sqrt{39}\times\sqrt{39}$ as well as the 6×6 surface of Ag/Ge(111) have been observed in a scanning tunneling microscopy (STM) study.¹ An electron-energy-loss spectroscopy (EELS) study of the 6×6 surface showed a peculiar semiconducting behavior in contrast to the metallic character of the $\sqrt{3}\times\sqrt{3}$ surface.² Inspired by the STM and EELS results, we have performed a detailed study of the surface electronic structure near the Fermi level for the three different periodicities of the Ag/Ge(111) system.

First, it is interesting to compare the different Ag/Ge(111) surfaces, which have attracted relatively little attention, to the closely related and extensively studied $\sqrt{3}\times\sqrt{3}$ and $\sqrt{21}\times\sqrt{21}$ surfaces of Ag/Si(111). STM observations show that the Ag/Si(111) and the Ag/Ge(111) surfaces are very similar, and they undergo almost the same surface reconstructions at coverages above 1 ML: from $\sqrt{3}\times\sqrt{3}$ via $\sqrt{21}\times\sqrt{21}$ to 6×6 for Ag/Si(111) and from $\sqrt{3}\times\sqrt{3}$ via $\sqrt{39}\times\sqrt{39}$ to 6×6 for Ag/Ge(111). The striking resemblance between the STM images of the $\sqrt{3}\times\sqrt{3}$ surfaces of Ag/Si(111) and Ag/Ge(111) suggests that the atomic structures are identical.³ That is, the honeycomb-chain-trimer (HCT) model⁴ should be applicable to both of them. In the

case of Ag/Si(111), the $\sqrt{21}\times\sqrt{21}$ phase appears below 250 K when ~ 0.15 ML of Ag is evaporated on the $\sqrt{3}\times\sqrt{3}$ surface.^{5,6} The $\sqrt{39}\times\sqrt{39}$ reconstruction of Ag/Ge(111) also appears at around 250 K but at a lower Ag coverage as expected from the larger unit cell. It has been reported that the $\sqrt{3}\times\sqrt{3}$ phase of Ag/Si(111) shows one metallic band,^{7,8} while the $\sqrt{21}\times\sqrt{21}$ phase shows two metallic bands.^{6,8} A recent theoretical calculation⁹ suggested that the upper band is an adatom-induced band (extra Ag adatoms on the $\sqrt{3}\times\sqrt{3}$ surface), while the lower band is derived from the underlying $\sqrt{3}\times\sqrt{3}$ surface. An interesting observation is that other noble metal (Au, Cu) and alkali-metal (Li, Na, K, Cs) adatoms can also form the $\sqrt{21}\times\sqrt{21}$ phase.⁶ It seems that the formation of the $\sqrt{21}\times\sqrt{21}$ phase is strongly related to the monovalency of the adatoms. That is, the total energy of the system is lowered by a continuous filling of the metallic surface bands by the *s* electron of the adatom. An interesting phenomenon observed for the $\sqrt{21}\times\sqrt{21}$ surface is the electrical conductance, which is significantly higher than the values for both the $\sqrt{3}\times\sqrt{3}$ and 6×6 surfaces. The high conductance is explained by the presence of the two metallic bands on the $\sqrt{21}\times\sqrt{21}$ surface.^{6,8} The electronic structure of the corresponding $\sqrt{39}\times\sqrt{39}$ surface of Ag/Ge(111) is presented in this paper, and it also shows two partially occupied surface bands. From previous studies of the Ag/Si(111) surfaces,^{5,6} the 6×6 phase appears to be stable only at a very low temperature (~ 100 K), while the 6×6 phase of Ag/Ge(111) is stable at room temperature. The electronic structures of the two 6×6 surfaces have not been reported so far.

In this paper, we present data from the different Ag/Ge(111) surfaces obtained by angle-resolved photoelectron spectroscopy (ARPES). We find that the Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ surface has four dispersing surface-state bands, two of which cross the Fermi level. The $\sqrt{39}\times\sqrt{39}$ surface of

FIG. 1. LEED patterns of Ag/Ge(111) surfaces as a function of Ag coverage θ (100 K). (a) $\theta \approx 1.0$ ML, $\sqrt{3} \times \sqrt{3}$ surface, 114 eV; (b) $\theta \approx 1.05$ ML, $\sqrt{39} \times \sqrt{39}$ surface, 115 eV; (c) $\theta \approx 1.2$ ML, 6×6 surface, 114 eV.

