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Abstract

The number of two-dimensional (2D) materials has grown steadily since the discovery of graphene. Each new 2D material demonstrated unusual physical properties offering a large flexibility in their tailoring for high-tech applications. Here, we report on the formation and characterization of an uncharted 2D material: 'Cu₂Te alloy monolayer on Cu(111) surface'. We have successfully grown a 2D binary Te-Cu alloy using a straightforward approach based on chemical deposition method. Low electron energy diffraction (LEED) and scanning tunneling microscopy (STM) results reveal the existence of a well-ordered alloy monolayer characterized by $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure, while the x-ray photoemission spectroscopy (XPS) measurements indicate the presence of single chemical environment of the Te atoms associated with the Te-Cu bonding. Analysis of the valence band properties by angle resolved photoemission spectroscopy (ARPES); in particular the electronic states close to the Fermi level suggests a strong hybridization between Te and Cu electronic states leading to an appearance of new dispersive bands localized at the surface alloy, which is confirmed by first-principles calculations. These bands are strongly influenced by the surface reconstruction and undergo a back-folding at the boundaries of the reduced surface Brillouin zone (SBZ). More interesting, a band gap of about 0.91 eV and a Rashba splitting in the conduction band are obtained. These findings taken together clearly prove the presence of 2D-type electron system within the Cu₂Te alloy layer, which is promising for spintronic application.

1. Introduction

In the recent years, there has been a growing interest in the study of two-dimensional (2D) layered materials that have fascinating physical and chemical properties and offer great opportunities to explore various areas such as energy storage, electronic devices and sensors [1]. In this respect, graphene, silicene, topological insulators and transition metal dichalcogenides (TMD) of the MX₂ form, where M the transition metal atoms (Cu, Mo, or W etc) and X the chalcogen atoms (S, Se or Te), are the most attractive materials because of their intriguing properties in a number of aspects [2–5]. Like graphene, 2D TMDs have very interesting electrical, chemical, mechanical or thermal properties when they have only one

atomic monolayer. TMD monolayers have recently emerged as very promising nanostructures for various technological applications in optics, electronics, catalysis and biosensors. In particular, studies have shown that TMD materials such as MoS₂ and MoSe₂ present a 2D electron system that exhibits remarkable properties [6, 7]. Interest in such systems has also been intensified by the recent discovery of a large enhancement in photoluminescence quantum efficiency [8] and a potential route to valleytronics in atomically thin layers of metal dichalcogenides [9, 10]. The recent renewed interest in TMD is due to the ultimate electronic components of transistor or phototransistor type, exploiting the properties of these materials [11, 12]. TMD monolayers and graphene have some common characteristics, for

example: they are derived from lamellar materials. They are distinguished by their electronic and optical properties and may be complementary for many technological challenges. Graphene has a hexagonal honeycomb arrangement, while the TMD monolayers consist of three atomic planes instead of one, the atoms of the transition metal form a plane sandwiched between two chalcogen planes. Each transition metal atom is connected to six chalcogen atoms, which they are in prismatic trigonal coordination with respect to the metal atoms. On the other hand, there exists another kind of chalcogen-based materials, named metal chalcogenide alloys that are also suitable for a large number of high-tech applications [13, 14]. As a model system, copper telluride (CuTe) alloy is a promising material for potential developments in several fields, such as in lithium ion batteries, photo-thermal therapy, detection of toxic CO, and thermoelectric uses [15–17]. It represents also a crucial element for the photovoltaic industry [18] and is conventionally employed as a back conductive contact layer for high-efficiency CdTe based solar cells [19, 20]. CuTe exists in a multitude of alloy phases with different allotropes [21, 22]. Depending on the Cu:Te relative composition a transition from semiconducting to metallic character is expected. Moreover, in a CuTe sheet containing quasi-1D Te-chain an appearance of *charge density wave phase* was recently observed at a significantly high temperature ($T_c = 335$ K) [23]. In addition, CuTe alloy may exhibit a Rashba-like spin orbit (RSO) splitting which is due to the surface inducing removal of the inversion symmetry along the normal direction [24]. In other words, the structural inversion asymmetry along the surface normal allows the lifting of degeneracy of the opposite spin states and thus leads to energy and wave vector separations. Such an effect is directly observed by angle resolved photoemission and has been studied in many other systems for which it was demonstrated that the surface alloy inducing large in-plane potential gradient leads to enhancing the RSO coupling [25–28]. Therefore, it is highly essential to analyze the effect of the alloying process in the electronic structures of such a system. Tellurium is the heaviest nonradioactive element in the chalcogen group. The bulk Te crystal is a mid-infrared semiconductor with a band gap of 0.33 eV and its band gap increases monotonically with decreasing thickness, reaching 0.92 eV in monolayer regime. In addition, tellurium has a metallic appearance, with p-type semiconductor properties, that it should be used in electronics and in the manufacture of electrical rectifiers for thermoelectric devices. So far, elaboration of Copper Telluride thin film has been done by physical vapor deposition (PVD). Previous LEED characterizations of this system suggested the formation of two superstructures ($2\sqrt{3} \times 2\sqrt{3}$)R30° and ($\sqrt{3} \times \sqrt{3}$)R30° at coverage θ_{Te} of 0.08 and 0.33 monolayers (ML), respectively. Analysis of the surface structure was performed

