Electronic structure of a monoatomic Cu$_2$Si layer on a Si(111) substrate

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(Received 31 October 2018; published 24 April 2019)

Fermi surfaces and band dispersion curves of a Cu$_2$Si layer on Si(111), quasi-“5×5” were mapped by angle-resolved photoemission spectroscopy using synchrotron radiation. Two metallic bands were observed within the Si bulk band gap, which are likely assigned to the electronic bands of the Cu$_2$Si layer. Additional bands were found in the Si bulk band gap that originate from the interactions between the substrate state and the Cu$_2$Si states that have the p$_z$ character. The present research aims at investigating the changes in the electronic structure of an atomic layer when prepared on a substrate.

DOI: 10.1103/PhysRevMaterials.3.044004

I. INTRODUCTION

Atomic layers have been significant playgrounds for low-dimensional physics. These systems have recently attracted both academic and technological interest due to observations and predictions of Dirac electrons. The mastery of Dirac electrons could lead to high-frequency and low-dissipation devices for electronic applications and be the next revolution in materials science. Dirac cones have been measured experimentally in layers of graphene [1,2] and have also been known to be obtained by Cu deposition [20,23,24], as shown in Fig. 1 by low-energy electron diffraction (LEED). The surface is “discommensurate” (incommensurate) with the substrate lattice, resulting in a quasi-“5×5” periodicity. The structure model, proposed by Zegenhagen et al. [20,21], has been widely accepted and was also confirmed recently [25]. As shown in Fig. 2, it consists of a surface tiled with the Cu$_2$Si quasi-“5×5” domains, lacking the long-range order of the Cu$_2$Si monolayer. The atomic structure of the Cu$_2$Si layer can be considered as replacement of upper Si atoms in the Si(111) topmost layer with the Cu atoms of the honeycomb lattice, as shown in Fig. 2. It is of note that, in the discommensurate phase, the degree of local Si-Si back-bonding depends on the individual sites, as presented in Fig. 2.

In the present research, we prepared the Si(111) quasi-“5×5” Cu surface and studied its electronic band structure by band-mappings with angle-resolved photoemission spectroscopy (ARPES) and by band calculations with density functional theory (DFT). Two partially occupied or metallic bands and fully occupied bands of the surface states were observed within the Si bulk band gap. These states likely originate from three electronic states of the Cu$_2$Si layer, evidencing the effect of interactions between the layer and the substrate.

II. EXPERIMENTAL SECTION

The experiments were conducted at the beamline BL-2A MUSASHI of Photon Factory, KEK, Japan. Measurements of angle-resolved photoemission spectroscopy were performed...
at 20 K. The samples were prepared in situ in a ultrahigh vacuum (UHV) chamber. Clean Si(111) surfaces with a 7 × 7 reconstruction were prepared by flashing at 1200 °C, followed by annealing at 850 °C. A Si wafer of n type (<0.02 Ω cm) was used. The Cu2Si layer was prepared by Cu deposition on the Si(111) 7 × 7 at 630 °C. A Cu evaporator was prepared using a tungsten filament and a copper wire (99.999% purity). At a Cu coverage of 1 monolayer (ML), as determined by a quartz balance, a quasi-“5 × 5” phase was confirmed by sharp LEED patterns, as shown in Fig. 1. This discommensurate surface reconstruction is in total agreement with anterior studies on this material [20,21,23,25].

First-principles calculations were performed using the projected augmented wave method (PAW) [26,27] as implemented in the Vienna Ab initio Simulation Package (VASP) [28–31] based on density functional theory with the Perdew-Burke-Ernzerhof (PBE) type of generalized gradient approximation (GGA) and GGA plus Hubbard U (PBE+U) scheme. The 12 × 12 × 1 Monkhorst-Pack k mesh and a cutoff energy of 400 eV are used in the self-consistent field calculations. The on-site Coulomb energy $U = 7.0$ eV [32] is adopted for Cu atoms in the PBE+U calculations. The geometries of all the systems are optimized with the total energies converged within 10-4 eV. To study the substrate effect in the Cu2Si/Si(111) systems, we put a Cu2Si 1 × 1 monolayer on top of a 12-layer Si 1 × 1 substrate with a Cu2Si lattice constant of 4.09 Å.

### III. RESULTS AND DISCUSSION

Figure 3(a) shows the photoemission Fermi surface map of the Cu2Si surface, taken at a photon energy of 70 eV and with linear-horizontal (LH) polarization. These parameters were experimentally determined as the optimal ones for a high resolution of the electronic bands. The observation of the Fermi surface clearly indicates that the surface is metallic. Contours of the Fermi surface are composed of a hexagon, exhibiting large photoemission intensity and fine intensity structures. The photoemission bands are composed of the original band and those coming from umklapp scattering associated with the quasi-“5 × 5” periodicity. The map of the Fermi surface is reproduced by taking into account two types of Fermi surfaces (hexagonal and flower-shaped) with a ±3° rotations and by tiling with the umklapp-scattering vectors, as shown in Figs. 3(b)–3(d). It is of note that the hexagonal and flower-shaped Fermi surfaces match with the energy contours of the α and β bands of the Cu2Si layer [22,33]. The tiling of the hexagonal (α) band is consistent with the previous band-mapping of the Si(111)quasi-“5 × 5”-Cu surface [24].

