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Spectroscopic studies of CdTe(111) bulk and surface electronic structure

Jie Ren^{1,2,3}, Li Fu^{1†}, Guang Bian⁴, Manhong Wong^{2,3}, Tao Wang¹, Gangqiang Zha¹, Wanqi Jie¹, T. Miller^{2,3}, M. Z. Hasan⁴, and T.-C. Chiang^{2,3,5*}

¹State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China
²Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080, USA
³Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, 104 South Goodwin Avenue, Urbana, Illinois 61801-2902, USA
⁴Joseph Henry Laboratory and Department of Physics, Princeton University, Princeton, New Jersey 08544, USA
⁵Synchrotron Radiation Center, University of Wisconsin-Madison, 3731 Schneider

Drive, Stoughton, WI 53589, USA

^{*}Corresponding author: tcchiang@illinois.edu

[†]Corresponding author: fuli@nwpu.edu.cn

ABSTRACT

Cadmium telluride (CdTe) is a direct band gap semiconducting material with broad applications in optoelectronic devices. Here we report on a high-resolution angle-resolved photoemission (ARPES) study of CdTe(111) surfaces prepared by sputtering and annealing that show a (2x2) reconstruction as observed by electron diffraction. The ARPES maps along high-symmetry directions show prominent features with their intensities modulated by varying the incident photon energy, thus suggesting important matrix element effects associated with photoemission. The results are in excellent agreement with first-principles calculations of the bulk band structure and one-dimensional density of states. A prominent surface state is observed that exhibits a (2x2) periodicity in agreement with the symmetry of the surface reconstruction.

I. INTRODUCTION

CdTe is a prototypical material in the zinc-blende II-VI semiconductor family. It is widely used in various devices including γ - and x-ray spectrometers, solar cells, optoelectronic and optoacoustic modulators, and infrared windows [1-5]. It serves as an excellent substrate for epitaxial growth of other II-VI compounds such as $Hg_xCd_{1-x}Te$ with a tunable band gap [6-8], and as a key parent material for the realization of the quantum spin Hall phase [9-11]. Experimental measurements of the bulk band structure of CdTe have been reported in previous studies [12-20], but only for the (100) and (110) surfaces. High-resolution band mapping of CdTe(111) is thus far lacking for this important technological face. The (111) face of CdTe has a three-fold symmetry and is well suited as a substrate for the epitaxial growth of functional films with trigonal or hexagonal symmetry, which is often the preferred orientational symmetry for film growth. Apart from the structural constraints imposed by epitaxial conditions, the bulk and surface electronic structures of the specific substrate orientation can have strong influence on the overall electronic structure of epitaxial structures.

In this work we present high-resolution angle-resolved photoemission spectroscopy (ARPES) measurements of CdTe (1 1 1) samples. A number of different photon energies were employed in the measurements for a consistent and conclusive mapping of the bands. The results are in excellent agreement with first-principles band structure calculations. The comparison with theory allows us to identify the orbital characters of the observed bands. A surface state at a binding energy about 4 eV is

identified for the (2x2) reconstructed surface.

II. EXPERIMENTS

Crystals of CdTe adopt the cubic zincblende structure with a lattice constant of a = 6.48 Å at room temperature. The structure is the same as that of diamond, but with Cd and Te atoms occupying two different sites in the unit cell [Fig. 1(a)]. Each Cd (Te) is surrounded by four Te (Cd) atoms to form a tetrahedral bonding configuration. The structure lacks a spatial inversion center and is therefore non-centrosymmetric. The shaded plane in Fig. 1(a) is the (111) cutting plane.

Large single crystals of CdTe were grown by a modified Bridgman method [21]. Wafers oriented in the (111) direction were cut and mechanically polished to yield $10x10x1 \text{ mm}^3$ samples. Because of the lack of inversion symmetry, the (111) surface is different from the $(\bar{1}\bar{1}\bar{1})$ surface. The nominally Cd-terminated surface, also known as the (111)-A face, is distinguished by chemical etching from the nominally Te-terminated surface, also known as the (111)-A face. The in-plane orientation of the sample was determined by Laue diffraction. An example of the diffraction pattern is shown in Fig. 1(d). The horizontal direction in the picture is $\operatorname{along} \overline{\Gamma KM}'$, also the $[1\bar{1}\bar{2}]$ direction.

The ARPES experiments were performed in an ultrahigh vacuum chamber. The sample surface was cleaned in situ by sputtering for 10 minutes with 500 eV Ar ions, followed by annealing for 3-5 minutes at a temperature of 300°C. The process was

repeated several times. The surface structure and symmetry were checked by reflection high-energy-electron diffraction (RHEED). Two patterns shown in Figs. 1(c) and (d) correspond to horizontal diffraction along $[1\bar{1}0]$ and $[11\bar{2}]$, respectively. The sharpness of the diffraction spots indicated a well-ordered surface. Half-order spots are evident in both pictures and are consistent with a (2x2) surface reconstruction.

