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Electrical properties and phase transition of CdTe under high pressure

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Abstract

In situ electrical resistivity measurement of powdered CdTe has been performed under high pressure using a diamond anvil cell equipped with a microcircuit. With the pressure increasing from 2.7 to 3.8 GPa, a sharp decrease in resistivity of over three orders of magnitude is observed. This is due to the appearance of rock-salt CdTe. At about 6.5 GPa a resistivity inflexion appears which has not been reported before. It is caused by the obvious decrease of band gap in certain symmetry directions of the Brillouin zone of rock-salt CdTe. From 6.5 to 10 GPa, the descending trend of the resistivity turns gently. At about 10 GPa, a cusp corresponding to the transition to the *Cmcm* phase is distinguished. Between 10 and 38 GPa, three leap points have been detected at 15.5 GPa, 22.2 GPa and 30 GPa, which imply abundant electronic phase transitions of CdTe. Resistivity measurements were also performed in a wide temperature range from liquid nitrogen temperature (77 K) to 450 K. It is proved that rock-salt CdTe does not show a typical metallic transport character. In the pressure range of 6.0–7.0 GPa, CdTe has a band gap of about 445 meV. The relationship of $\ln \rho$ to $1/T$ is also fitted linearly to yield the ionization energy of impurities at different pressures.

1. Introduction

Cadmium telluride (CdTe) is a typical compound of chalcogenides. Because of wide application in technology, its many properties have been the subject of high pressure studies. CdTe is a direct-gap semiconductor with a band gap of about 1.5 eV [1] and occurs in a zincblende structure under atmospheric conditions. Under pressure CdTe undergoes a series of structural phase transitions and the basic sequence has been well documented, with the zincblende to rock-salt transition occurring at 3.5 GPa [2–4] and the rock-salt to β -tin transition at about 10 GPa [3, 5]. A further transition, to an orthorhombic structure with space group

Pmm2, has been reported at about 12 GPa [6]. However, using an angle-dispersive diffraction technique and synchrotron radiation, Nelmes *et al* [7–9] showed that in fact CdTe has two closely spaced transitions near 3.5 GPa: first zinc-blende to cinnabar and then cinnabar to rock-salt. The triple point of three solid phases, namely zinc-blende, cinnabar and rock-salt, was determined by energy dispersive x-ray diffraction by Balchan *et al* [10] and Martinez-Garcia *et al* [11]. They found that the cinnabar phase appeared only in a very narrow pressure range and could be isolated only during unloading. In order to investigate the structural phase transitions in CdTe above 5 GPa, Nelmes *et al* [7–9] performed detailed angle-dispersive diffraction measurements on CdTe to 28 GPa. They found that at 10 GPa the rock-salt phase of CdTe transformed continuously into a *Cmcm* structure that remained stable to at least 28 GPa. The sequence of structural phase transitions given by theory is in agreement with that observed in experiments [12]. However, there exists debate about the electrical characters of these high pressure phases: early in 1962, Samara *et al* [13] observed that at 85–90 kbar the resistivity of CdTe dropped very sharply to about $10^{-4} \Omega \text{ cm}$; Minomura *et al* [7] measured the temperature coefficient of resistance of CdTe at 130 kbar and showed that CdTe was indeed metallic in the sense that the resistance increased with the temperature; Gonzalez *et al* [8] measured the optical absorption edge of CdTe and found that the rock-salt CdTe was not metallic but showed a broad absorption edge with onset near 0.08 eV at 6.8 GPa; Güder *et al* [9] calculated the electronic structures of rock-salt CdTe at different pressures and showed that rock-salt CdTe was a semi-metal. Because the reflectance experiments in the mid-infrared range did not indicate metallic behavior, they attributed the semi-metallic character of rock-salt CdTe to the limitations of DFT-LDA methods and assumed that rock-salt CdTe was a low gap semiconductor. And at 10 GPa the shrinking and disappearance of the transparency region was interpreted as the occurrence of a phase transition to the *Cmcm* metallic phase. In addition, a Hall effect experiment was conducted by Segura *et al* [14] and they thought it was more reasonable that the rock-salt CdTe phase was semi-metallic.

