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SEMICONDUCTOR–METAL–SEMICONDUCTOR PHASE TRANSITION OF CdS UNDER HIGH PRESSURE

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Pressure induced phase transition of CdS was investigated by Raman spectroscopy and *in situ* electrical resistivity measurement on DAC. Both of the experiments confirmed CdS undergoes phase transition from wurtzite to intermediate to rocksalt structure. From simple data of pressure dependence of resistivity, it is cursorily estimated that these three phases of CdS are all semiconductors, but deeper investigation by resistivity measurement at high pressure and varied temperature shows that wurtzite and rocksalt phase of CdS are semiconductors, and intermediate phase is metal actually.

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1. Introduction

It is an interesting phenomenon that pressure can change the electrical properties of matter. Generally it narrows the energy bandgaps of matter and hence the matter could transform from insulator to semiconductor or from semiconductor to metal [1-5]. However, recent research on Li and Na radically changed people's outlook about the changes of bandgap by pressure. It is showed that Li and Na transformed from metal to insulator with energy bandgaps broadening rather than narrowing [6, 7]. In some IV-VI and III-V binary compound, such as GaN and SiC, pressure induced phase transitions are not simple as from semiconductor to metal. Theoretical calculations indicated that SiC and GaN undergo semiconductor-metal-semiconductor phase transition [8, 9], however it was not confirmed by experiment. CdS is II-VI semiconductor having pressure induced phase transition from wurtzite (WZ) to intermediate to rocksalt (RS) structure. Whether the phase transition of CdS is similar to those of GaN and SiC is not cleared both in theories and experiments, and therefore need to investigate deeply.

In this paper, the phase transition of CdS and the electrical properties of different high pressure phases were studied by diamond anvil cell (DAC) based electrical measurements and Raman spectroscopy.

2. Experiments

CdS powder was bought from Alfa Aesar Company with purity of 99.999% in WZ structure. In the experiments, structural phase transition of CdS was detected by an HR-800

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LABRAM confocal Raman microscope (JY Company, France). The optical source was 514.5 nm argon-ion laser and had a power of 20 mW. The photospheric facula was 15 μm in diameter. All spectra were recorded at room temperature. A mixture of methanol and ethanol with volume ratio of 4:1 was used as pressure transmitting medium.

Resistivity measurements under high pressure were performed on a DAC. Thin film detection electrodes in Van der Pauw configuration were prepared on diamond anvil and then encapsulated by Al_2O_3 layer as shown in Fig. 1(a). The inset of figure 1(a) is the photograph of the microcircuit corresponding with Fig 1(a). The preparation process in detail was similar to previous works [10, 11]. T-301 stainless steel gasket was preindented to 50μm in thickness and then drilled with a hole in diameter of 150 μm. For better insulation, a 2-μm-thick Al_2O_3 layer was also sputtered onto the gasket. Pressure calibrator was a piece of ruby crystal [12] and no pressure medium was used. The cross section of sample configuration in DAC was illustrated in Fig. 1(b).

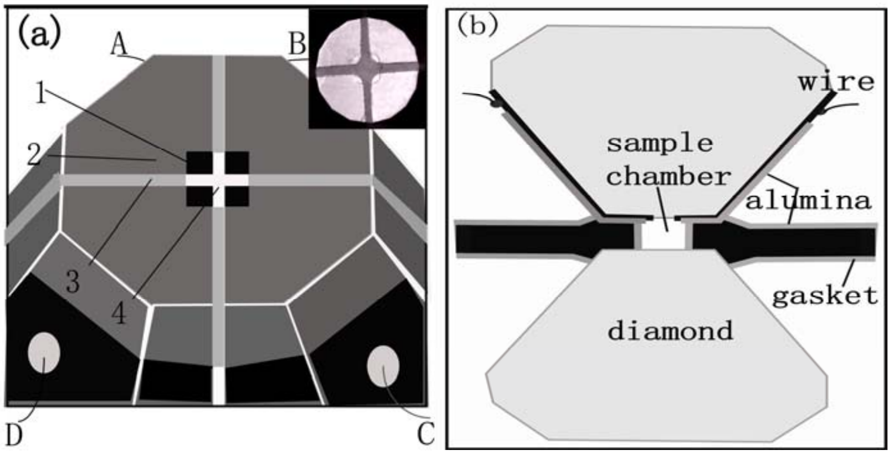

Fig. 1(a) The configuration of a microcircuit on a designed diamond anvil cell. 1,exposed Mo electrode; 2, Al_2O_3 layer on the Mo above the electrode; 3, Al_2O_3 layer on the diamond anvil cell; 4 exposed diamond anvil; (b) The cross section of the designed diamond-anvil-cel; A, B, C, and D are the four contact terminals of the microcircuit.