Photoemission measurements were performed at the Synchrotron Radiation Center (SRC) of the University of Wisconsin-Madison. The chemical composition of the surface was probed by photoemission from the core levels. Fig. 1(e) shows a spectrum taken with 80 eV photons, and the Cd 4*d* and Te 4*p* peaks are indicated. The intensity ratio between the two core levels is 0.38, which is consistent with prior studies of CdTe (111)-A prepared by molecular beam epitaxy [23]. ARPES measurements were performed with an energy resolution of about 15 meV. The bulk and surface Brillouin zones (BBZ and SBZ) are shown in Fig. 2(a). The k_x , k_y , and k_z axes are chosen to be along $[11\overline{2}]$, $[1\overline{10}]$, and [111], respectively. The X and L points in the BBZ are projected onto the \overline{M} points of the (111) SBZ. The (1x1) unreconstructed (dashed lines) and the (2x2) reconstructed (solid lines) SBZ are depicted in Fig. 2(b).

III. RESULTS AND DISCUSSION

Band structure mapping were performed along $\overline{\Gamma M}$ and $\overline{\Gamma KM}$ ' of the SBZ. These two directions are oriented within the planes $\Gamma X\Gamma$ '-*LL'L*" and $\Gamma KL'$ -*LK'X*' of the BBZ which are marked by red and blue shaded quadrangles, respectively, in Fig. 2(a). Figs. 3(a) and 4(a) show ARPES maps measured with 25 eV photons along the $\overline{\Gamma M}$ and $\overline{\Gamma K M}$ ' directions, respectively. Figs. 3(b) and 4(b) show the second derivatives along the energy axis of the same data for an enhanced view of the band features. The valence band maximum is located at 0.75 eV below the Fermi level, which is consistent with the high electrical resistivity of our CdTe wafers.

For comparison with the experiment, first-principles electronic band structure calculations were performed with a plane-wave basis set and HGH-type pseudopotentials [24] using the ABINIT algorithm based on the local density approximation including spin-orbit coupling [25, 26]. The projected bulk band structure within the $\Gamma X \Gamma' - LL'L''$ plane [red shaded plane in Fig. 2(a), projected onto the $\overline{\Gamma M}$ direction] is shown in Fig.3 (c). The "edge" bands along $\Gamma X \Gamma$ ' and LL'L" are plotted as blue and yellow curves, respectively. Such edge bands often correspond to prominent ARPES features because of a high density of states [27], but not always. Likewise, prominent ARPES features are not necessarily derived from edge bands, as high density of state features can happen elsewhere. There are two sets of bands sit close to the Fermi levels labeled as Γ_7 and Γ_8 in terms of the representations of the point group at Γ (marked with the red arrows). These two bands are hole-like, derived from the Te 5p orbitals, and they play dominant roles in the electronic and optical properties of CdTe. The Γ_8 band splits into a heavy-hole band Γ_8^+ and a light-hole band Γ_8 -. Likewise, the calculated projected bulk band results for the $\Gamma KL' - LK' X'$ plane [blue shaded plane in Fig. 2(a), projected onto the $\overline{\Gamma KM'}$ direction] are presented in Fig. 4(c). The edge bands are indicated by blue and yellow curves.

Band mapping discussed above assumes that the photoemission is dominated by indirect transitions, and no direct transition peaks appear in the region of interest. Direct transition peaks disperse with photon energy and can be very intense. By contrast, indirect transitions reflect the projected band structure and do not vary in energy positions as a function of photon energy. To verify that our analysis is not affected by direct transitions, we have repeated ARPES mapping measurements for several different photon energies. A few data sets taken at photon energies of 19, 25, and 30 eV are shown in the top panels in Figs. 5 and 6 for emission directions within the $\Gamma X \Gamma' - LL'L''$ plane and the $\Gamma K L' - LK'X'$ plane, respectively. The corresponding second-derivative maps are presented in the lower panels, Figs. 5(d)-(f) and 6(d)-(f). All major features show little energy dispersion, but the photoemission intensities vary substantially as a function of photon energy. Note that second derivative maps generally highlight the band edge positions, but such maps could be somewhat affected by background emission or tails of neighboring peaks. Data taken at different photon energies can help clarify these occurrences. The results reveal that the valence bands near the gap are best revealed at 25 eV [Figs. 5(b) and (e) and Figs. 6(b) and (e)]. The strong intensity variations as a function of photon energy are not unexpected as the photoemission cross sections can vary differently for different bands.