In fact, the definitive way to establish whether the high pressure phase is metallic is to study the resistivity and its temperature dependence, but because of the unsolved contact resistance problem, Samara *et al* [13] just gave the change trend of the resistance with pressure, and the resistivity of the high pressure phase was also just estimated based on sample geometry and on comparison with metallic samples of known electrical resistivity. Furthermore, no experiment was carried out to investigate the transport mechanism. In the experiments of Minomura *et al* [7], because of the limited temperature range, the transport mechanism cannot be comprehensively reflected.

In present study, an integrated microcircuit, which can avoid the effects of contact resistance and the deformation of the electrodes, was used to investigate the pressure dependence of the electrical resistivity of CdTe at room temperature. In order to study the transport mechanism of high pressure phases of CdTe (semiconductor, metal or semi-metal), the electrical resistivity experiments were also conducted in the temperature range from liquid nitrogen (77 K) to 450 K and resolved the doubt about the transport mechanism of rock-salt CdTe. By fitting the curve of the temperature dependence of resistivity, we have obtained information about the band gap of CdTe and the activation energy of impurities in CdTe.

2. Experimental detail

A Mao-Bell type diamond anvil cell (DAC) was utilized to generate high pressure. The diamond anvils had a culet of $500 \mu\text{m}$ in diameter. We chose molybdenum as the electrode material and alumina as the insulator and protective material in the resistivity measurement for the reasons discussed in [15]. A radio frequency magnetron sputtering system was used to

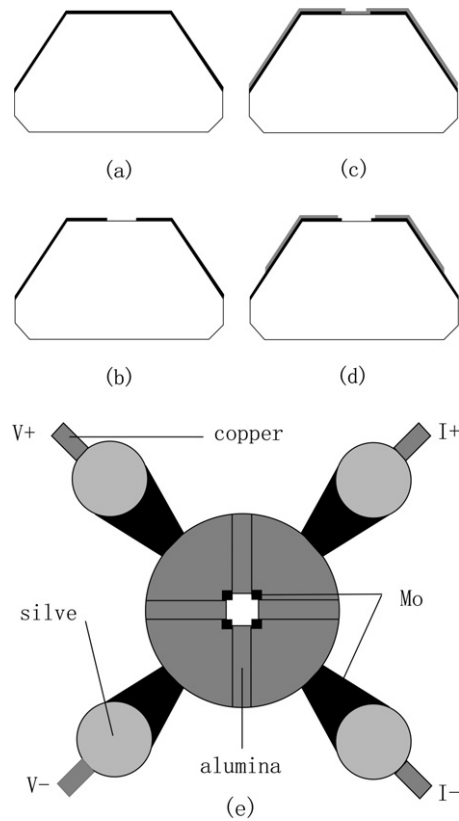


Figure 1. Manufacturing process and configuration of a microcircuit on a diamond anvil. (a) 300 nm Mo thin film sputtered onto the diamond anvil. (b) Mo thin film patterned into the designed circuit. (c) Sputtered alumina layer. (d) Some parts of alumina chemically removed to expose the Mo electrodes. (e) The configuration of a complete microcircuit, V_+ , V_- , I_+ and I_- represent the positive and negative voltage and current ends.

Table 1. The experimental parameters of the sputtering film.

Item	Experimental parameter
Sputtering technology	Radio frequency magnetron sputtering
Working gas	Pure Ar and pure oxygen gases
Working pressure	1.0 Pa
Sputtering power	90 W (Mo), 110 W (alumina)
Distance of the underlay	5 cm
Temperature of the underlay	600 K
Sputtering time	4 min (Mo), 3 h (alumina)

sputter the film on our diamond anvil and the experimental parameters are shown in table 1. A photolithographic technique was used to pattern the molybdenum and alumina film. The fabrication process for the microcircuit is shown in figures 1(a)–(d). The diamond anvil was first cleaned chemically. Then a 0.3 μm -thick molybdenum film was deposited on it. In order to enhance the adhesion of the molybdenum film, the anvil was heated to 600 K during the sputtering process. Then the film was patterned into the van der Pauw type circuit as shown