by Surface Extended x-ray Absorption Fine-Structure (SEXAFS) and indicated that the Te atoms substitute Cu atoms in the outermost Cu layer [29]. Apart from these few works mentioned above, the Te/Cu(111) system has not been sufficiently studied and, in particular, information on the electronic band structure is missing. In the present paper we provide a systematic study combining four main surface investigation methods: (i) Low energy electron diffraction (LEED) to analyze the crystal structure of the sample surface; (ii) low temperature tunneling microscopy (STM) to access the crystal structure at the atomic scale; (iii) x-ray photo-emission spectroscopy (XPS) to probe core levels; and (iv) angle-resolved photoemission (ARPES) to analyze the valence band properties, by taking advantage of the synchrotron light. To compare with theory, First-principles calculations of the band structure have been made. The main objective is to study the electronic properties of Te films on the surface of Cu(111) of the highest possible structural quality using the chemical deposition method, with a view to studying the fundamental adsorption properties of chalcogen atoms on metallic surfaces. The complexity and richness of the alloy phases of this material and the ability to match electronic properties by modifying the relative composition, makes Te/Cu system more important for scientific research. Formation of Cu₂Te surface alloy is the most favorable which confirms the theoretical predictions and agrees with other experimental results [30–33]. Like in other metal applications, the alloy forms essentially at the level of the surface and exhibits a ($\sqrt{3} \times \sqrt{3}$)R30° type reconstruction [34–37]. The present study focuses on the properties of binary Cu₂Te alloy monolayer when it is formed on Cu(111) surface. It highlights 2D electron behavior of this material and can open up novel avenues towards new technological developments.

2. Results and discussion

Experimentally, we have used a new approach based on chemical deposition method from Na₂Te aqueous solution for the elaboration of Cu₂Te alloy monolayer on Cu(111) substrate. Besides being simple, inexpensive, convenient, and especially safe, this method yields to high-quality and thin alloy with large size film and has already been used for other systems [30, 38, 39]. Detailed XPS analysis at the different elaboration steps is given in the supplementary information (available online at stacks.iop.org/TDM/7/035010/mmedia). We describe here the photoemission spectra of the Te-4d core level, shown in figure 1. The latter presents the spectrum measured just after deposition compared to that obtained on the sample after annealing at 500 °C. The two spectra were analyzed using a fit with Voigt-type peaks to determine the different possible components. There are four spectroscopic contributions, labelled by the letters A, B, C and D,

