# Correlation between spectroscopic and transport experiments under pressure in II-VI semiconductors (CdTe, ZnO)

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# Summary

In this paper we discuss the reliability of transport measurements under pressure as a source of accurate information on the electronic structure of semiconductors by correlating transport and spectroscopic experiments. First we will discuss transport and optical results on the rock-salt phase of CdTe, showing the complementarity of the information on the material's electronic structure yielded by each method. Then, on the base of recent results on ZnO, we will focus in some optical measurements that are directly related to the transport properties of semiconductors: Burnstein-Moss band-gap shift and free carrier absorption. These experiments yield the high frequency values of standard transport parameters and allow for useful correlations with resistivity and Hall effect measurements under pressure.

# I. Introduction

Even if transport measurements have been widely used in high pressure research since the foundational period (Bridgman 1921) and have been applied to semiconductor physics since the very beginning (Bridgman 1951), since the appearance of the diamond anvil cell, optical measurements have certainly been the technique of choice in high pressure semiconductor research. The Paul's empirical rule (Paul 1961) is an example of the important role played both transport and optical experiments under pressure in the study of the electronic structure of semiconductors.

In this paper we will present some results on the correlation of transport and optical experiments under pressure in two technologically important semiconductors (CdTe and ZnO).

# II. Experimental details

CdTe crystals were grown by the Bridgman method. Samples for transport measurements were cut with a diamond saw and thinned to the right thickness. CdTe thin films for optical measurements were grown by MOCVD on GaS substrates as described in Güder 2003.

Ga doped ZnO thin films were grown by Pulsed Laser Deposition (PLD) on GaS and mica substrates. Targets were prepared from high purity (99.999) ZnO and  $Ga_2O_3$  powders. In order to improve the target homogeneity powders previously dispersed in pure ethanol before mixing. After drying and compressing the pellets were annealed at 950°C for 12 hours in air atmosphere. Targets with Ga atomic proportion from 0.25 to 5% Ga (with respect to the total cation content) were prepared by this method. The PLD system and deposition conditions have been described in Sans 2004.

Samples for optical measurements in the DAC were free-standing films that can be easily separated from the mica substrates. Samples for transport measurements were deposited on GaS substrates.

For optical absorption measurements in the UV-VIS-NIR range under pressure, a sample was placed together with a ruby chip into a 200-mm diameter hole drilled on a 50-mm thick Inconel gasket and inserted between the diamonds of a membrane-type DAC (Le Toullec 1988). Methanol-ethanol-water (16:3:1) was used as a pressure transmitting medium and the pressure was determined through the ruby luminescence linear scale (Piermarini 1975). The optical set-up was similar to the one described in Le Toullec 1988. It consists of a deuterium lamp, fused silica lenses, reflecting optics objectives and an UV-VIS spectrometer, which allows for transmission measurements up to the absorption edge of IIA diamonds (about 5.5 eV).

Hall effect and resistivity measurements under pressure up to 12 GPa were made with steelbelted Bridgman tungsten carbide anvils, using annealed pyrophyllite as gaskets and hexagonal BN as pressure transmitting medium. The experimental set-up has been described in Errandonea 1997.

### III. Results and discussion

#### III.a.- Rock-salt CdTe

Fig. 1 shows the pressure dependence of the carrier concentration in a CdTe sample as obtained from HE measurements. It remains virtually constant up to the zinc-blende to rock-salt (RS) phase transition, which is observed as an abrupt increase at about 4 Gpa. It is worth noticing that, at a smaller scale, the onset of the transition is announced by a progressive increase of the carrier concentration above 3 GPa. After the abrupt change between 4 and 4.5 Gpa, a much slower increase is observed up to 6 Gpa, pressure above which the carrier concentration remains constant up to 10Gpa.

In optical absorption measurements the the zinc-blende to RS phase transition is observed at 3.8+0.2 GPa as a drastic decrease of the sample transmittance. The sample becomes virtually opaque between 3.9 and 4.5 GPa. At this pressure, a range of relative transparency is observed between 1,2 and 2.2 eV.





Fig. 2: Transmittance of a CdTe sample in the RS phase at several pressures.

RS-CdTe

2.4

Figure 2 shows how, as pressure increases up to 10 GPa, the sample transmittance increases in the whole transparency range and the overall transmitted intensity increases by more than one order of magnitude. It must be stressed that even in the highest transparency range (between 9 and 10 GPa), the maximum transmittance of the sample is about 2.5 %. Different behaviours are observed in the low and high energy tails of the transparency range:

while the low energy tail tends to saturate and remains virtually constant above 6 GPa, the high energy edge moves monotonously to higher photon energies as pressure increases. Above 10 GPa the transparency region gradually shrinks and disappears at about 11 GPa, pressure at which the transmitted intensity is below the stray light level of our spectroscopic system. These results were explained in Güder 2003, on the basis of an FDA-LDA calculated band structure, by assuming that RS-CdTe is an indirect semiconductor with a small gap (probably a few hundred meV). At low carrier concentrations, the indirect transition would give rise to intense absorption in the VIS/NIR range. At high carrier concentrations (thermally excited or coming from electrically active defects), carriers would fill the VBM and CBM states and the contribution of indirect transitions to the absorption coefficient would be strongly reduced. If we neglect the contribution of indirect transitions, the absorption coefficient would be modelled with a free carrier absorption tail (proportional to the squared photon wavelength) and a direct gap contribution:

