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Role of Atomic Interaction in Electronic Hybridization in Two-Dimensional Ag₂Ge Nanosheets

Abstract

We performed low-temperature scanning tunneling microscopy, low-energy electron diffraction, angle-resolved photoemission spectroscopy, and in situ Raman spectroscopy to investigate the exotic electronic characteristics of the two-dimensional Ag₂Ge surface alloy associated with Ge-Ag interactions. The dynamics of Ge insertion into the Ag(111) substrate has been identified, which is distinct due to the metalloid nature of Ge. The ordered structure of the Ag₂Ge alloy is determined by the Ag-Ge interaction, which can be controlled by the coverage of Ge atoms on the Ag(111) surface. The linear dispersions of surface states across the Fermi level have been identified in Ag₂Ge by angle-resolved photoelectron spectroscopy, which suggests that Ag₂Ge could be a potential candidate material for high-performance electronic applications.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Liu, Y., Zhuang, J., Liu, C., Wang, J., Xu, X., Li, Z., Zhong, J. & Du, Y. (2017). Role of Atomic Interaction in Electronic Hybridization in Two-Dimensional Ag₂Ge Nanosheets. *The Journal of Physical Chemistry C: Energy Conversion and Storage, Optical and Electronic Devices, Interfaces, Nanomaterials, and Hard Matter*, 121 (31), 16754-16760.

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Abstract

We performed low-temperature scanning tunneling microscopy, low-energy electron diffraction, angle-resolved photoemission spectroscopy, and *in-situ* Raman spectroscopy to investigate exotic electronic characteristics in two-dimensional Ag₂Ge surface alloy associated with Ge-Ag interactions. The dynamics of Ge insertion into the Ag(111) substrate is identified, which is distinct due to the metalloid nature of Ge. The ordered structure of Ag₂Ge alloy is determined by the Ag-Ge interaction which can be controlled by the coverage of Ge atoms on the Ag(111) surface. The linear dispersions of surface states across the Fermi level have been identified in Ag₂Ge by ARPES, which suggests that Ag₂Ge could be a potential candidate material for high-performance electronic applications.

1. Introduction

Two-dimensional (2D) surface alloys, which feature electronic hybridization between substrate atoms and top-layer metal adatoms, have attracted considerable attention, due to their exotic electronic characteristics, which are distinct from those of their bulk counterparts. For instance, the Rashba-Bychkov (RB) effect, which is observed in noble metal substrate surfaces due to the broken spatial inversion symmetry of the bulk crystals, is significantly enhanced in the ordered 2D surface alloys by the introduction of an in-plane potential gradient, evoking potential applications in magnetic data storage and spintronic devices.¹⁻¹¹ As a typical metallic substrate, Ag(111) has turned out to be suitable surface for the formation of Ag_2M surface alloy ($M = \text{Bi}^2, \text{Sn}^4, \text{Pb}^{5,6}, \text{or Sb}^7$) with $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ reconstruction after the deposition of $1/3$ monolayer of metal atoms. Exotic characteristics were observed in such Ag_2M surface alloys. The corresponding atomic reconstructions and electronic structures are believed to be determined by the Ag- M interatomic interactions. For instance, RB splitting is observed in Ag_2Bi alloy³, while it is absent in the case of Ag_2Sn alloy because of the decreased spin-orbit coupling strength with decreasing atomic number⁴. In contrast, light nonmetal elements, *e.g.* C and Si in group IV, prefer to form the 2D allotropes graphene¹² and silicene¹³⁻²⁵ with Dirac fermion characteristics on the Ag(111) surface due to their weak interaction with Ag atoms. This suggests that the nature of the adsorbed element indeed determines the surface configuration on the Ag(111) surface, and therefore, induces distinct electronic properties.