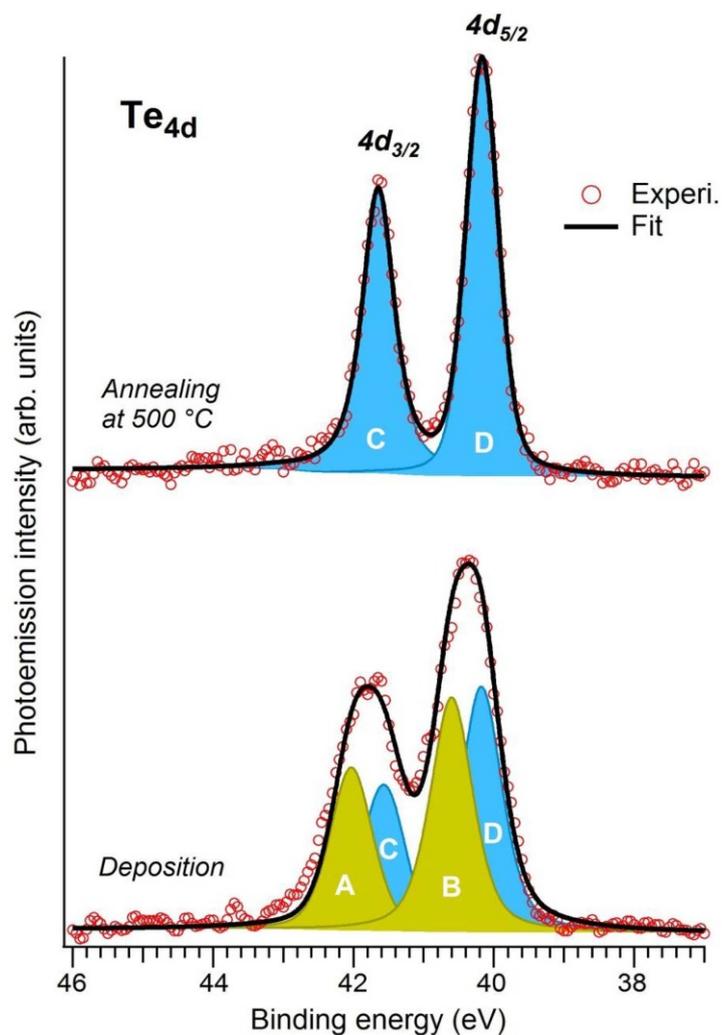


Figure 1. Te-4d core level spectra (red circles) and their de-convolutions (solid line overlapping the data points) recorded using a photon energy of 260 eV at normal emission. The lower spectrum is obtained on as-deposited film while the upper one is measured on the same sample after annealing at 500 °C. For the fitting, Voigt-type peaks were used to identify the different spectroscopic contributions marked A, B, C, D and characterized by a linewidth of 0.7 eV without asymmetry effect, which suggests a semiconductor character of the deposited film.

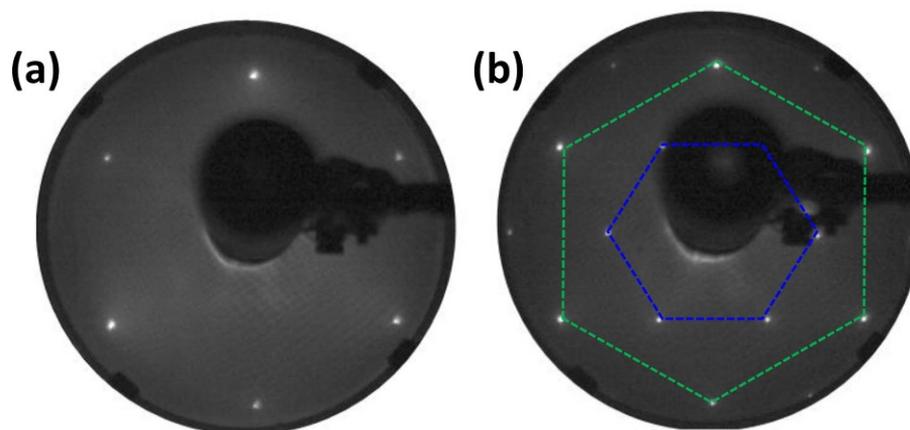
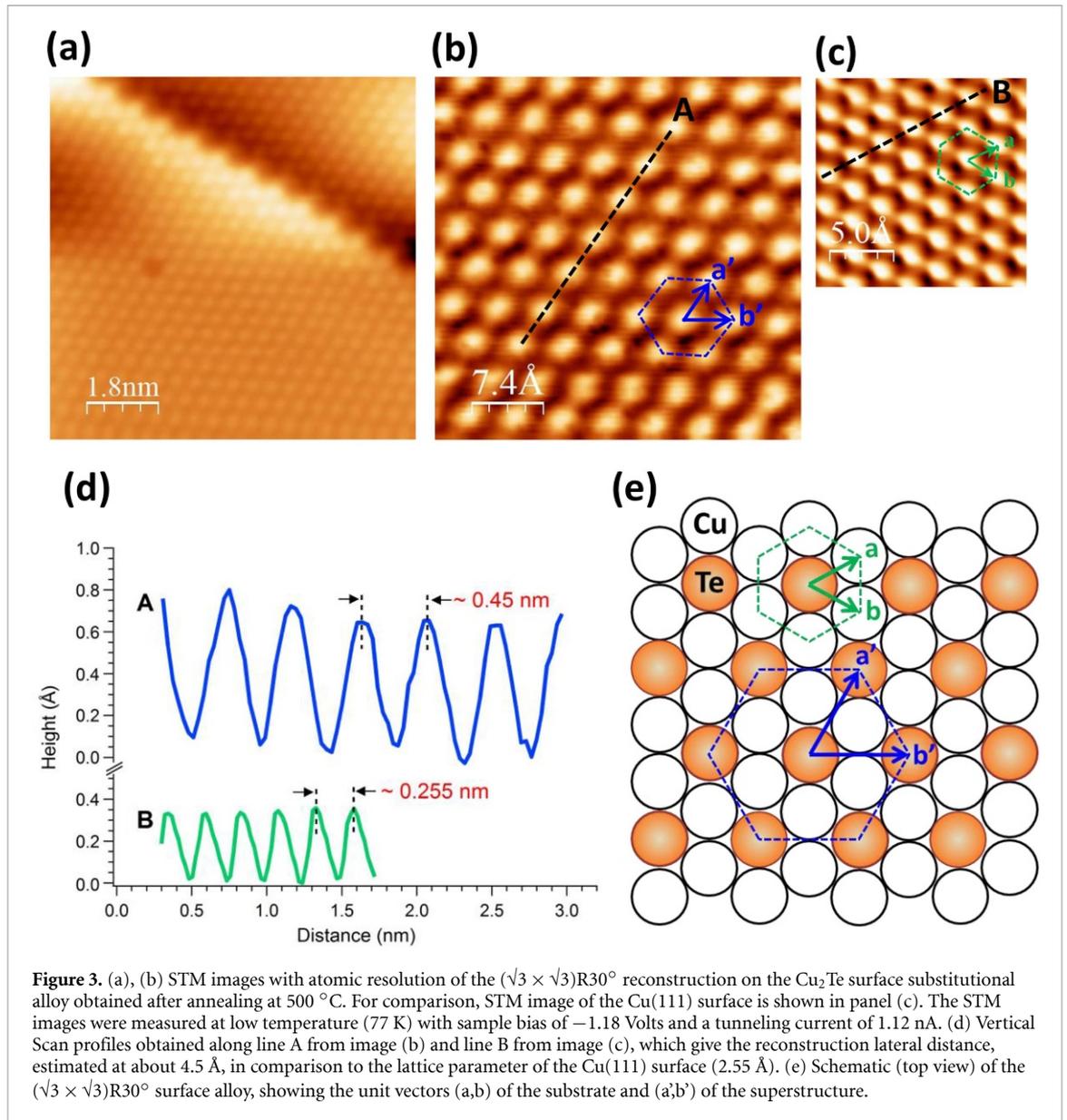