The electronic band structure was measured along two directions in the reciprocal space: Γ−M and Γ−K of the Si(111) 1 × 1 Brillouin zone surface. The results are shown in Figs. 4 and 5. Starting with Fig. 4, one can recognize the silicon bulk bands [34] at the Γ point. The bulk bands are composed of many subbands that are generated due to the quantum confinement by the narrow space-charge layer [35]. The white dotted line in the figure traces the edge of the bulk bands and,
FIG. 3. Study of the Fermi surface of Cu$_2$Si. (a) Constant energy contour map measured using 70-eV linear horizontal polarized photons at the Fermi level. Two bands, one hexagonal ($\alpha$) and one flower-shaped ($\beta$), are observed, as well as lighter patterns arising from umklapp scattering. (b) Schematic representation of the hexagonal $\alpha$ band, in green, and its umklapp tiling, in black. The umklapp vectors, by which the $\alpha$ band is translated, are represented by the arrows centered on $\Gamma$, and the Si(111) Brillouin zone is represented by the dashed hexagon. (c) Schematic representation of the flower-shaped $\beta$ band, in red, and its umklapp tiling, in black. (d) Superposition of (a), (b), and (c), creating the complete quasi-“5×5” umklapp scattering of the Fermi surface.

Within the bulk band gap, one can identify dispersion curves of the $\alpha$ band that crosses the Fermi level ($E_F$). The Fermi vector along the $\Gamma$-$M$ direction is 0.42 Å$^{-1}$, which is similar to the previously reported value [24]. The metallic $\beta$ band, fainter, is also identified. Other bands, indicated by arrows in the figure, correspond to replica bands by the quasi-“5×5” umklapp scattering [24].

Along the $\Gamma$-$K$ direction (Fig. 5), one can clearly observe the two metallic bands, $\alpha$ and $\beta$, that cross the Fermi level. The Fermi vectors along the $\Gamma$-$K$ direction are estimated to be 0.48 and 0.54 Å$^{-1}$ for the $\alpha$ and $\beta$ bands, respectively. It is of note that previous research on Si(111) [24] reported one of the bands, $\alpha$. In the figure, one can also find replica bands of the quasi-“5×5” umklapp scattering [24]. We confirm observation of no other band at the Fermi level for different photon energies (hν = 35, 40, 50, 60, 80, 100 and 105 eV), which are not shown here.

The $\alpha$ and $\beta$ bands observed in the present research are hole pockets and also have similar dispersion curves (Fermi surfaces) to those of the $\alpha$ and $\beta$ bands in Ref. [22]. Thus, it is natural to consider that origins of the $\alpha$ and $\beta$ states are $\alpha_+$ and $\beta_+$ of the freestanding layer, respectively. A comparison between Fermi vectors for three different systems is presented in Table I. Taking parameters of the freestanding Cu$_2$Si as a reference, the wave vectors show opposite shifts between the Cu and Si substrates. The $k_F$ values become smaller on Cu(111) but larger on Si(111), indicating a lower and higher shift in energy of the $\alpha$ and $\beta$ bands, respectively.

Concerning the $\gamma$– band in the freestanding Cu$_2$Si layer, it was not observed under the present experimental conditions at the Fermi level for the Si(111)quasi-“5×5”-Cu surface, which is sharply in contrast to behaviors of $\alpha$ and $\beta$ bands. We infer that this difference is due to the orbital symmetry. According to the previous report [22], the $\alpha_+$ and $\beta_+$ states have the mixed Si $p_x/p_y$ and Cu $p_x/p_y$ characters. On the other hand, the $\gamma$– state has the Si $p_z$ and Cu $p_z$ character [22]. In the layer, the $\alpha_+$ and $\beta_+$ states distribute in-plane, while the $\gamma$– state extends out-of-plane. Thus, it is expected that the $p_z$ states in the Cu$_2$Si layer make interactions with Si dangling-bond ($p_z$) states of the Si(111) substrate, resulting in formation of the bonding states. This picture is consistent with the structural model of the Si(111)quasi-“5×5”-Cu surface in...
TABLE I. Fermi vectors \( k_F \) in the three systems: freestanding \( \text{Cu}_2\text{Si}, \text{Cu}_2\text{Si}/\text{Cu}(111) \), and \( \text{Cu}_2\text{Si}/\text{Si}(111) \), for bands \( \alpha \) and \( \beta \), along the \( \Gamma-K \) and \( \Gamma-M \) directions. The unit is \( \text{Å}^{-1} \). Values of the freestanding layer are obtained from the DFT calculation, while those of the \( \text{Cu}_2\text{Si}/\text{Cu}(111) \) are supplied from the previous research [22]. For \( \text{Cu}_2\text{Si}/\text{Si}(111) \), values are experimentally determined with accuracy of \( \pm 0.02 \text{ Å}^{-1} \).