As a typical metalloid element in group IV, germanium (Ge) only takes on a

diamond structure with sp^3 hybridization of the valence electrons in bulk form, similar to C and Si in their bulk crystals²⁶. Very recently, it was reported that the 2D allotrope of Ge, germanene, had been successfully epitaxially grown on MoS_2 ²⁷ and metallic substrates²⁸⁻³⁶, including $\text{Au}(111)$ ³⁰⁻³², $\text{Pt}(111)$ ³³, $\text{Al}(111)$ ^{34,35} and $\text{Cu}(111)$ ³⁶ surfaces. The interaction between the substrates and the Ge atoms is believed to depress the Ge-Ge sp^3 hybridization and lead to a mixed sp^2/sp^3 state between neighboring Ge atoms. Consequently, low-buckled 2D germanene nanosheets with a honeycomb lattice structure can be formed on the substrates. So far, there are no reports about germanene on $\text{Ag}(111)$. Instead, Ag_2Ge alloy has been observed by low-energy electron diffraction (LEED) and reflective high-energy electron diffraction (RHEED) measurements after deposition of Ge atoms on $\text{Ag}(111)$.^{26,37,38} Unexpected surface band splitting behavior at the M points of the Brillouin zone (BZ) in Ag_2Ge alloy was reported, which is attributed to its novel atomic structure, where a striped appearance is induced by the long-range $\sqrt{3}\times\sqrt{3}$ modulation.^{26,38} These preliminary reports suggest that the interaction between Ag and metalloid Ge is significantly different from what occurs with either semiconducting Si or metallic Sn and Bi, although this is still unclear. Thus, the growth dynamics of 2D Ag_2Ge alloys on the $\text{Ag}(111)$ surface are also not clear. Since all the inferences about Ge on the $\text{Ag}(111)$ surface are solely based on the behavior of Ag_2Ge alloy, whether germanene can be epitaxially grown on $\text{Ag}(111)$ surfaces remains an open question. Thus, revealing the atomic and electronic interactions between Ge and Ag during the deposition of Ge on $\text{Ag}(111)$ surfaces is very much needed to illustrate these issues.

In this work, we have investigated the growth kinetics and mutual interaction of Ge on Ag(111) substrate by low-temperature scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) measurements. It was found that Ge atoms insert themselves into the Ag(111) surface to replace Ag atoms at the initial stage of Ge deposition at room temperature. With high coverage of Ge, a partially ordered honeycomb structure accompanied by amorphous regions appears, forming continuous triangle-like networks. An ordered honeycomb Ge monolayer with a striped appearance is formed under the conditions of high substrate temperature and sufficient Ge coverage. *In-situ* Raman spectra and ARPES results have revealed the metallic nature of this monolayer 2D surface alloy. Our work provides a comprehensive understanding of the evolution of monolayer Ge on Ag(111), which is desirable for high-quality alloy fabrication and exploring its novel physics and potential applications.

2. Experimental

All the samples used in this work were fabricated in a preparation chamber in a low-temperature STM/scanning near-field optical microscopy system (LT-STM-SNOM, SNOM1400, Unisoku Co.). The Ag(111) substrate was cleaned by cycles of Ar⁺ ion sputtering for 30 min at 5×10^{-5} Torr and then annealed at 773 K for 30 min. The cleanliness of the Ag(111) substrate was confirmed by LT-STM. Ge was deposited on the Ag(111) surface from a homemade W-wire-twisted Ta-boat filled with Ge crystal. STM images were obtained in constant-current mode and processed by WsXM software.³⁹ The Raman laser ($\lambda = 532$ nm) was delivered through a

single-mode optical fiber into the measurement chamber of the STM-SNOM system. *In-situ* LEED and ARPES characterizations were performed at the Photoelectron Spectroscopy Station in the Beijing Synchrotron Radiation Facility (BSRF) using a SCIENTA R4000 analyzer. All the measurements were carried out in ultrahigh vacuum (UHV, $< 1 \times 10^{-10}$ Torr) at 77 K.

3. Results and discussion

Figure 1(a) shows STM images of a clean Ag(111) surface with large flat terraces. The atomic structure of the Ag(111) surface with a hexagonal arrangement of atoms is shown in Figure 1(b). The distance between nearest neighbor Ag atoms is 0.28 ± 0.01 nm, corresponding to the Ag(111) surface lattice. After deposition of a small amount of Ge atoms at room temperature, no obvious change was observed in the flatness of the Ag(111) terraces, as shown in Figure 1(c). As shown in Figure 1(d), the isolated dark spots in the high-resolution STM image suggest that the local density of states (LDOS) or out-of-plane height at these spots was altered after Ge deposition. Interestingly, these randomly distributed spots do not affect the hexagonal atomic structures and periodicity of the Ag(111) surface. A similar phenomenon was reported for Si atoms in previous reports, which became intermixed with the Ag(111) substrate at the high temperature used to facilitate the surface precipitation of Si onto Ag(111).¹⁴ Considering the smaller radius of the Ge atom ($r_{\text{Ge}} = 0.122$ nm) than that of the Ag atom ($r_{\text{Ag}} = 0.144$ nm), the Ge atoms can intermix with and substitute for Ag atoms in the Ag(111) surface, leading to a smaller height at the positions where Ge atoms substitute for Ag atoms. Furthermore, due to the metalloid nature of Ge, the LDOS is

much depressed at these substituted positions. Therefore, we attribute these dark spots to the Ge atoms which have inserted themselves into the Ag (111) surface plane and substituted for surface Ag atoms.