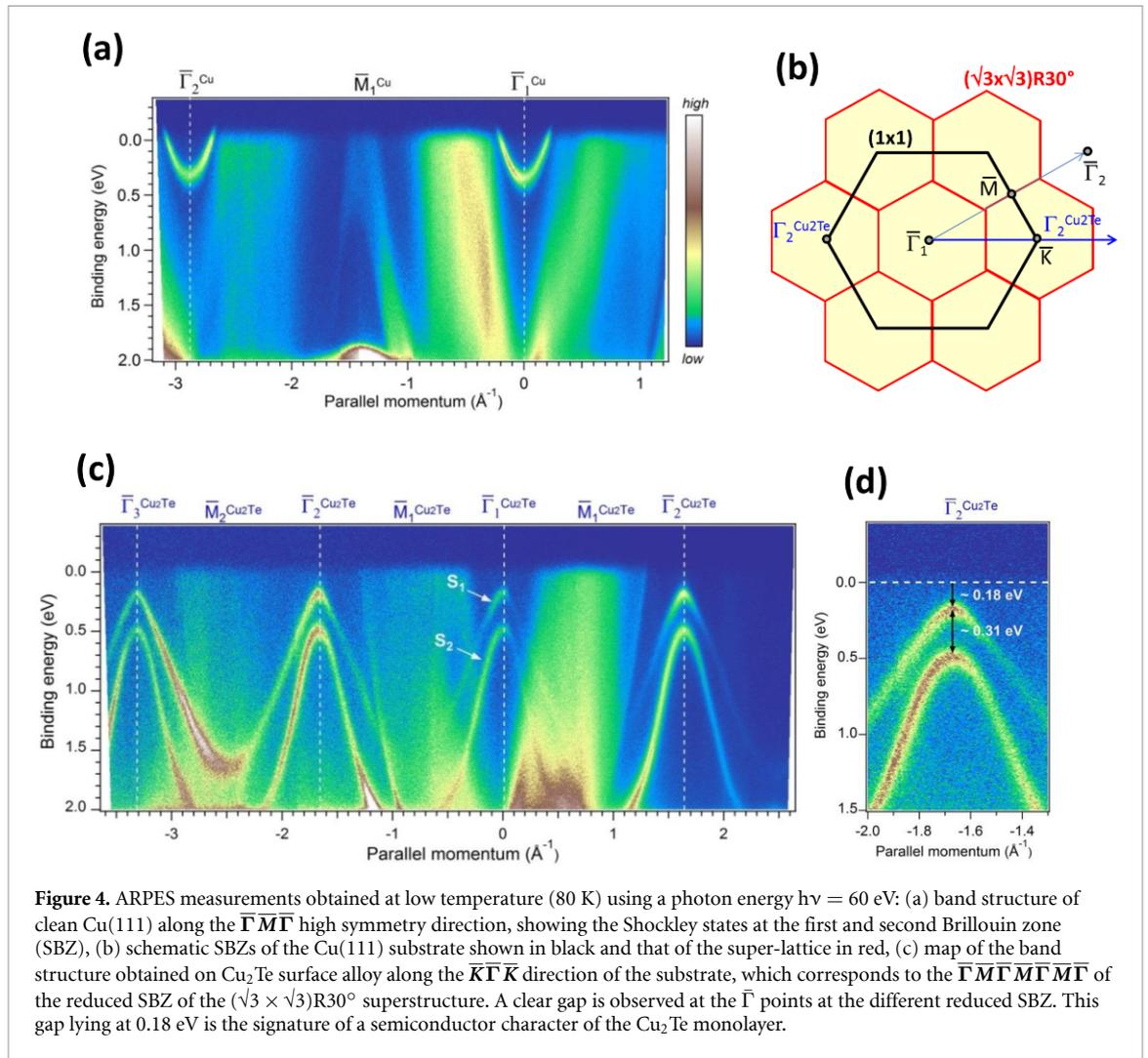
Figure 2. LEED diffraction patterns obtained on: (a) clean Cu(111) surface, (b) after deposition of Te followed by annealing at 500 °C. These images have been measured at energy of 80 eV from sample kept at low temperature (80 K). Dashed hexagonal guidelines highlight the reciprocal surface lattices of Cu(111) in green and of the Cu_2Te monolayer in blue, respectively.