$$\alpha(\hbar\omega) = \frac{A}{(\hbar\omega)^2} + B\left(\frac{\pi}{2} + \arctan\frac{\hbar\omega - E_{gd}}{\Gamma}\right) \qquad \text{(Equation 1)}$$

where is the photon energy, A and B stand for the relative intensity of free carrier and bandto-band absorption,  $E_{gd}$  is the direct gap energy and  $\Gamma$  is the direct transition width. Red line plots of Fig. 2 correspond to the calculated transmittances  $T_c = e^{-\alpha d}$ , where d is the sample thickness (1µm) and a is given by equation 1, after fitting T<sub>c</sub> to the sample transmittance at several pressures. The direct gap so estimated turns out to be 1.9 eV at 4.7 GPa, with a pressure coefficient of 90±15 meV/GPa.

Fig. 3 shows the IR-visible reflectance of a CdTe sample in three phases. In the zinc-blende phase reflectance exhibit the sample interference fringe pattern below the band gap (1.72 eV



Fig. 3: Reflectance of a CdTe sample in three different phases



Fig. 4: Band structure of RS CdTe

at 4.7 GPa), while both the RS and *Cmcm* phases exhibit a plasma reflection structure, with plasma energies of about 1.1 eV in the RS phase and 1.7 eV in the *Cmcm* phase. From the expression of the plasma energy  $E_p = \hbar \sqrt{\frac{e^2 n}{m^* \varepsilon_e}}$  and given the carrier concentration measured by HE, and assuming a value for the electronic dielectric constant typical of a low gap comised duster (a, 15a) and communication the electronic dielectric constant typical of a low

gap semiconductor ( $\epsilon_e \sim 15\epsilon_0$ ) one can estimate the electron effective mass to be  $m_e^* \sim 0.06m_0$ . The filling of the conduction band corresponding to these effective mass and concentration would place the Fermi level at 0.73 eV above the CBM. On the basis of the HE and IR reflectance here reported (Figs. 1 and 3) the low gap model would be confirmed only in the assumption that electrons in RS-CdTe are generated by extrinsic donor defects generated in the phase transition. Given the constancy of the electron concentration above 6 GPa observed in two different kind of samples, as well as the reversibility of the electron concentration in the down-stroke, it seems more reasonable to assume that the free carriers are of intrinsic origin. This assumption necessarily leads to a semi-metallic character, as such high electron concentrations would not be observed in an intrinsic semiconductor at room temperature, even with a band gap as low as a few tens of meV. Fig.4 shows a sketch of the proposed band structure of RS-CdTe around the Fermi level. Given the symmetry of the different points of the FCC Brillouin zone, the conduction band consists of 3 equivalent valleys at X, while the valence band consists of 4 equivalent valleys at L and 24 in the GK direction. The density of states in the valence band is expected to be much larger than the one in the conduction band. This is the reason why the Fermi level is assumed to be at a larger energy from the bottom of the conduction band minimum in the band sketch of Fig. 4.

#### III.a.- Ga doped ZnO

Figs. 5 and 6 show the pressure dependence of the carrier concentration and electron mobility in several Ga-doped ZnO thin films deposited on GaS between ambient pressure and about 12 GPa. Fig. 5 shows how the electron concentration remains practically constant between ambient pressure and 10 GPa, pressure at which a decrease by about a factor 2 is observed. Fig. 6 shows no clear decrease of the electron mobility in any of the samples.



Fig. 5: Pressure dependence of the carrier concentration in several Ga-doped ZnO



Fig. 6: Pressure dependence of electron mobility in several Ga-doped ZnO samples

The phase transition from the wurtzite (W) to the rock-salt (RS) phase is known to occur at about 9.5 GPa from X-ray diffraction and absorption experiments (Bates 1962, Recio 1998, Decremps 2003).



Fig. 7: Change of the ZnO absorption edge in the W to RS phase transition.



Fig. 8: Optical absorption in Ga-doped ZnO films with different electron concentrations.

In optical absorption experiments under pressure the W to RS transition occurs at about  $9.5 \pm 0.2$  Gpa in monocrystals and is observed as a neat change in the shape of the absorption coefficient for both bulk monocrystals (Segura 2003). The absorption edge exhibits a structure related to the wurtzite phase up to 16 GPa. Above that pressure, and contrary to what happens for most high-pressure phases of II-VI semiconductors, the sample does not exhibit any trace of light scattering and the absorption edge can be accurately measured.

Figure 7 shows the change of the absorption coefficient for in the W to RS transition for a ZnO thin film in mica, for which the transition was observed at a slightly higher pressure (11 Gpa). The absorption edge of RS-ZnO films is shifted to higher energies and, at the pressure transition appears as a structureless edge shifted to much higher photon energies (with respect to the W-ZnO edge).