In the electrical resistivity measurements, a 10 μA (I_1) direct current was first applied from *A* to *B* and the voltage drop (V_1) between *D* and *C* was recorded. Then, the same current (I_2) was applied from *A* to *D* and the voltage drop (V_2) between *B* and *C* was recorded. The electrical resistivity of the sample was determined by the van der Pauw equation: [13]

$$\exp(-\pi L R_A / \rho_s) + \exp(-\pi L R_B / \rho_s) = 1, \qquad (1)$$

where R_A and R_B are the measured resistances ($R_A=V_1/I_1$,$R_B=V_2/R_2$), ρ_s is the electrical resistivity. The sample thickness L could be deduced by subtracting the net height of two diamond anvils from the total distance measured by milscale between the back facets of the two anvils [14].

3. Results and discussion

3.1 High pressure Raman spectra

The Raman spectra of CdS at various high pressures are shown in Fig. 2. These Raman spectra are dominated by the progression in the longitudinal optical phonon (LO) mode. The LO and 2LO mode frequency of CdS are observed respectively at 300 cm^{-1} and 604 cm^{-1} at ambient conditions，but they disappeared as the pressure was increased over 4.46 GPa. The disappearances of LO and 2LO mode frequency indicate the occurrence of RS phase in CdS, which could be proved by the inactivity of RS phase of CdS to the Raman scattering [15]. Below 4.46 GPa, LO and 2LO mode frequency shift to higher wavenumbers with pressure increasing, however, two different pressure dependences of Raman shift could be found as shown in Fig. 2(b). The Raman shift discontinuity took place at 2.70 ± 0.20 GPa. It indicates that as CdS transforms from WZ phase to RS phase, it undergoes an intermediate phase transition at 2.70 ± 0.20 GPa first. Therefore the phase transition of CdS under high pressure should be WZ to intermediate to RS phase. When refers to the transition from WZ to RS structure, an intermediate phase was studied in previous papers[9,16-22], but its characteristic has been little known.

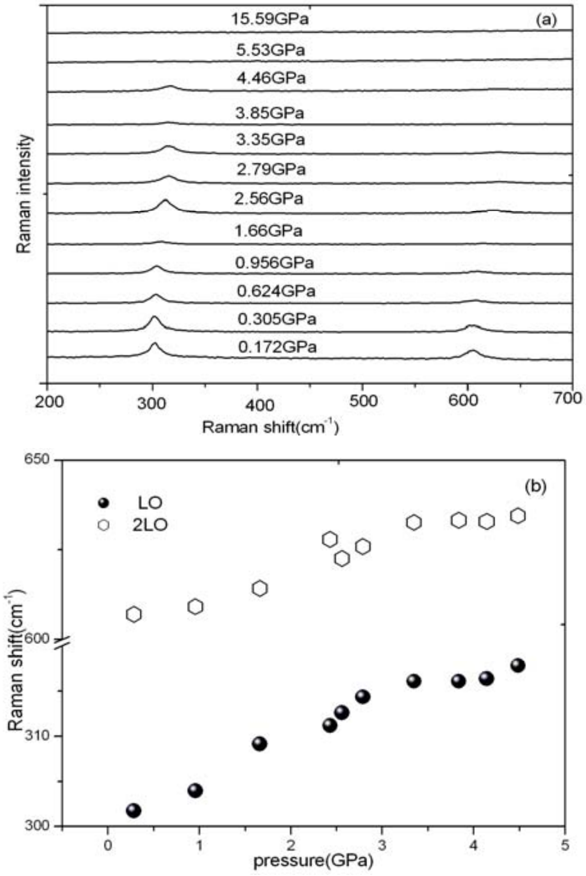

Fig. 2 (a) Resonant-Raman-scattering Spectra of CdS under different pressure;
(b) The dependence of the LO and 2LO Raman peak with pressure.