A better comparison between theory and experiment is to plot the one-dimensional density of states as a function of the in-plane momentum. We defined a rectangular mesh with 301 points for in-plane momentum along either $\overline{\Gamma M}$ or $\overline{\Gamma K M}$ ' and 250 points in energy ranging from -5.35 eV to -0.75 eV, and we counted how many

projected bulk states fell into each mesh grid. The resulting counts, shown in Figs. 3(d) and 4(d), are proportional to the density of states and should resemble the ARPES maps. A comparison with the data indeed reveals an excellent agreement in terms of the band dispersion relations, and to some extent, the relative intensities.

However, some prominent features in the data, labeled in Figs. 5 and 6 by S, are not reproduced by the density of states. The dispersion relations of these features do not depend on photon energy, although the intensities vary. These are logically assigned to be surface states (or resonances) as they do not correspond to any known bulk electronic features. To highlight these states, Figs. 7(a) and (b) show the photoemission energy distribution curves obtained at the $\overline{\Gamma}$ point for photon energies of 19, 25, and, 30 eV for the two scan directions. Feature S at -4.3 eV is the dominant one under some experimental conditions. Such surface states are not unfamiliar; InAs, InSb, and ZnSe are known to show similar surface states [28, 29]. It is important to note that the dispersion of state S is consistent with the (2x2)periodicity. In other words, The same parabolic dispersion near $\overline{\Gamma}$ is repeated at \overline{M} , which becomes the zone center after folding the SBZ. This band folding effect is quite evident in Fig. 5, but no so in Fig. 6 as the feature is relatively weak. Bulk bands are not expected to fold under surface reconstruction. Thus, the observed periodicity is strong evidence for the surface nature of state S.

IV. CONCLUSIONS

The electronic structure of CdTe(111)-A face with a (2x2) reconstruction has been

studied by high-resolution ARPES along major high symmetry directions. A number of photon energies are employed to ensure that the ARPES maps correspond to density of states features, and no strong direct transitions are present. The results are compared to first-principles calculations of the bulk band structure and the density of states, and there is overall good agreement. The intensity variations observed in the ARPES maps as a function of photon energy can be attributed to matrix element (or cross section) effects. A prominent surface state at ~4 eV binding energy is observed and identified by comparison with the results from bulk band calculations. The observed dispersion of this state shows a (2x2) periodicity, which provides strong evidence for its surface character. Our results provide a knowledge base relevant to using this surface as a substrate platform for building up device structures.

Acknowledgments

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Figures

FIG. 1 (color online). (a) Crystal structure and the (111) plane in CdTe. (b) Laue diffraction pattern of the CdTe(111) crystal. (c) and (d) RHEED patterns with horizontal diffraction along $[1\bar{1}0]$ and $[11\bar{2}]$, respectively. (e) Photoemission from core levels of CdTe measured with 80 eV photons.



FIG. 2 (color online). (a) Bulk Brillouin zone (BBZ) and (111) surface Brillouin (SBZ) zone with high symmetry points indicated. (b) The (1x1) unreconstructed (dashed line) and the (2x2) reconstructed (solid lines) SBZ.



FIG. 3 (color online). (a) APRES map taken along $\overline{\Gamma M}$ in the (111) SBZ measured with 25 eV photons. (b) Second derivative map of (a). (c) Calculated projected bulk bands along $\overline{\Gamma M}$. (d) Calculated one-dimensional density of states.



FIG. 4 (color online). (a) APRES map taken along $\overline{\Gamma K M}$ ' in the (111) SBZ measured with 25 eV photons. \overline{M} ' is in the second BZ. (b) Second derivative map of (a). (c) Calculated projected bulk bands along $\overline{\Gamma K M}$ '. (d) Calculated one-dimensional density of states.



FIG. 5 (color online). ARPES maps taken along $\overline{\Gamma M}$ in the (111) SBZ measured with (a) 19 eV, (b) 25 eV, and (c) 30 eV photons. (d)-(f) The corresponding second derivative maps.



FIG. 6 (color online). ARPES maps taken along $\overline{\Gamma K M}$ ' in the (111) SBZ measured with (a) 19 eV, (b) 25 eV, and (c) 30 eV photons. (d)-(f) The corresponding second derivative maps.



FIG. 7 (color online). Photoemission energy distribution curves taken at the $\overline{\Gamma}$ point with photon energies of 19, 25, and, 30 eV and with the photoemission analyzer aligned along (a) $\overline{\Gamma M}$ and (b) $\overline{\Gamma K M}$ ', respectively. The surface state S is indicated.