Fig. 9: Pressure dependence of the absorption edge of a Ga-doped ZnO sample.

Fig. 10: Pressure dependence optical gap of Ga-doped ZnO thin films.

Doping ZnO with Ga has two effects on the optical properties that are clearly visible on the spectra shown in Fig. 8. On the one side, the Burstein-Moss effect shifts the absorption edge to higher photon energies due to the conduction band filling by free carriers generated from the ionization od the Ga-

related donor. On the other side, a free carrier absorption edge appears on the low photon energy spectrum. It must be outlined that, given the small thickness of the ZnO films and the longer wavelength limit of our spectroscopic system (1700 nm), the free carrier edge was observed only in samples with carrier concentrations larger than  $6 \, 10^{20} \, \text{cm}^{-3}$ .

Fig. 10 shows the pressure evolution of both effects for a Ga doped ZnO film with a carrier concentration of the order of  $6 \ 10^{20} \text{ cm}^{-3}$ . The Burtein-Moss shifted absorption edge moves to higher photons energies, monotonously, with a pressure coefficient that decreases with increasing the carrier concentration, as shown in Fig. 8. The free carrier edge does not exhibit, within the experimental errors, any dependendence on pressure up to the phase transition.



Fig. 11: Change of the absorption edge in the W to RS transition in Ga-doped ZnO sample.

Fig. 12: Change of the free carrier edge in the W to RS transition in Ga-doped ZnO sample.

Fig. 11 illustrates the W to RS transition in a Ga-doped ZnO film with a carrier concentration of 10<sup>20</sup> cm<sup>-3</sup>. The phase transition to the RS phase in Ga-doped ZnO films has en effect similar to the one observed in undoped samples. The step-like absorption edge of W-ZnO changes to a much smoother edge as shown in Fig. 11. It is interesting to nottice that the pressure transition to the RS phase tends to increase with the Ga concentration and the transition is not complete unless the pressure is rised to 14-16 GPa.

As regards the free carrier absorption edge, in samples with the highest free carrier concentration, it is also observed in the RS phase, with a reduction of its intensity, coherent with the decrease of the carrier concentration, as measured by Hall effect (see Fig 12).

# **IV. Conclusions**

In the two cases here studied, transport and optical measurements have been shown to be complementary. In the case of CdTe, the information provided by HE measurements has been crucial to decide between the low-gap semiconductor and semimetal models for RS-CdTe, in favor of the second option. In the case of ZnO, the information provided by both techniques has been shown to be fully coherent. Further analysis of results here reported are needed in order to extract more precise details about the electronic structure of wurtzite and rock-salt ZnO.

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## References

BATES CH, White W. B. and Roy R. (1962). New high-pressure polymorph of zinc oxide. Science **137**, 993.

BRIDGMAN P.W. (1921). Electrical resistance under pressure, including certain liquid metals:black phosphorous. Proc. Amer. Acad. Arts Sci. **56**, 126-131.

BRIDGMAN P.W. (1951). The effect of pressure on the electrical resistance of certain semiconductors. Proc. Amer. Acad. Arts Sci. **79**, 127-148.

DECREMPS F., Datchi F., Saitta A.M., Polian A., Pascarelli S., Di Cicco A., Itie J.P., Baudelet F. (2003). Local structure of Condensed zinc oxide. Phys. Rev. B **68** (10), 104101.

ERRANDONEA D, Segura A, SanchezRoyo JF, Muñoz V, Grima P, Chevy A, Ulrich C (1977). Investigation of conduction-band structure, electron-scattering mechanisms, and phase transitions in indium selenide by means of transport measurements under pressure. Phys. Rev. B **55** (24), 16217-16225.

GÜDER H. S., Gilliland S.J., Sans J. A., Segura A., González J., Mora I., Muñoz V., and Muñoz A. (2003). Electronic structure and optical properties of CdTe rock-salt high pressure phase. Phys. Stat. Sol. (b) **235** (2), 509–513

LE TOULLEC R., Pinceaux J. P. and Loubeyre P. (1988) High Pressure Research 1, 77.

PAUL W. (1961). Band structure of intermetallic semiconductors from pressure experiments. J. Appl. Phys **32**, Supplement, 2092-2095.

PIERMARINI G. J., Block S., Barnett J. D. and Forman R.A. (1975). Calibration of the pressure dependence of the R1 ruby fluorescence line to 195 kbar. J. Appl. Phys. **46**, 2774-2780.

RECIO J.M., Blanco M.A., Luaña V., Pandey, Gerward L. and Olsen J. S. (1998). Compressibility of the high-pressure rocksalt phase of ZnO. Phys. Rev. B **58**, 8949-8954.

SANS J.A., Segura A., Mollar M., Marí B. (2004). Optical properties of thin films of ZnO prepared by pulsed laser deposition. Thin Solid Films **453–454**, 251–255.

SEGURA A, Sans JA, Manjon FJ, Munoz A, Herrera-Cabrera MJ (2003). Optical properties and electronic structure of rock-salt ZnO under pressure. Appl. Phys. Lett. **83** (2), 278-280.