3.2. *In situ* resistivity measurements

The electrical properties of high-pressure phase transition of CdS were revealed by electrical resistivity measurement on DAC. Fig. 3 shows the pressure dependence of electrical resistivity at room temperature. Initially the electrical resistivity decreased abruptly with two orders of magnitude. After 2.10 GPa, it increased slightly, which indicates that the phase transition of CdS from WZ to intermediate phase took place. The phase transition pressure detected by electrical resistivity measurement is consistent with the result of Raman experiment. Little discrepancy in phase transition pressure with the Raman experiment is due to no pressure media was added in electrical resistivity measurement. After 5.17 GPa, the electrical resistivity began to decrease again, which reflects the occurrence of phase transition of CdS from intermediate to RS structure. From the simple data of the pressure dependence of electrical resistivity, it is hard to deeply reveal the electrical properties of CdS in different phases. The only known is that the electrical resistivity of CdS in WZ phase was 1684.30~140.93 Ω·cm, intermediate phase 150.72~294.41 Ω·cm, and RS phase 151.75~2.24 Ω·cm, and it is glancingly and temporarily estimated that WZ, intermediate and RS phase of CdS are semiconductors.

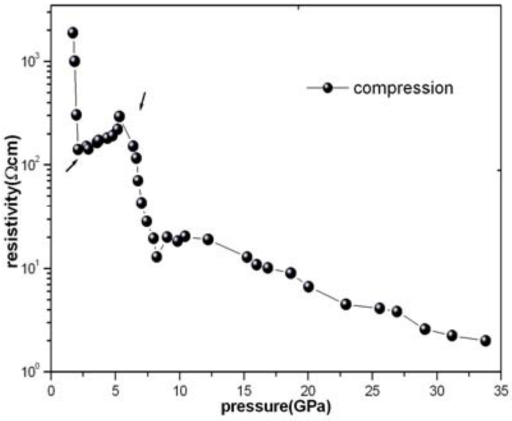

Fig. 3 Pressure dependence of CdS electrical resistivity

In order to make a deeper insight into the electrical properties of CdS under high pressure, electrical resistivity measurements were also measured at high pressure and varied temperature. Fig. 4 shows the electrical resistivity versus temperature at various pressures. At 1.42 GPa at which CdS was in WZ phase, the electrical resistivity increased with temperature increasing. Similar phenomenon could be found in RS phase of CdS at 18.87 GPa. It indicates that WZ and RS phase of CdS are semiconductors, and it is consistent with previous theoretical results. However, CdS at 2.66 GPa in intermediate phase presented totally different behavior in temperature dependence of resistivity. Its resistivity decreases with increasing temperature, suggesting the intermediate phase of CdS is metal actually.

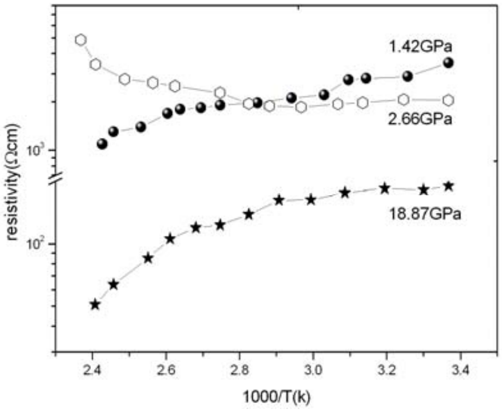

Fig. 4.Temperature dependence of resistivity at different pressures.

Note that WZ and RS phase of CdS are semiconductors, and hence the change of activation energy with pressure can be calculated from Eqs. (1) and (2) for these two phases.

$$\rho = \rho_0 e^{\frac{E}{KT}} \tag{1}$$

$$\frac{d(\ln \rho)}{dP} = \left(\frac{1}{kT}\right)\left(\frac{\partial E}{\partial P}\right) \tag{2}$$

where E represents activation energy, k is the Boltzmann constant, T is the temperature, and ρ_0 generally is a constant. By linear fitting to the curve ln $\rho \sim P$ from Fig. 3, the pressure dependence of the activation energy was presented in Tab. 1. For CdS in WZ phase, dE/dP was -9.7×10^{-2} eV/GPa. In the case of RS phase, dE/dP was -2.38×10^{-3} eV/GPa.

Table. 1 Pressure dependence of active energy in CdS.

Pressure region(GPa)	dE/dP(eV/GPa)
0 - 2.10	-9.7×10^{-2}
9.03-33.85	-2.38×10^{-3}

4. Conclusions

In summary, pressure induced phase transition of CdS was investigated by Raman spectroscopy and electrical resistivity measurement on DAC. Both of the experiments suggested the occurrence of the CdS phase transition from WZ to intermediate to RS phase. Besides, electrical resistivity measurements indicated that CdS undergoes semiconductor – metal – semiconductor phase transition under high pressure.

Acknowledgments

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