which are positioned at binding energies of **42.02**, **40.60**, **41.60** and **40.18** eV, respectively. The 4d levels are characterized by spin-orbit coupling and therefore two sublevels $4d_{3/2}$ and $4d_{5/2}$ must be obtained from the same chemical environment. The difference in energy between the two peaks $\text{Te}4d_{3/2}$ and $\text{Te}4d_{5/2}$ is due to the spin-orbit interaction, which depends on the coupling between the electron's spin moment $s = 1/2$, and its orbital kinetic moment $l = 2$. The difference in energy related to this coupling is about **1.42** eV for Te. The two spectroscopic structures **A** and **B** correspond in fact to the levels associated with the so-called bulk Te atoms according to others studies [21]. That is, they come from a chemical environment characterized by Te-Te bonds. Doublet **C** and **D** is also associated with levels $\text{Te}4d_{3/2}$ and $\text{Te}4d_{5/2}$, but must come from another chemical environment characterized by the Te-Cu bond. The formation of such a chemical bond induced an energy shift of the 4d core level estimated to be **0.42** eV, which is in

agreement with the results given in ref [21]. This effect originates from a charge redistribution process between Cu and Te atoms. After annealing at 500°C , a significant change in the photoemission spectrum is observed. The two features associated with the Te-Te bond (indicated by **A** and **B**) have completely vanished. This result indicates that annealing causes complete desorption of the upper layers of Te. We only observe peaks associated with the Te-Cu bond, suggesting the presence of single alloy monolayer on the surface.

In figures 2(a), (b), we present the LEED patterns measured on the sample at different preparation conditions. On clean $\text{Cu}(111)$, one observes white dots corresponding to the diffraction spots and forming an hexagonal symmetry, which is a characteristic of the reciprocal lattice of the $\text{Cu}(111)$ surface. The diffraction spots are very sharp on low background, proving a clean and very orderly surface. After a chemical deposition of Te on this surface, no



