

Atomic and Electronic Structures of  $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}(110)$  Surface \*

ZHA Gang-Qiang(查钢强)<sup>1\*\*</sup>, JIE Wan-Qi(介万奇)<sup>1</sup>, ZHANG Wen-Hua(张文华)<sup>2</sup>,  
LI Qiang(李强)<sup>1</sup>, XU Fa-Qiang(徐法强)<sup>2</sup>

<sup>1</sup>State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072

<sup>2</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029

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X-Ray diffraction is used to analyse the lattice structure of  $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$  (CZT), and the lattice constant is measured to be 0.647 nm. The atomic structure of the clean CZT(110) surface obtained by  $\text{Ar}^+$  etching in vacuum is observed by low-energy electron diffraction, where no surface reconstruction is discovered. Angle-resolved photoemission spectroscopy was used to characterize the surface state of the clean CZT (110) surface, by which we find a 1.5-eV-wide surface band with the peak at 0.9 eV below the Fermi energy containing about  $6.9 \times 10^{14}$  electrons/cm<sup>2</sup>, approximately one electron per surface atom.

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In recent years, there has been increasing interest in the II-VI compound semiconductor  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  (CZT) because of its excellent photoelectric properties. Since the lattice constants of CZT change with the  $x$  values matching with that of  $\text{Hg}_{1-y}\text{Cd}_y\text{Te}$ , CZT is the most suitable substrate material for  $\text{Hg}_{1-y}\text{Cd}_y\text{Te}$  epitaxial growth. Furthermore, CZT has been extensively adopted to make x-ray and  $\gamma$ -ray detectors, photoelectricity modulators, solar cells, and laser windows, etc.<sup>[1,2]</sup>

The surface of CZT is a special area with features different from the bulk material. Taken as substrates, the atomic structure of the CZT surface will affect the epitaxial growth. As a detector material, the electronic structure will be a critical factor to determine the equipment performance, especially the leakage current of detectors and the ohmic contact of electrodes.<sup>[3,4]</sup> However, the surface of CZT has not been analysed in detail up to date. In this Letter, we present an investigation of atomic and electronic structure of the CZT (110) surface.

CZT has a zinc-blende-structure like CdTe with a fraction of Cd substituted by Zn as shown in Fig. 1, where every atom is surrounded by four heteroatoms. A Cd (Zn) atom and the four most-near Te atoms are combined by covalent bonds.<sup>[5]</sup> If the Cd (Zn) atom locates in the centre of the regular tetrahedron, the four Te atoms will locate at the vertexes of the regular tetrahedron. The orientations and angles of these covalent bonds are the same as those in the diamond structure.

From  $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$  powder milled from single crystal grown by the Bridgman method, we obtained the x-ray diffraction pattern of CZT with PANalytical X'Pert Pro, as shown in Fig. 2.

Various interplanar spacings obtained from the pattern of x-ray diffraction using the Bragg formula  $2d \sin \theta = n\lambda$  are listed in Table 1. The crystal lattice of CZT was determined to be 0.6468 nm by using the formula  $a = \sqrt{3}d_{111}$ , where  $d_{111}$  is the interplanar spacing of (111) planes. Our result agrees with the linearity rule presented by van Scyoc *et al.*<sup>[6]</sup>

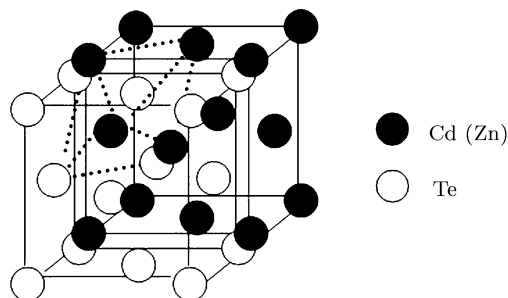


Fig. 1. The lattice structure of CZT.

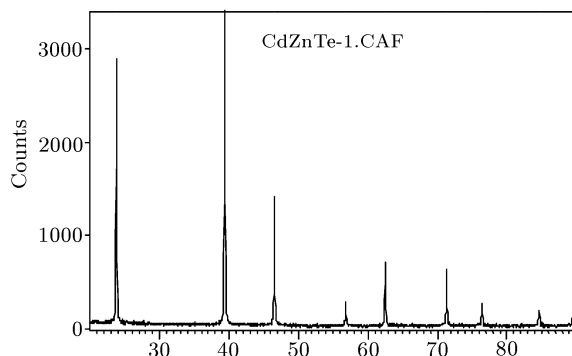


Fig. 2. X-ray diffraction pattern for  $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$  powder milled from single crystal.

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\*\* Email: zha\_gq@163.com

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Table 1. Interplanar spacings of various planes.