Ag/Ge(111) has six dispersing bands and two of them cross the Fermi level. The presence of additional Ag on the $\sqrt{3} \times \sqrt{3}$ surface seems to lead to an increased filling of the two partially occupied surface bands. The 6×6 surface of Ag/Ge(111) has five dispersing bands. However, in contrast to the metallic behavior of the $\sqrt{3} \times \sqrt{3}$ and the $\sqrt{39} \times \sqrt{39}$ surfaces, the 6×6 surface shows a semiconducting character with a gap of around 0.2 eV with respect to the Fermi level. A continuous filling of the lower partially occupied surface band seems to pull it down entirely below the Fermi level, while the upper metallic band is absent or might have been lifted up above the Fermi level, resulting in the observed band gap.

The photoemission study was performed at beam line 33 at the Max-I synchrotron radiation facility in Lund, Sweden. The angle-resolved valence-band spectra presented here were obtained with a total-energy resolution of ≈ 50 meV and an angular resolution of $\pm 2^\circ$. The pressure of the preparation chamber was around 4×10^{-10} Torr during evaporation and the pressure in the photoemission chamber was around 1×10^{-10} Torr during data collection. Cleaning of the Ge(111) sample (Sb-doped, $3 \Omega \text{ cm}$) was done by repeated sputtering (Ar^+ , 0.5 kV) and annealing cycles ($\approx 600^\circ \text{C}$, 5 min). This cleaning procedure was stopped when low-energy electron diffraction (LEED) showed a $c(2 \times 8)$ pattern with well-defined $8 \times$ spots. Ag was evaporated onto the Ge sample from a tungsten filament source calibrated by a quartz crystal monitor. Evaporation of 1 ML of Ag followed by annealing at 300°C for 2 min resulted in a sharp $\sqrt{3} \times \sqrt{3}$ LEED pattern [Fig. 1(a)]. A $\sqrt{39} \times \sqrt{39}$ surface [Fig. 1(b)], which is visible by LEED at temperatures below ~ 250 K, may be obtained either by an evaporation of a small amount of Ag onto the $\sqrt{3} \times \sqrt{3}$ surface, or by annealing the

FIG. 2. ARPES spectra recorded from the Ag/Ge(111) surfaces with a photon energy of 21.2 eV at 100 K. The emission angles correspond to $k_{\parallel}$ points throughout the first and second $\sqrt{3} \times \sqrt{3}$ SBZ (see inset at the top), along the $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ line. (a) $\sqrt{3} \times \sqrt{3}$ surface; (b) $\sqrt{39} \times \sqrt{39}$ surface; (c) 6×6 surface.

6×6 surface. The 6×6 surface [Fig. 1(c)] was formed by adding ~ 0.2 ML of Ag on the $\sqrt{3} \times \sqrt{3}$ surface. Regarding the $\sqrt{3} \times \sqrt{3}$ surface, it should be pointed out that at low temperature there was always a tiny ringlike diffraction around the $\sqrt{3} \times$ spots in the LEED patterns [Fig. 1(a)]. The sample was annealed up to 500°C for several minutes in order to remove the tiny extra diffraction in the LEED patterns. Above 500°C , 4×4 LEED spots were found in the center of the sample. Finally, we had to accept the presence of the extra ringlike diffraction pattern, which most likely indicates that there is a tiny amount of additional Ag on the $\sqrt{3} \times \sqrt{3}$ surface. The diffraction ring of the $\sqrt{3} \times \sqrt{3}$ surface is smaller than that of the $\sqrt{39} \times \sqrt{39}$ surface, implying a “unit cell” that is larger than the $\sqrt{39} \times \sqrt{39}$ unit cell, and the Ag adatoms are therefore expected to be widely separated.