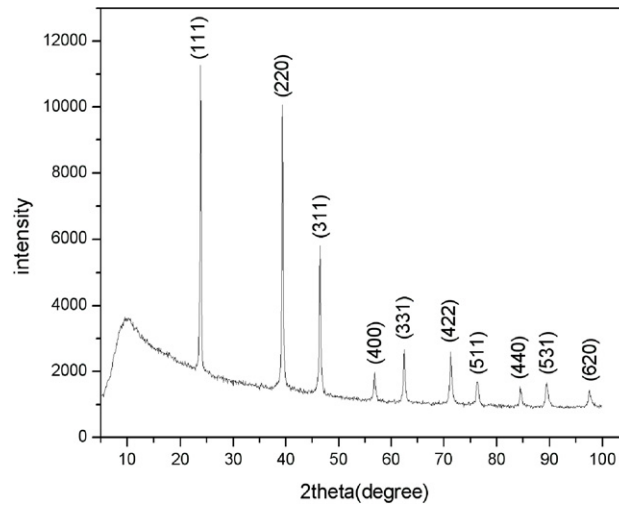


Figure 2. The x-ray diffraction spectrum of CdTe at ambient conditions.

in figure 1(b). The four-section electrodes were used as current and voltage ends, respectively, as marked in figure 1(e). The microcircuit and diamond culet were then encapsulated with a $2\ \mu\text{m}$ -thick alumina protective layer, as shown in figure 1(c). Finally part of the alumina layer was removed by calcium phosphate solution, as shown in figure 1(d). A detection window with a size of $120 \times 120\ \mu\text{m}^2$ was created in the center of the diamond culet and the electrode ends were exposed, as shown in figure 1(e). A stainless steel gasket was pre-indented, and then a $200\ \mu\text{m}$ diameter hole was drilled at the center of the indented mark as the sample chamber. For better insulation, a $2\ \mu\text{m}$ -thick alumina film was also deposited onto the drilled gasket. A ruby crystal of $5\ \mu\text{m}$ was placed in the centre of the sample chamber as the pressure calibrator. To avoid introducing additional electrical resistivity no pressure medium was used. During the whole pressing course, the fluorescence spectrum of ruby showed two separate peaks at all times, indicating that the pressure gradient was less. The sample was powdered CdTe bought from Alfa Aesar Co. with a purity of 99.999%. The original structure of the sample was confirmed to be the zinc-blende structure according to the x-ray diffraction spectrum at ambient conditions shown in figure 2.

In the experiments to measure electrical resistivity, a constant direct current I_1 was introduced from I_+ to I_- and the voltage drop, obtained with a Hewlett Packard 3458 A multimeter, between V_+ and V_- was recorded as V_1 . Likewise, a constant direct current I_2 was introduced from I_+ to V_+ , and the voltage drop between I_- and V_- was recorded as V_2 . The electrical resistivity was calculated through van der Pauw's equation

$$\exp(-\pi LR_1/\rho) + \exp(-\pi LR_2/\rho) = 1 \quad (1)$$

where $R_1 = V_1/I_1$ and $R_2 = V_2/I_2$ represent the resistance, ρ and L represent the resistivity and thickness of the sample, respectively. The pressure-induced change in thickness of the sample was determined by measuring the change in distance of the back facet of two diamond anvils using a micrometer and the error introduced by the anvil deformation was taken into account in our measurement. The thickness difference between compression and decompression was considered to reflect the change in anvil thickness at high pressure and was used in the sample thickness correction. The overall maximum relative error of resistivity in our experiment was estimated to be less than 10%.

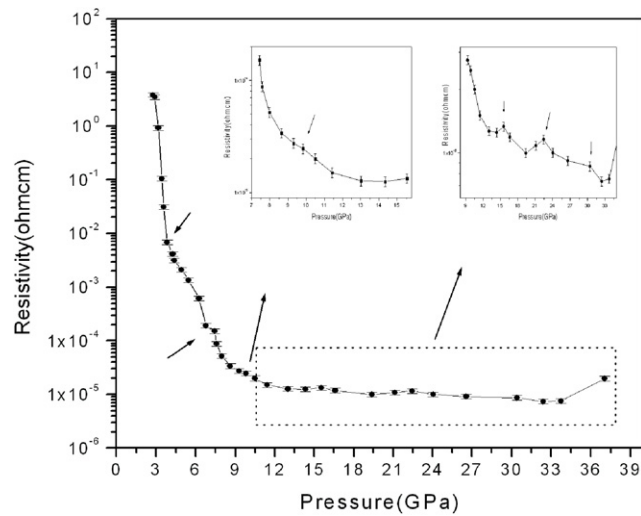


Figure 3. The pressure dependence of the electrical resistivity of CdTe at room temperature. The arrowheads point out the electrical resistivity anomalies. Inset: enlargements of near 10 GPa and after 10 GPa.