<table>
<thead>
<tr>
<th>Direction</th>
<th>band</th>
<th>( \text{Cu}_2\text{Si} )</th>
<th>( \text{Cu}_2\text{Si}/\text{Cu}(111) )</th>
<th>( \text{Cu}_2\text{Si}/\text{Si}(111) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma-K )</td>
<td>( \alpha )</td>
<td>0.37</td>
<td>0.23</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>( \beta )</td>
<td>0.39</td>
<td>0.27</td>
<td>0.54</td>
</tr>
<tr>
<td>( \Gamma-M )</td>
<td>( \alpha )</td>
<td>0.34</td>
<td>0.21</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>( \beta )</td>
<td>0.30</td>
<td>0.31</td>
<td>0.65</td>
</tr>
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Fig. 2(b), underlining the bonding between the Si atoms from the surface and the bulk. As shown in Fig. 5, one can recognize electronic band at binding energy of 1–2 eV that are different from the \( \alpha \) and \( \beta \) (replica) bands. Since the dispersion curves are located within the bulk band gap, the bands are assigned to the surface that are likely originated from the \( \gamma \) band. In order to confirm the picture, the DFT calculation was held on the \( \text{Cu}_2\text{Si}/\text{Si}(111) \).

In Fig. 6, the calculated band structures of a \( \text{Cu}_2\text{Si} \) monolayer are presented for the freestanding layer and for the layer grown on a \( \text{Si}(111) \) substrate. For the freestanding \( \text{Cu}_2\text{Si} \), Fig. 6(a), the band structure is consistent with the previous report [22]. Three metallic bands are labeled: two hole pockets, \( \alpha_+ \) and \( \beta_+ \), and one electron pocket, \( \gamma_- \), at the \( \Gamma \) point. The bands cross each other in regions with linear dispersion and generate two loops of the nodal lines [22]. Wave functions of the \( \alpha_+ \) and \( \beta_+ \) bands have even parity, while that of the \( \gamma_- \) band has odd parity. On the \( \text{Si} \) substrate, we made calculation with the commensurate \( \text{Cu}_2\text{Si}/\text{Si}(111) \) structure to model the \( \text{Si}(111) \)-quasi-“5×5”-\( \text{Cu} \) surface. Despite the simplicity, the model is sufficient to capture electronic change coming from by the back-bond formation between the overlayer and the substrate. As shown in Fig. 6(b), the \( \alpha \) and \( \beta \) bands remain almost unchanged while the \( \gamma_- \) band changes significantly. Furthermore, comparing Figs. 6(a) and 6(b), one recognizes additional bands around the \( K \) point at binding energy of 1–2 eV in (b), as expected in Fig. 5. The calculation supports our experimental results, evidencing that the \( \gamma \) band is much influenced than the \( \alpha \) and \( \beta \) bands. It is of note that the calculation model reproduces only a part of the discommensurate phase. We leave open the possibility of the existence of the metallic freestanding-like \( \gamma \) band if there is a domain of the \( \text{Cu}_2\text{Si} \) layer on the surface that does not have local bonding with the substrate Si atoms.

**IV. CONCLUSIONS**

In summary, we mapped Fermi surfaces and band dispersion curves of a \( \text{Cu}_2\text{Si} \) layer on \( \text{Si}(111) \), with a quasi-“5×5” surface reconstruction, by angle-resolved photoemission spectroscopy and compared the result with the DFT band calculation. We found that electronic states with \( x-y \) (in-plane) character remained unchanged but those with \( z \) (out-of-plane) character are modified when the overlayer is prepared on a \( \text{Si} \) substrate. The present research demonstrates the electronic evolution of a monolayer in various environments, linking the theoretically predicted freestanding monolayer to the one prepared on a substrate.

**ACKNOWLEDGMENTS**

This work was supported by the Grant-in-Aid for Specially Promoted Research (KAKENHI 18H03874) from the Japan Society for the Promotion of Science, and by a grant from the Labex MATISSE. The preliminary experiment was performed at facilities of the Synchrotron Radiation Research Organization, the University of Tokyo. The computational work was supported by the Ministry of Science and Technology, Taiwan. H.T.J. also thanks the CQT-NTHU-MOE, NCHC, and CINC-NTU, Taiwan, for technical support. Baojie Feng is acknowledged for providing information on the \( \text{Cu}_2\text{Si}/\text{Cu}(111) \) system.


ELECTRONIC STRUCTURE OF A MONOATOMIC Cu2Si … PHYSICAL REVIEW MATERIALS 3, 044004 (2019).


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