Figure 2(a) shows a set of angle-resolved photoemission spectra from the low temperature (LT), (100 K) $\sqrt{3} \times \sqrt{3}$ surface along the $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ line of the $\sqrt{3} \times \sqrt{3}$ surface Brillouin zone (SBZ) (see inset in Fig. 2). Four surface states were detected and they are labeled S_1 , S_2 , S_3 , and S_4 . The $\sqrt{3} \times \sqrt{3}$ surface has a metallic character, as evidenced by S_1 crossing the Fermi level (E_F) at an emission angle of -36° . The S_1 surface state shows a small downwards dispersion with a minimum energy of -0.1 eV at $\theta_e = -32^\circ$, which

corresponds to the $\bar{\Gamma}$ point of the second $\sqrt{3} \times \sqrt{3}$ SBZ. The second surface state S_2 , which we also assign to a metallic band, has a dispersion with a minimum energy of -0.3 eV at the $\bar{\Gamma}$ point. The other two dominant surface states, denoted S_3 and S_4 , are degenerate at the $\bar{\Gamma}$ point with an initial energy of 1.12 eV below E_F . We also observed that these two surface states are degenerate at the $\bar{K}$ point along the $\bar{\Gamma}-\bar{K}-\bar{M}$ line. Here it is interesting to compare our data with the previous studies of the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface.⁷⁻¹⁰ On the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface, there are three surface states S_1 , S_2 (S'_2), and S_3 (S'_3),⁷ where S_1 is a metallic band. Just by comparing, it can be concluded that the surface states S_3 and S_4 of Ag/Ge(111) are identical with the surface states “ S_2 ” (S'_2) and “ S_3 ” (S'_3) of Ag/Si(111), as evidenced by the similarity of their appearance and their symmetry properties observed in the valence-band spectra. In accordance with the case of Ag/Si(111),⁷ the S_3 state shows an even symmetry with a strong p_z character (Si $3p_z$), while the S_4 state shows an odd symmetry with respect to the mirror plane containing the surface normal and the $[11\bar{2}]$ direction. There is, however, one difference between the two $\sqrt{3} \times \sqrt{3}$ surfaces concerning the surface states near the Fermi level. There is only one metallic band in the case of Ag/Si(111), while there are two metallic bands in the case of Ag/Ge(111). From the other reports of the Ag/Si(111) surfaces,^{6,8} it is well known that there might be two metallic bands if a tiny amount of extra Au (Cu) is deposited on the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface to form the $\sqrt{21} \times \sqrt{21}$ surface. By using first-principles calculations, a recent theoretical study⁹ suggested that the upper band of the $\sqrt{21} \times \sqrt{21}$ phase is an adatom-induced band, while the lower band is derived from the underlying $\sqrt{3} \times \sqrt{3}$ surface. Applying the same conclusions to the Ag/Ge(111) case, the surface state S_2 of the Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ surface should be identical with “ S_1 ” of the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface. The surface state S_1 of Ag/Ge(111) should correspond to Ag adatom states of a few extra Ag atoms on the $\sqrt{3} \times \sqrt{3}$ surface, which is consistent with LEED observation of weak ringlike diffraction around the $\sqrt{3} \times \sqrt{3}$ spots at low temperature. Our results strongly suggest that the $\sqrt{3} \times \sqrt{3}$ surfaces of Ag/Ge(111) and Ag/Si(111) have the same local atomic geometry, as evidenced by their surface electronic structures, which is also consistent with previous STM studies.¹⁻³

Figure 1(b) shows the LEED pattern of the $\sqrt{39} \times \sqrt{39}$ reconstruction. The dominant features are the $\sqrt{3} \times \sqrt{3}$ LEED spots plus the $\sqrt{39} \times \sqrt{39}$ superstructure (ringlike diffraction). The high-resolution STM image in Ref. 1 indicates the presence of one Ag adatom per $\sqrt{39} \times \sqrt{39}$ unit cell (one bright protrusion in each corner), which corresponds to an additional Ag coverage of 0.026 ML on top of the $\sqrt{3} \times \sqrt{3}$ surface. The small amount of Ag atoms needed to form the $\sqrt{39} \times \sqrt{39}$ reconstruction explains why it is really difficult to obtain a pure $\sqrt{3} \times \sqrt{3}$ surface without any ringlike diffraction around the $\sqrt{3} \times \sqrt{3}$ spots at low temperature. Figure 2(b) shows a set of angle-resolved photoemission spectra