When the density of deposited Ge atoms reaches 1/3 of the pristine density of the surface Ag atoms, defined as 1/3 monolayer coverage, the evolution of the surface is completely different at room temperature, as shown in Figure 2(a)-2(c). Figure 2(a) displays a typical STM image acquired for the empty state ($V_{\text{sample}} = 3 \text{ V}$) of the sample, which consists of triangle-like patterns with filleted corners (component I) and fuzzy stripes (component II). The occupied-state STM image ($V_{\text{sample}} = -2 \text{ V}$), as shown in Figure 2(b), displays similar triangle patterns with the same size as those in Figure 2(a), but with the contrast reversed, indicating distinct electronic structures for components I and II. High-resolution STM images were obtained in order to shed light on the atomic structures of both components. We found that it was hard to resolve any atomic arrangement in component I, possibly due to its disordered/amorphous structure. In contrast, a clear honeycomb structure is revealed in the regions of component II, as shown in Figure 2(c). The distance between bright protrusions of the honeycomb lattice, measured along the red dashed line in Figure 2(c), is around $0.28 \pm 0.01 \text{ nm}$. This value is closed to the periodicity of $1 \times 1 \text{ Ag}(111)$. The distance between neighboring dark suppression spots along the green dashed line in Figure 2(c) gives a periodicity of $\sim 0.51 \pm 0.01 \text{ nm}$, as shown in Figure 2(d), which is about $\sqrt{3}$ times the lattice constant with respect to $1 \times 1 \text{ Ag}(111)$. Thus, the honeycomb arrangement with a $\sqrt{3} \times \sqrt{3}$ superstructure is most likely generated by the

destruction of or substitution for one in every three Ag atoms in the Ag(111) surface after Ge deposition. In this case, structural compression is expected in the region of component II, which is relaxed by the formation of bright stripes. Considering the low mobility of Ge atoms on the Ag(111) surface at room temperature, it is proposed that the structural compression would lead to the generation of a small honeycomb network along with the amorphous-like areas.

In order to verify this assumption, we increased the substrate temperature to 600 K during Ge deposition up to coverage of $1/3$ monolayer. A long-range-ordered honeycomb network was obtained, as expected. Figure 3(a) displays an STM image of the sample grown at 600 K, in which the striped structure of the surface is clearly revealed. The stripes are aligned along three different directions with an orientation angle of 120° . It should note that the striped patterns do not change their periodicity and wavelike modulation when the sample bias is varied in the STM measurement. It is concluded that the STM image in Figure 3 reflects the surface topographic features of the sample surface. As shown in Figure 3(b), both the honeycomb periodicity and the long-range modulation are clearly visible. Furthermore, the periodicity of the long-range modulation, labeled by a white parallelogram in Figure 3(b), is 6 times as great as the periodicity of the local $\sqrt{3} \times \sqrt{3}$ honeycomb cell. An atomic resolution STM image of the striped structures is displayed in Figure 3(c). The lattice parameters of the refined structure in Figure 3(c) can be calculated from the distance between the neighboring dark suppression spots, which is around 0.51 nm. This value is the same as that of the lattice in component II in Figure 2(c), which corresponds to $\sqrt{3}$ times the

Ag-Ag distance. Therefore, the parallelogram in Figure 3(b) can be essentially described by a $\sqrt{3}\times\sqrt{3}$ reconstruction with respect to the 1×1 Ag(111).

LEED measurements are performed to explore macroscopically the structural characterization in the reciprocal space. The LEED pattern of pristine Ag(111) substrate displays six symmetric bright spots, labeled by the red circle in Figure 4(a). After a small amount of Ge atoms were deposited on Ag(111) surface at 600 K, there are six additional inner spots appearing in the LEED results, as shown in Figure 4(b). This pattern originates from a $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure (as labeled by the yellow circle) with respect to the substrate lattice. The spots of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure become bright and clear with increasing Ge coverage, consistent with the microscopic results obtained by STM measurements.