3. Results and discussion

3.1. The pressure dependence of the electrical resistivity at room temperature

Figure 3 shows the pressure dependence of the electrical resistivity of powder CdTe at room temperature. It can be seen that when the pressure increases from 2.7 to 3.8 GPa the resistivity drops sharply over three orders of magnitude, which is similar to the result of Samara *et al* [13]. This is due to the appearance of rock-salt CdTe at 3.8 GPa [5, 16, 17]. Between 3.5 and 3.8 GPa, the cinnabar CdTe remains stable, and there is no abnormal resistivity change observed. Just in this pressure range the pressure was difficult to raise, due to the bigger compressibility of the cinnabar phase [16]. Above 3.8 GPa, the change in resistivity with increasing pressure is obviously slower than that before 3.8 GPa, which is quite different from that reported by Samara *et al* [13]. At about 6.5 GPa an inflexion in resistivity occurs which was not observed by Samara *et al* [13]. From 6.5 to 10 GPa, the descending trend of resistivity becomes much slower. Since in the pressure range from 3.8 to 10 GPa no structural phase transition was reported [17], the inflexion observed at about 6.5 GPa cannot be due to the structural phase transition in CdTe. When the pressure reaches 10 GPa, a cusp is discerned at which rock-salt CdTe transformed to the phase with the *Cmcm* space group, which was believed to be the metallic phase of CdTe [13, 9]. However, a clear difference from the report by Samara *et al* [13] is that the change is sluggish not abrupt. Between 10 and 38 GPa, three leap points at 15, 22.2 and 30 GPa can be seen, which have not been reported before [13]. Because the *Cmcm* remains stable up to at least 28 GPa [17], these leaps may be caused by electronic phase transitions.

3.2. The temperature dependence of the electrical resistivity at different pressures

The resistivity measurement was also performed at the temperature ranging from liquid nitrogen temperature (77 K) to 450 K to study the transport mechanism of high pressure phases of CdTe. The temperature dependence of the electrical resistivity in the temperature range from 77 to 280 K is shown in figure 4(a). It can be seen that the resistivity always decreases with the