from the LT $\sqrt{39} \times \sqrt{39}$ surface along the $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ line of the $\sqrt{3} \times \sqrt{3}$ SBZ. Six surface states were detected (S_1 , S_2 , S_3 , S_4 , S_5 , and S_6). As with the $\sqrt{3} \times \sqrt{3}$ surface, the $\sqrt{39} \times \sqrt{39}$ surface also has a metallic character, as evidenced by S_1 crossing the Fermi level at $\theta_e = -39^\circ$. The second surface state S_2 is located at -0.26 eV below E_F at $\theta_e = -27.5^\circ$ and it disperses steeply downwards to a minimum energy of -0.52 eV at $\theta_e = 34^\circ$. It is natural to suggest that S_1 and S_2 of the $\sqrt{39} \times \sqrt{39}$ and $\sqrt{3} \times \sqrt{3}$ surfaces have the same origins, since just a tiny amount of Ag was deposited on the $\sqrt{3} \times \sqrt{3}$ surface and one can expect that the local atomic structure should remain. Nevertheless, a significant difference is that S_2 has been pulled down by 0.22 eV as a result of an increased occupation caused by the extra Ag atoms. This is also similar to what happens on the Ag/Si(111) $\sqrt{21} \times \sqrt{21}$ Au (Cu) surfaces, i.e., two partially occupied surface states are pulled down as a small amount of Au (Cu) is deposited on the $\sqrt{3} \times \sqrt{3}$ surface.^{6,8} The other surface states S_3 and S_4 have also been pulled down (by 0.3 eV) compared to the $\sqrt{3} \times \sqrt{3}$ surface. Interestingly, the STM study¹ provided another useful piece of information about the local atomic structure of the $\sqrt{39} \times \sqrt{39}$ surface. It seems that the additional Ag adatoms are sitting on the Ag trimer sites of the $\sqrt{3} \times \sqrt{3}$ surface (bright protrusions in the STM image of Ref. 1), forming the $\sqrt{39} \times \sqrt{39}$ unit cell. A similar picture for the Ag/Si(111) $\sqrt{21} \times \sqrt{21}$ surface is also supported by both STM (Ref. 10) and theoretical calculations,⁹ i.e., the extra Ag atoms prefer to sit on the Ag trimer sites instead of Si trimer sites. Conductance measurement on the Ag/Si(111) surfaces⁶ showed that the $\sqrt{21} \times \sqrt{21}$ phase has a much higher electrical conductance compared to both the $\sqrt{3} \times \sqrt{3}$ and 6×6 phases. The striking resemblance between the upper two surface-state bands of the $\sqrt{39} \times \sqrt{39}$ and the $\sqrt{21} \times \sqrt{21}$ surfaces points to a similar situation for Ag/Ge(111). That is, the $\sqrt{39} \times \sqrt{39}$ surface may also show an anomalously high conductance due to the two strong surface metallic bands S_1 and S_2 . Actually, this idea is supported by our photoemission data since the $\sqrt{39} \times \sqrt{39}$ surface has a stronger metallic character than the $\sqrt{3} \times \sqrt{3}$ surface and the 6×6 surface shows an interesting semiconducting character.

Figure 1(c) shows the LEED pattern of the 6×6 surface after ~ 0.2 ML of Ag was deposited on the $\sqrt{3} \times \sqrt{3}$ surface. The 6×6 LEED pattern has some special characteristics. First, its $\sqrt{3} \times \sqrt{3}$ spots are very strong while the 6×6 spots appear weaker for most energies [Fig. 1(c), obtained at 114 eV, is an exception]. Second, the diffraction pattern shows a complicated intensity variation as a function of electron energy. Actually, the LEED patterns are consistent with the STM image in Ref. 1, which indicates that the local $\sqrt{3} \times \sqrt{3}$ atomic structure still remains and the 6×6 structure corresponds to a complicated arrangement of adatoms inside the unit cell. The additional Ag adatoms still seem to sit on the Ag trimer sites, and the coverage may be estimated to ~ 0.22 ML from the number of bright protrusions in the 6×6 unit cell. Figure 2(c) shows a set of angle-resolved photoemission spectra obtained at LT from the 6×6 surface

FIG. 3. Dispersions of the surface states on Ag/Ge(111) along the $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ line of the $\sqrt{3}\times\sqrt{3}$ SBZ (see inset at the top). The dot size indicates the relative intensity of the different surface states. (a) $\sqrt{3}\times\sqrt{3}$ surface; (b) $\sqrt{39}\times\sqrt{39}$ surface; (c) 6×6 surface.