The Ag(111) substrate is a unique surface for a group of 2D surface alloys with remarkable 2D electronic profiles. In particular, the $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure could also be identified in Ag_2M alloy ($M = \text{Bi}^2$, $\text{Pb}^{5,6}$, Sb^7 , or Sn^4) when $1/3$ monolayer of M atoms was deposited on Ag(111). Thus, our experimental observations indicate that the honeycomb arrangement of the $\sqrt{3}\times\sqrt{3}$ reconstruction is related to Ag_2Ge -ordered surface alloy, where one out of three Ag atoms in the surface layer was replaced by a Ge atom, as shown in Figure 4(d). The wavelike striped patterns could be correlated with the meandering stripes observed at room temperature (Figure 2). This structural feature is the result of the relaxation of the compression force induced by the difference in the radii between Ge atoms and Ag atoms after Ge insertion. The deviation of the atomic arrangement from the ideal $\sqrt{3}\times\sqrt{3}$ periodicity can be

identified in the high-resolution STM image [Figure 3(c)], where the honeycomb structure appears to be slightly stretched in the valleys compared to the ridges of the stripes. Moreover, the rows of Ge atoms along the $\vec{a}$ direction of 6-fold periodicity appear slightly wiggly, which gives rise to the twisted angle for the line through the dark suppression spots along the ridges with respect to the line through the dark suppression spots in the valleys. All these results reflect a distortion evoked by the compression relaxation. Due to the hexagonal symmetry of Ag₂Ge alloy, we would expect there to be three directions for the striped patterns separated by 120°, which is demonstrated by the STM results in Figure 3(a).

Raman spectroscopy is an insightful tool for probing the phonon dynamics associated with 2D materials, which can be distinguished from that of their three-dimensional (3D) bulk parent. The phonon vibrational properties of the Ge/Ag(111) system were investigated by *in-situ* Raman measurements to prevent possible oxidization during *ex-situ* measurements. The Raman spectra of Ag(111) substrate and Ge(111) wafer are displayed in Figure 4(e) as references. No Raman signal of Ag(111) can be detected due to the Rayleigh scattering. In the Raman spectrum of the Ge(111) surface, the characteristic peak at 303 cm⁻¹ corresponds to the frequency of the *in-plane* transverse optical (iTO) and *in-plane* longitudinal optical (iLO) phonon branches at the Γ point for germanium atoms, *i.e.* a doubly degenerate E_{2g} mode.⁴⁰ The Raman spectrum of Ag₂Ge was acquired and is shown in Figure 4(e), where no Raman signal could be detected. Since the E_{2g} peak is the fingerprint of the bond stretching of all germanium atom pairs, the Raman spectrum

implies the absence of Ge-Ge covalent bonds after 1/3 monolayer of Ge has been deposited on the Ag(111) surface. The Raman results confirm the generation of metallic 2D Ag₂Ge surface alloy rather than a monolayer of 2D germanium nanosheets in the Ge/Ag(111) system.

The electronic band structure of Ag₂Ge alloy on Ag(111) surface was probed by ARPES with high energy and momentum resolution. Figure 5(a) displays the occupied states of Ag₂Ge along the Γ -M- Γ direction of the $\sqrt{3}\times\sqrt{3}$ superstructure. The Shockley surface state of Ag(111) substrate in the proximity of the Γ point could no longer be observed, but the typical bulk *sp* band of Ag crossing the Fermi level (E_F) at around $1 \text{ \AA}^{-1}$ still exists, implying a structural modulation on the Ag(111) surface. Two well-resolved surface bands with linear dispersion, S_1 and S_2 , are around the Γ point and lies across the Fermi level at $\sim 0.10 \pm 0.01 \text{ \AA}^{-1}$ (S_1) and $\sim 0.28 \pm 0.02 \text{ \AA}^{-1}$ (S_2), respectively. Another band labelled as S_3 could also be identified at around the center (Γ point) of the second Brillouin zone (BZ) of Ag₂Ge alloy. The nature of the S_3 band is same as that of S_1 band, although only one dispersion branch could be detected due to the measurement range. All these bands are absent in pristine Ag(111) and assigned to Ge-related bands. The S_2 band exhibits an upward parabolic-like variation crossing the Fermi level along the direction perpendicular to $k_{//}$, thus giving a clear indication of the metallic nature of the S_2 band. This metallic character of the S_2 band is consistent with our Ag₂Ge alloy mode. Figure 5(c) shows the constant energy (k_x, k_y) contour plots (CECP) at various binding energies from the Fermi level to 1.6 eV below the Fermi level with energy intervals of 0.2 eV. Each constant energy