LEED pattern was observed indicating that the surface became very messy and was certainly not sufficiently clean, which is consistent with the XPS data that showed the presence of oxygen and carbon on the surface, see supplementary information. To have an ordered surface it was necessary to anneal the sample and effectively after annealing at 500 °C clear diffraction spots appeared. We observe the reappearance of Cu(111) spots and in addition the presence of new spots that form a reduced hexagonal structure rotated by 30° compared to that of the Cu substrate. This is attributed to the existence of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ type reconstruction on the surface. According to the XPS results, at this temperature a surface alloy develops and the coverage rate of Te can be estimated to be 0.33 ml. This result is consistent with the literature [31] indicating of the presence of a single Cu_2Te monolayer on the Cu(111) surface. Moreover, this system exhibits high environmental stability when exposed to the ambient atmosphere and is resistant to high temperature, up to 500 °C (more detail is given in the supplementary information). The STM image of this alloy surface is reported in figure 3(a), where one can see two terraces separated by a step edge

covered by Cu_2Te alloy monolayer with a periodic hexagonal structure. We report in panels (b) and (c) atomic resolution STM images of Cu_2Te alloy and of clean Cu(111) surface, respectively. Figure 3(d) shows the line profiles measured along line A from image (b) and along line (B) from image (c), respectively. We obtain exactly a periodicity of ~ 0.45 nm which corresponds to $\sqrt{3}$ times the nearest-neighbor distance of Cu(111) surface (0.255 nm), in good agreement with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure shown in the LEED experiments. Figure 3(e) schematizes the corresponding structure and the arrangement of the Te atoms within the Cu(111) surface. It illustrates the positions of the Te atoms that substitute Cu atoms of the outermost plane of the surface. The Cu_2Te monolayer is formed over the entire surface of Cu(111), i.e. a monolayer with a diameter of 8 cm, and is homogeneously well-ordered on a large scale.

Maps of the band structure obtained by ARPES on clean Cu(111) surface and on Cu_2Te alloy monolayer on Cu(111) are displayed in figure 4. These maps, showing the photoelectron intensity as a function of binding energy and parallel momentum, were measured along high symmetry directions and over