Miller indices	$2\theta$ (deg)	$d$ -spacing (nm)
(111)	23.8065	0.373461
(220)	39.3390	0.228851
(311)	46.4837	0.195204
(400)	56.8798	0.161747
(331)	62.5362	0.148408

The spacing of (111) planes is the largest one, therefore the length of the covalent bond is the longest. Because the atoms all are Cd (Zn) or Te in (111) planes, the (111) planes are the dipole ones where the binding energy including the Coulomb force interaction decided by the effective charges of Te and Cd (Zn) is quite strong. While (110) planes of CZT are the nonpolar ones where the number of Cd (Zn) atoms is the same as Te, and the Coulomb force between Cd (Zn) and Te are counteracted. Therefore, the CZT(110) planes have lower sum-up binding energy, and are easier to be split than (111) planes.

We cut the CZT (110) wafers from CZT ingot grown by the Bridgman method. The sample was pre-treated with polishing mechanically and etching uniformly by 5 vol% Br–MeOH solution, and followed by a rinse in de-ionized water. To dislodge oxygen and other impurity atoms adsorbed on the surface, the

sample was etched for 20 min by Ar<sup>+</sup> with different ionization voltages (1.5, 1.2, 1.0, 0.8, 0.6 kV) and annealed in-situ in a vacuum preparation chamber. The pattern of low-energy electron diffraction (LEED) of CZT (110) surface is shown in Fig. 3.

The energy of incident electron  $E_e$  is 113 eV, and the wavelength is<sup>[7]</sup>

$$\lambda = \frac{1.23}{\sqrt{E_e}} = 0.116 \text{ nm}. \tag{1}$$

According to the formula

$$a = \frac{\lambda L}{R}, \tag{2}$$

where  $L$  is the effective length of the diffractometer,  $a$  is the spacing of lattice planes,  $R$  is the distance of diffraction spot,  $R_1$  is measured to be 1.07 cm, and  $R_2$  is measured to be 1.51 cm, so the lattice constant is determined to be 0.650 nm. From this result, we know that the bond length of CZT (110) surface has changed slightly, but the surface atoms are not reconstructed. This result agrees well with the data reported in Refs. [8–10]. Figure 4 shows the geometrical structure of the ideal terminated CZT (110) surface.

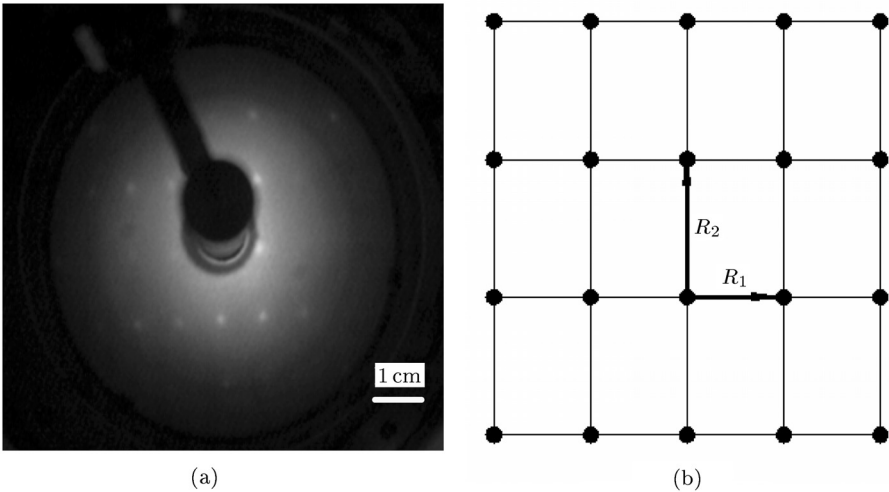


Fig. 3. LEED photograph of the Cd<sub>0.96</sub>Zn<sub>0.04</sub>Te (110) surface: (a) the pattern of LEED, (b) the labelled pattern of LEED.

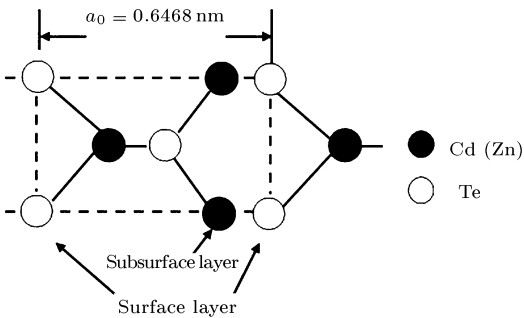
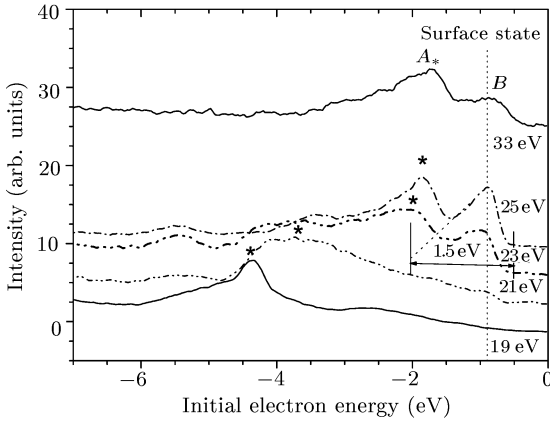


Fig. 4. Schematic of the atomic structure of CZT(110) surface.