contour of the band structure displays a vertical, circularly shaped band variation as a result of the projection of a cone. The cone point is estimated to be around 0.4-0.5 eV above the Fermi level from the linear-like energy momentum dispersion. Thus, the S_1 band at the Γ point is possibly attributable to the Dirac cone originating from Ag_2Ge . In principle, a two-dimensional electron gas (2DES) can be transformed into Dirac fermions after it is decorated by a suitable periodic array of gates.⁴¹ Due to its metalloid nature, the deposited Ge is expected to be at negative potential relative to the buried 2DES on the $\text{Ag}(111)$ substrate and to deplete electrons. Thus, the triangular Ge arrangement leaves the electrons in a graphene-like honeycomb pattern and could be described by the Dirac Hamiltonian, leading to the formation of “composite graphene” with Dirac fermion characteristics. More results on the electronic properties, however, such as quasi-particle chirality and X-shaped band dispersion in ARPES measurements, are needed to judge whether the Dirac fermions exist in 2D Ag_2Ge alloy or not.

4 Conclusions

In summary, the interaction between Ge and the $\text{Ag}(111)$ surface has been identified by *in-situ* Raman spectroscopy, and by LEED, STM, and ARPES measurements. After a small amount of Ge deposition, Ge atoms insert themselves into the $\text{Ag}(111)$ surface at room temperature. With increasing Ge deposition, Ag_2Ge alloy with honeycomb topography is generated in the enclosed triangle-like regions of the stripes. Due to the low mobility at room temperature and the compression strain effect evoked by the inserted Ge atoms, Ag_2Ge alloy is arranged in the form of

meandering features coexistent with the amorphous areas. The long-range striped structure of Ag₂Ge alloy is generated at a high deposition temperature when the coverage of Ge reaches 1/3 monolayer. Based on the STM results, a structural model of Ag₂Ge alloy is proposed, where one out of three Ag atoms at the Ag(111) surface is replaced by a Ge atom to reproduce the ($\sqrt{3}\times\sqrt{3}$)R30° surface alloy. The *in-situ* Raman spectra and ARPES results provide clear evidence for the formation of metallic Ag₂Ge alloy.

Acknowledgements

This work was supported by the Australian Research Council (ARC) through two Discovery Projects (DP140102581 and DP160102627), Linkage Infrastructure, Equipment and Facilities (LIEF) grants (LE100100081 and LE110100099), the National Natural Science Foundation of China (11474244), the National Basic Research Program of China (2015CB921103), and the Program for Changjiang Scholars and Innovative Research Team in University (IRT13093). The authors would like to acknowledge support by the University of Wollongong through a University Research Council (URC) Small Grant in 2014. The authors thank Dr. T. Silver for her valuable comments on this work.

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Figures and figure captions

Figure 1

Figure 1. (a) STM topographic image ($100 \text{ nm} \times 100 \text{ nm}$, $V_{\text{bias}} = 3 \text{ V}$, $I = 0.05 \text{ nA}$) and (b) high-resolution STM image ($5 \text{ nm} \times 5 \text{ nm}$, $V_{\text{bias}} = 0.136 \text{ V}$, $I = 0.05 \text{ nA}$) of bare Ag(111) surface. The atomically resolved STM image reveals the hexagonal structure of the Ag(111) surface with a lattice constant of $0.28 \pm 0.01 \text{ nm}$. (c) STM topographic image ($100 \text{ nm} \times 100 \text{ nm}$, $V_{\text{bias}} = 3 \text{ V}$, $I = 0.05 \text{ nA}$) and (d) high-resolution STM image ($5 \text{ nm} \times 5 \text{ nm}$, $V_{\text{bias}} = 0.1 \text{ V}$, $I = 0.05 \text{ nA}$) of a small amount of Ge atoms deposited on the Ag(111) surface at room temperature. The randomly distributed dark spots represent Ge atoms, which insert themselves into the Ag (111) surface plane and substitute for surface Ag atoms without destroying the

hexagonal structure of the Ag(111) surface.