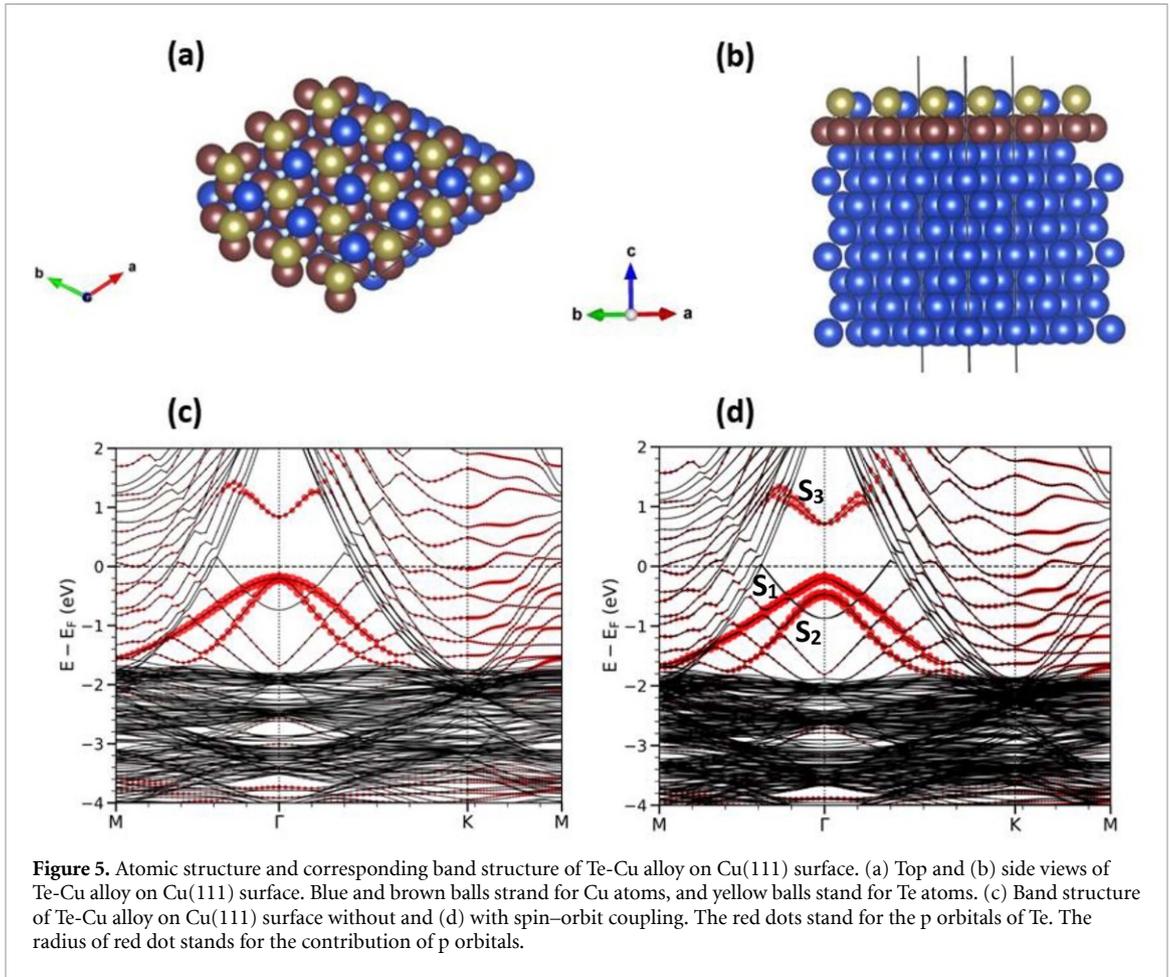


Figure 5. Atomic structure and corresponding band structure of Te-Cu alloy on Cu(111) surface. (a) Top and (b) side views of Te-Cu alloy on Cu(111) surface. Blue and brown balls stand for Cu atoms, and yellow balls stand for Te atoms. (c) Band structure of Te-Cu alloy on Cu(111) surface without and (d) with spin-orbit coupling. The red dots stand for the p orbitals of Te. The radius of red dot stands for the contribution of p orbitals.

large areas of the Surface Brillouin Zone (SBZ), as indicated in panel b of figure 4. First, on Cu(111) one observes the expected so-called Shockley state bands at the $\bar{\Gamma}$ -points of the first and second SBZs. The distance in k between the two bands of the Shockley states permits to determine the distance $|\bar{\Gamma}_1 - \bar{M}| = |\bar{\Gamma}_1 - \bar{\Gamma}_2|/2 = 1.43 \text{ \AA}^{-1}$, thus the distance $|\bar{\Gamma}_1 - \bar{K}| = |\bar{\Gamma}_1 - \bar{M}|/\cos 30^\circ = 1.65 \text{ \AA}^{-1}$. These values appear very consistent with the SBZ parameters of the Cu(111) surface. Besides the Shockley states one observes other bands, some of them are significantly broad. These bands are attributed to the copper sp -states. The formation of Cu_2Te monolayer on the surface creates a significant change in the band structure as it is shown in figure 4(c). The map of the band structure obtained on this surface was measured along the $\bar{\Gamma} - \bar{K}$ direction of the substrate, which is equivalent to the $\bar{\Gamma} - \bar{M}$ direction of the Cu_2Te super-cell. One observes that the Cu(111) Shockley states completely disappeared and two new bands are observed, S_1 and S_2 , characterized by binding energy minima at 0.18 and 0.49 eV, respectively and exhibit a parabolic-type dispersion with negative effective masses. These bands originate from the alloy monolayer and can be interpreted as the result of a hybridization process between the sp -states of Cu(111) and the electronic states of Te.

More interesting, we observe replicas of those bands around the $\bar{\Gamma}$ points of the second and even third reduced SBZs of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ super-structure. This effect usually called ‘back folding’ is a typical case for 2D electron systems [40]. In fact, in surface with commensurate superstructure, the size of the SBZ is significantly reduced and the electron dispersion is influenced by the super-lattice potential. This is immediately observed in the photoemission data. Moreover, the energy position of the S_1 band suggests a semiconductor character of the alloy monolayer and a band gap is obtained at the $\bar{\Gamma}$ -points at a binding energy of about 0.18 ± 0.01 eV, as shown in figure 4(c).

Figures 5(a) and (b) show the top and side views of Cu_2Te monolayer on Cu(111) substrate. There is one Te atom in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ supercell. After relaxation, Te is alloy with Cu in the topmost layer with buckling of 0.00836 \AA , see figure 5(b). Figures 5(c) and (d) show the band structures along $\bar{M} - \bar{\Gamma} - \bar{K} - \bar{M}$ path without and with spin-orbit coupling (SOC), respectively. The major difference between the two band structures is the top valence band splitting around $\bar{\Gamma}$ point. We can find that the band structure with SOC in figure 5(d) is consistent with ARPES in figure 4(c). This indicates that SOC is strong in such system and cannot be neglected in the

calculation. Moreover, the energy splitting of S_1 and S_2 states at $\bar{\Gamma}$ point is **0.27 eV** from figure 5(d), which is consistent with experimental value of **0.31 eV** from figure 4(c). From the p orbital projection for top most Te-Cu layer in figures 5(c) and (d), we can attribute S_1 and S_2 bands from p orbital of Te-Cu layer. Also, we can find a bandgap of **0.91 eV** from Te-Cu layer. Because of strong SOC effect of Te and inversion symmetry breaking of system, it is also expected Rashba spin splitting [24] around the $\bar{\Gamma}$ point. Figure 5(d) clearly shows Rashba splitting of conduction band edge (S_3) around $\bar{\Gamma}$ point, indicating possibility application of such system in spintronic applications.