along the $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ line of the $\sqrt{3}\times\sqrt{3}$ SBZ. Five surface states were detected (S_2 , S_3 , S_4 , S_5 , and S_6). In contrast to the metallic character of the $\sqrt{39}\times\sqrt{39}$ and the $\sqrt{3}\times\sqrt{3}$ surfaces, the 6×6 surface shows a semiconducting behavior, as evidenced by a clear gap of 0.2 eV with respect to E_F at $\theta_e = -38^\circ$. This result is consistent with an earlier EELS observation.² In comparison with the $\sqrt{3}\times\sqrt{3}$ and the $\sqrt{39}\times\sqrt{39}$ surfaces, the dramatic difference is that S_2 becomes stronger and disperses downwards at $\theta_e = -39^\circ$, while the metallic band S_1 is missing. It is found that S_2 is located at -0.2 eV below E_F at $\theta_e = -38^\circ$ and it disperses downwards to -0.55 eV at $\theta_e = -34^\circ$. For smaller emission angles, the S_2 peak becomes very weak. The dispersion and line shape of the spectra suggest that S_2 has the same origin for all Ag/Ge(111) surfaces. A continuous deposition of additional Ag seems to dramatically change the S_1 and S_2 bands. That is, S_2 is completely pulled down below the Fermi level, while we find that S_1 does not exist for the 6×6 surface or it has moved up above the Fermi level.

Figure 3 shows the band structures of the three surfaces ($\sqrt{3}\times\sqrt{3}$, $\sqrt{39}\times\sqrt{39}$, and 6×6) along the $\bar{\Gamma}-\bar{M}-\bar{\Gamma}$ line of the $\sqrt{3}\times\sqrt{3}$ SBZ. The three panels clearly show the changes

observed for the different surface-state bands. The downward displacement of the S_3 and S_4 surface bands on the $\sqrt{39}\times\sqrt{39}$ surface is very evident when comparing Figs. 3(a) and 3(b). The presence of the S_1 and S_2 surface bands on the $\sqrt{3}\times\sqrt{3}$ surface indicates that S_3 and S_4 would be positioned closer to the Fermi level on an ideal $\sqrt{3}\times\sqrt{3}$ surface, i.e., a surface without extra Ag atoms. Another two surface bands, S_5 and S_6 , are present on the $\sqrt{39}\times\sqrt{39}$ and 6×6 phases. As a matter of fact, the S_5 state appears as a shoulder also in the spectra from the $\sqrt{3}\times\sqrt{3}$ surface [see Fig. 2(a)]. Except for the global downward shift of the surface bands caused by the extra Ag adatoms, one can envision a local effect on the surface-state structure. A Ag trimer with a Ag adatom may be regarded as a defect of the $\sqrt{3}\times\sqrt{3}$ surface, which could lead to locally modified surface states. We tentatively assign the S_5 and S_6 states to such local perturbations. When the distance between the adatom-trimer features decreases, as in the case of the 6×6 phase, one can expect a stronger interaction and a larger dispersion as shown in Fig. 3(c) for the 6×6 surface.

In conclusion, the surface electronic structures of three surfaces ($\sqrt{3}\times\sqrt{3}$, $\sqrt{39}\times\sqrt{39}$, and 6×6) have been investigated by ARPES. Four surface-state bands are found on the $\sqrt{3}\times\sqrt{3}$ surface, two of which are partially occupied metallic states (S_1 and S_2). This partial occupation is caused by a small number of extra Ag atoms on the $\sqrt{3}\times\sqrt{3}$ surface. Six surface-state bands are found on the strongly metallic $\sqrt{39}\times\sqrt{39}$ surface, with S_2 0.2 eV deeper compared to the $\sqrt{3}\times\sqrt{3}$ surface. The existence of two metallic surface bands on the $\sqrt{39}\times\sqrt{39}$ surface suggests a close resemblance to the $\sqrt{21}\times\sqrt{21}$ surface of Ag/Si(111). The 6×6 surface has five surface-state bands but no band crosses the Fermi level. The photoemission data show that the partially occupied band (S_2) is completely filled, while the other metallic band (S_1) is missing or is located above the Fermi level. The result is an interesting semiconducting character of the 6×6 phase, with a gap of 0.2 eV with respect to E_F , which is in contrast to the metallic behavior of the $\sqrt{3}\times\sqrt{3}$ and $\sqrt{39}\times\sqrt{39}$ surfaces.

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