Figure 2

Figure 2. (a) STM topographic image of $1/3$ monolayer of Ge atoms deposited on an Ag(111) surface at room temperature ($100 \text{ nm} \times 100 \text{ nm}$, $V_{\text{bias}} = 3 \text{ V}$, $I = 0.05 \text{ nA}$). (b) Enlarged STM image of intercalated region [cyan frame in (a)] ($50 \text{ nm} \times 50 \text{ nm}$, $V_{\text{bias}} = -2 \text{ V}$, $I = 0.05 \text{ nA}$). It shows clear triangle-like patterns with filleted corners (component I, blue frame I) and fuzzy stripes (component II, blue frame II). (c) High-resolution STM image of frame II in (b) ($5 \text{ nm} \times 5 \text{ nm}$, $V_{\text{bias}} = 2.5 \text{ V}$, $I = 0.05 \text{ nA}$), which reveals the honeycomb structure. The black rhombus represents the $\sqrt{3} \times \sqrt{3}$ unit cell. (d) Line profiles along the solid lines in (c), which indicate the unit cell with a lattice constant of 0.51 nm (green line) and the honeycomb structure with side lengths of 0.29 nm (red line).

Figure 3

Figure 3. (a) STM topographic image of $1/3$ monolayer of Ge atoms deposited on an Ag(111) surface at 600 K ($100 \text{ nm} \times 100 \text{ nm}$, $V_{\text{bias}} = 1.5 \text{ V}$, $I = 0.05 \text{ nA}$), which reveals a striped structure aligned along different directions with an orientation angle of 120° . (b) Enlarged STM image of intercalated region [cyan frame in (a)] ($15 \text{ nm} \times 15 \text{ nm}$, $V_{\text{bias}} = -8 \text{ mV}$, $I = 0.05 \text{ nA}$), in which a long-range modulated $6\sqrt{3} \times \sqrt{3}$ reconstruction is labeled with a white parallelogram. The purple arrows show the directions of the $6\sqrt{3} \times \sqrt{3}$ reconstruction. (c) High-resolution STM image acquired in the blue frame in (b) ($5 \text{ nm} \times 5 \text{ nm}$, $V_{\text{bias}} = 2.5 \text{ V}$, $I = 0.05 \text{ nA}$). The orientation of Ag_2Ge is at $\sim 30^\circ$ from the $[1\bar{1}0]$ direction of the Ag(111) surface. The black rhombus represents a $\sqrt{3} \times \sqrt{3}$ unit cell. (d) Line profiles along the solid lines in (c),

which indicate a unit cell with a lattice constant of 0.51 nm (green line) and a honeycomb structure with side lengths of 0.29 nm (red line).

Figure 4

Figure 4. LEED patterns of (a) pristine Ag(111) substrate, (b) after a small amount of Ge atoms was deposited on the Ag(111) substrate, and (c) after 1/3 monolayer of Ge atoms was deposited on the Ag(111) substrate at 600 K. These patterns were collected with primary electron energy of 86 eV (a) and 63 eV (b, c). The six outer spots are ascribed to the six-fold symmetry of the Ag(111) substrate, which is marked by the red circle. The six inner spots originate from the Ge/Ag(111) ($\sqrt{3}\times\sqrt{3}$)R30° superstructure, which is marked by the yellow open circle. (d) Side view and top view along the $[1\bar{1}0]$ Ag direction of the atomic configuration of the Ag₂Ge ($\sqrt{3}\times\sqrt{3}$)R30° superstructure. The yellow and gray spheres represent Ge and Ag atoms, respectively. The unit cell of $\sqrt{3}\times\sqrt{3}$ Ag₂Ge is outlined by the black rhombus. (e) Raman spectra of Ag₂Ge alloy, and Ge(111) and Ag(111) crystal.

Figure 5

Figure 5. (a) Energy vs. k dispersion measured by ARPES for 1/3 monolayer Ge atoms deposited on Ag(111) substrate at 600 K band along the Γ -M- Γ direction of the Ag_2Ge alloy BZ. S_1 , S_2 , and S_3 label highly dispersive surface bands, which stem from Ge atom deposition on Ag(111). (b) Constant energy contour at 0.4 eV below the Fermi level and schematic diagram of the BZ for $\sqrt{3} \times \sqrt{3}$ superstructures of Ag_2Ge grown on Ag(111): the dashed green hexagon and solid orange hexagons correspond to Ag (111) and Ag_2Ge , respectively. (c) Equidistant constant energy contours of the band structure of S_1 and S_2 at the Γ point.

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