3. Conclusion

In summary, we were able to form a Cu_2Te alloy monolayer on Cu(111) by means of chemical deposition method followed by high temperature annealing. Using the extremely surface-sensitive LEED and STM techniques, we have demonstrated the presence of a high-degree and long-range order on the surface. Both techniques indicated the existence of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction. The XPS data revealed the presence of a single chemical environment of the Te atoms, which is associated with the Cu-Te bond in the alloy monolayer. A binding energy shift of the Te core level is observed, which could be the signature of a significant charge transfer process accompanying the formation of the alloy. Detailed analysis by ARPES showed a radical change of the band structure. The Shockley state band of the Cu(111) surface disappeared after the formation of the Cu_2Te monolayer and new dispersive bands have developed, which are from p orbitals of Te-Cu layer based on first-principles calculations. Most importantly, these peculiar bands are back-folded under the influence of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure. Moreover, a band gap of 0.91 eV is obtained that proves the semiconductor character of the Cu_2Te monolayer. All these results represent a clear proof of new type of 2D material constituted by the Cu_2Te monolayer, which is potential for spintronic application.

4. Materials and methods

8 cm diameter circular shape Cu(111) substrate was prepared *in-situ* in UHV using several cycles of Ar + sputtering followed by annealing at high temperature ($P_{\text{Ar}+} = 5.10^{-5}$ mbar and $T = 500$ °C). Then, thick film of Te was obtained after deposition of drops of Na_2Te aqueous solution on the clean Cu(111) substrate. The prepared surface was afterwards well rinsed with Milli-Q water and dried under Argon flow before reintroducing into the UHV analysis chamber. This operation was carried out under Argon atmosphere around the load-lock of the experimental setup to minimize the exposure of the sample to air. To obtain ordered structure on the surface,

an annealing procedure was applied and a study as a function of the annealing temperature has been performed until obtaining the required and the most stable structure. The sample surface was first characterized by LEED and STM to analyze the crystalline structure and the atomic detail of the surface reconstructions. To probe the electronic structure, we have done photoemission measurements using the advantage of the synchrotron radiation. Both core level photoemission and ARPES of the band structure have been made. The Te-4d core levels have been measured to determine the chemical environment of the Te atoms on the surface. Afterwards, low energy electronic region in the vicinity to the Fermi level was analyzed in detail over a large part of the Surface Brillouin Zone.

The photoemission experiments were carried out using the synchrotron radiation at TEMPO beamline of Synchrotron SOLEIL, France. The XPS data were recorded by means of a Scienta SES 2002 electron spectrometer and the ARPES results were obtained by using a freshly installed MBS A-1 analyzer. The energy resolution of the core levels shown here is estimated at 50 meV, while it is of about 10 meV for the ARPES data. All the XPS spectra were calibrated with Au $4f_{7/2}$ at a binding energy of 84 eV on a clean Au substrate. The valence band data were taken at $h\nu = 60$ eV and calibrated with respect to the Fermi level. The LEED technique was used to probe the surface crystalline structure and to orient the sample along high-symmetry direction of the SBZ for the ARPES experiments. Low-temperature STM measurements were performed at ISMO-Orsay Institute (France) using Omicron high resolution STM system. The corresponding bias and tunnel current are indicated in the images, respectively. All the measurements were performed under ultra-high vacuum of 10^{-10} mbar and the STM images were calibrated due to possible thermal drift during the scanning.

To interpret the experimental electronic structure, we perform First-principles calculations by using Vienna *ab initio* simulation package (VASP) code [41] based on density functional theory (DFT). The functional of Perdew, Burke and Ernzerhof (PBE) and the projector augmented wave (PAW) method [42] together with van der Waals (vdW) interaction (DFT-D3) [43] were used. We also use a plane-wave cutoff energy of 375 eV, and a precise $6 \times 6 \times 1$ mesh for k-point sampling. Structural optimization is continued until the residual force has converged to less than 0.01 eV/Å. The spin-orbit coupling (SOC) effect was taken into consideration for band structure calculations because of the high atomic SOC strength of Te and due to the presence of surface alloy that induces a large in-plane potential gradient. The Cu substrate was modeled by using nine Cu layers. The topmost layer was covered by a Te layer in $\sqrt{3} \times \sqrt{3}$ supercell. A 20 Å thick vacuum spacing was used to

avoid interaction between neighboring slabs due to the periodic condition.

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