The surface-state of the ideal clean CZT (110) surface was measured by angle-resolved photoemission spectroscope VGX900 in an ultrahigh-vacuum chamber ( $1 \times 10^{-10}$  Torr). The experiments were carried out at the surface physics station of the National Synchrotron Radiation Laboratory in Hefei, China. We changed the photon energy from 19 eV to 33 eV and kept the incidence angle to be 15°. The energy distribution curves (EDCs) obtained from the clean CZT (110) surface are shown in Fig.5. Peak A, which varies with photon energy, is from bulk-state direct ( $k$ -conservation) transitions. The CZT is a direct-gap

semiconductor, and the final-state energy of transition electrons approaches the Fermi energy with the increase of the photon energy. At 0.9 eV below the Fermi energy, peak *B*, which does not vary with photon energy, indicates to be the surface state.<sup>[11,12]</sup>



**Fig. 5.** Electron energy-distribution curves recorded at normal emission for various photo energies from CZT (110) surface. The angle of incidence is  $\alpha = 15^\circ$ .

There are four valence-band electrons distributed over an energy range of 10.8 eV for each of the  $2.94 \times 10^{22} \text{ cm}^{-3}$  bulk atoms. At 25 eV, the valence-band part of the EDC is 5.5 eV, and the ratio of surface-to-bulk emission is 0.096.<sup>[13]</sup> Provided that matrix elements are the same for surface and bulk transitions, the electron escape depth is estimated to be 1.2 nm.<sup>[13]</sup> We obtain<sup>[14]</sup>

$$n_s = 4 \times (2.94 \times 10^{22}) \times (5.5/10.8) \times 0.096 \times (1.2 \times 10^{-9}) \approx 6.9 \times 10^{14} \text{ electrons/cm}^2 \quad (3)$$

for the surface electron density. The result agrees the simple model of the CZT (110) cleavage plane in which one filled and one empty surface state are taken for each of the  $6.7 \times 10^{14} \text{ cm}^{-2}$  broken bonds gives charge. We find that the two-dimensional first-order band con-

taining  $6.9 \times 10^{14} \text{ electrons/cm}^2$  is 1.5 eV, which agrees well with that of Wanger and Spicer's observation on silicon.<sup>[15]</sup>

In conclusion, we have investigated the lattice structure of CZT by x-ray diffraction, and the lattice constant is determined to be 0.6468 nm. The binding energy of nonpolar CZT (110) which determines the plane to be a cleavage one is the lowest. Using LEED, we observe the atomic structure of the clean CZT (110) surface obtained by  $\text{Ar}^+$  etching in vacuum. The surface reconstruction is not found. We have found a 1.5-eV-wide surface band with a peak at 0.9 eV below the Fermi energy containing about  $6.9 \times 10^{14} \text{ electrons/cm}^2$ , i.e. approximately one electron per surface atom.

## References

- [1] Li G Q et al 2003 *Chin. Phys. Lett.* **20** 1600
- [2] Li G Q et al 2004 *Chin. Phys. Lett.* **21** 367
- [3] Wang L J et al 1999 *J. Functional Mater. Devices* **5** 91 (in Chinese)
- [4] Yoon H, van Scyoc J M and Goorsky M S 1997 *J. Electron. Mater.* **26** 529
- [5] Liu E K, Zhu B S and Luo J S 1994 *Semiconductor Physics* (Beijing: National Defence Industry) p 195 (in Chinese)
- [6] van Scyoc J M, Lund J C, Morse D H and Antolak A J 1996 *J. Electron. Mater.* **25** 1324
- [7] Zhang H, Liu S Y and Zhang G Y 2004 *Quantum-Mechanical Description of Chemical Adsorption* (Beijing: Science) (in Chinese)
- [8] Zhang H F, Li Y P and Fang R C 1995 *Acta Phys. Sin.* **44** 280 (in Chinese)
- [9] Jia Y, Fan X and Ma B X 1997 *Acta Phys. Sin.* **46** 1999 (in Chinese)
- [10] Kendelewicz T et al 1995 *Phys. Rev. B* **51** 10774
- [11] Qu H, Nilsson P O and Kanski J 1989 *Phys. Rev. B* **39** 5276
- [12] Magnusson K O and Flodstrom S A 1988 *Phys. Rev. B* **38** 5384
- [13] Wagner L F and Spicer W E 1972 *Phys. Rev. Lett.* **28** 1381
- [14] Eastman D E and Grobman W D 1972 *Phys. Rev. Lett.* **28** 1378
- [15] Wagner L F and Spicer W E 1972 *Bull. Am. Phys. Soc.* **17** 134