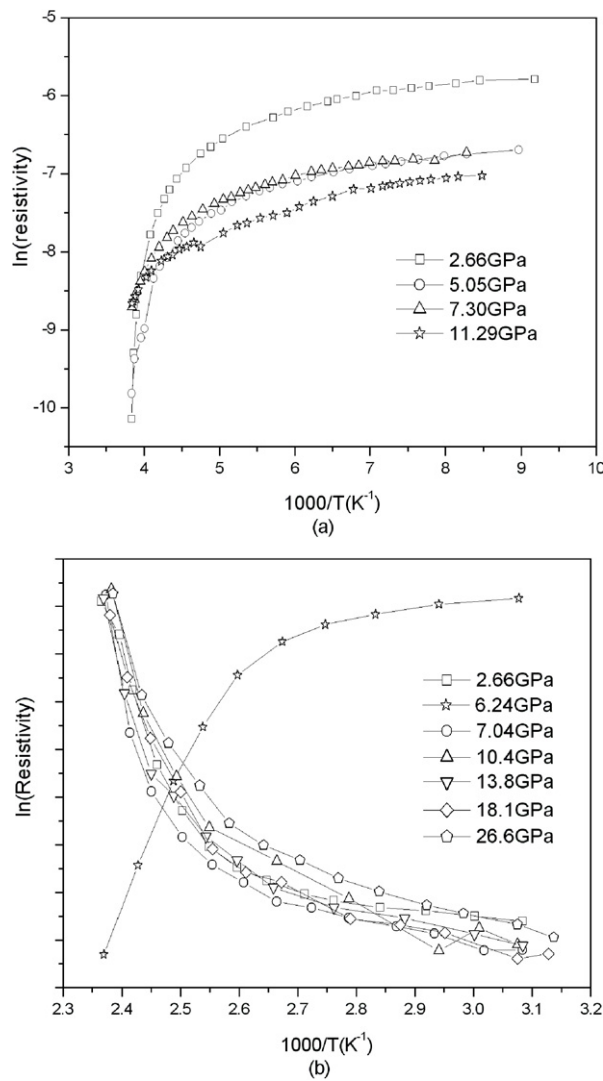


Figure 4. The reciprocal temperature dependence of the logarithm of resistivity at low temperature (a) and high temperature (b).

increasing temperature in the pressure range studied. But in the temperature range from 300 to 450 K, the situation seems to be different. Only at about 6.24 GPa does the resistivity decrease with temperature (in accordance with the result of Gonzalez *et al* [8]); at other pressures the resistivity always increases with temperature. The reciprocal temperature dependence of the logarithm of resistivity at high temperature is shown in figure 4(b). It is obvious that between 3.8 and 10 GPa rock-salt CdTe does not show a typical metallic character.

More attention should be paid to the inflexion at about 6.24 GPa (more accurately is from 6.0 to 7.0 GPa), the decrease in resistivity with temperature observed corresponds to the intrinsic activation of CdTe. For an impurity semiconductor the wider the band gap the higher the temperature needed for carriers to get into the intrinsic activation region. Considering CdTe

Table 2. The ionization (activation) energy and band gap at different pressures.

Pressure (GPa)	Ionization or activation energy (meV)	Band gap (meV)
2.66	15.5	
5.05	16.3	
6.24		445
7.30	18.1	
11.29	19.0	

in the same temperature range, only at about 6.2 GPa did we observe the intrinsic activation, so we deduce that at about 6.24 GPa CdTe is a narrow band gap semiconductor. This result supports the experimental view of Güder *et al* [9]. But the reasons why the resistivity inflexion and the different change of resistivity with temperature happened in the pressure range from 6.0 to 7.0 GPa still need to be investigated in theory.

3.3. Fitting to the curve of resistivity versus temperature in different temperature ranges

The electrical resistivity ρ of a semiconductor is sensitive to temperature; it can be written as

$$\rho = \rho_0 \exp(\Delta E/kT) \quad (2)$$

where ρ_0 is a constant (which lumps together the mobility and effective mass of the charge carriers and the density of states), k is the Boltzmann constant and T is the temperature. In the extrinsic range, ΔE is the ionization or activation energy of the impurity. In the intrinsic range, $\Delta E = E_g/2$, where E_g is the band gap. By fitting to the curve of $\ln \rho \sim 1/T$ in different temperature ranges we can obtain the ionization energy of the impurity and the band gap. The fitting results are shown in table 2. It can be seen that with increasing pressure the ionization energy increases slowly and at about 6.2 GPa a band gap of about 445 meV is obtained.

From [1, 8, 15], one can conclude that the band gap of zinc-blende CdTe shows a linear increase with pressure. While there are some disagreements about the pressure dependence of the band gap of rock-salt CdTe [9, 14]. Our experimental results show that the band gap of rock-salt CdTe first decreases before 6.24 GPa and then increases with pressure.

4. Conclusions

Using *in situ* electrical resistivity measurement we obtained the pressure and temperature dependences of the resistivity of CdTe. With increasing pressure we observed resistivity anomalies at 3.8 GPa and at 10 GPa which correspond to the structural phase transitions to a rock-salt structure and then to a *Cmcm* structure, respectively. The electronic phase transitions of CdTe happening at about 6.5, 15.5, 22.2 and 30 GPa were also found. The abnormal resistivity change at about 6.5 GPa is due to an abnormal change of band structure. The rock-salt CdTe at this pressure is confirmed by electrical resistivity measurement to be a semiconductor with a band gap of about 445 meV. With increasing pressure the ionization energy of impurities in CdTe increases slowly.

Acknowledgments

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