ELECTROABSORPTION BY IMPURITIES AND DEFECTS IN SEMI-INSULATING CdTe

G. NEU, Y. MARFAING, R. TRIBOULET and M. ESCORNE

Laboratoire de Physique des Solides, C. N. R. S.,
1, place A. Briand, 92190 Meudon/Bellevue, France

Résumé. — Des expériences d'électroabsorption extrinsèque permettent de comparer les spectres des défauts dans CdTe compensé non dopé et dopé au chlore de 1,2 à 1,6 eV. Trois groupes de transitions sont relevés :

- des transitions bande de valence-niveaux donneurs semi-profonds ($E_c - 0,02$ à $0,03$ eV) liés à la présence du chlore et d'impuretés du groupe III,
- des transitions à partir de niveaux accepteurs peu profonds ($E_o + 0,05$ eV) vers la bande de conduction,
- une transition de basse énergie ($E_c + 0,13$ eV). Cette dernière est étudiée en fonction de l'orientation du cristal et de la polarisation de la lumière afin de préciser la nature du défaut qu'elle implique, et particulièrement sa symétrie.

Abstract. — Electroabsorption experiments have been conducted on semi-insulating CdTe prepared by THM without intentional doping, and with addition of chlorine. Three groups of optical transitions due to localized levels have been observed in the photon energy range from 1.2 eV to 1.6 eV :

- transitions from the valence band to shallow donor levels ($E_c - 0.02, 0.03$ eV), associated with chlorine or group III donors,
- transitions from shallow acceptors ($E_v + 0.05$ eV) to the conduction band,
- transitions from a deep acceptor level ($E_v + 0.13$ eV) to a shallow donor level.

The latter level is usually attributed to a donor-cadmium vacancy complex, which prompted us to undertake a more systematic study of the transition. Various electroabsorption spectra were recorded as a function of temperature, crystal orientation and light polarization. Strong dichroic effects were observed, the analysis of which should allow one to determine the symmetry of the complex involved.

1. Introduction. — Extrinsic electromodulation experiments have already provided much information on impurity centers in semiconductors [1, 4]. Early work [5, 6] on CdTe has shown the existence of localized levels, which probably imply the presence of native defects. These defects play an important role in the electrical compensation of the material. In the case of a high degree of compensation a study of the centers involved using electroabsorption seems particularly suitable, owing to the high resistivity of the material.

Therefore, we have undertaken spectroscopy of semi-deep, localized levels in semi-insulating samples, using the electric field as a modulation parameter.

Two kinds of samples prepared by the solution growth technique THM were studied : the ones grown at 700 °C were not intentionally doped, and the other ones, grown at 900 °C were doped with chlorine to a level of $2 \times 10^{17} \text{ cm}^{-3}$.

1.1 ELECTROABSORPTION SPECTRA. — The spectra recorded at 77 K on undoped samples (Fig. 1a) display two sets of oscillations : the larger, D_1 , is located near the start of the absorption edge. The

signal spreads out around 1.565 eV. A second group of oscillations, A_1 , is centered around 1.545 eV. The signal amplitudes are proportional to the square of the electric field. At low temperature (Fig. 1b), the shape of D_1 as well as its quadratic amplitude are not modified. This signal corresponds to an optical transition from the valence band to a donor level located 30 meV below the conduction band at 77 K.

FIG. 1. — Electroabsorption spectra at 77 K (a) and 4.2 K (b) for undoped CdTe. a) $E = 5\,000$ V/cm, b) $E = 1\,000$ V/cm.

The theoretical analysis of such electroabsorption signals can be rather easily formulated in the case of a valence band to hydrogenic donor level transition [7]. Calculating the optical transition probability between the valence band states perturbed by the field, F , and the ground state of the donor, the absorption coefficient, α , is obtained as :

$$\alpha = \alpha_0 + A(\hbar \Delta\omega) F^2$$

where α_0 is the absorption coefficient at zero field as given for example by Dumke [8], and $A(\hbar \Delta\omega)$ is a function of the incident light energy. This analysis allows us to explain the quadratic variation of the amplitude with electric field.

At 4.2 K the set A_1 consists of a series of narrow oscillations around 1.55 eV. This signal can be assigned to a transition from acceptor levels localized at about 55 meV above the valence band to the conduction band. The displacement of A_1 with temperature is normal. However, D_1 , taking as reference the energy at which the signal equals zero, increases by 19 meV when the temperature is reduced from 77 K to 4.2 K, whereas the bandgap energy only increases by 11 meV.

This behavior indicates an anomalous variation of donor ionization energy as a function of temperature. This variation was previously observed in photo-capacitance [9] and piezoreflectance experiments [10]. This level also seems to be the origin of the luminescence line observed at 1.584 eV at 4.2 K in undoped or indium doped material. Since in undoped material the residual donors are postulated to be of group III, the donor center D_1 can be associated with group III impurities occupying non substitutional sites or complexed with native defects.

The electroabsorption spectrum in the same range of energy is modified by the presence of chlo-

rine (Fig. 2). At 70 K, with unpolarized light, the high energy region displays two peaks which increase as the square of the field. The peak D_2 , located around 1.563 eV is preceded by a weaker peak A_2 at 1.54 eV. The low energy region shows a wide negative peak C_2 around 1.48 eV, which increases linearly with the field. Thus besides donor-type and acceptor-type transitions, a new transition C_2 has appeared.

Figure 2 also shows the evolution of the spectrum at low field with decreasing temperature ; two salient features are observed :

(i) The C_2 peak which exists at 70 K disappeared at 40 K.

(ii) A new high energy peak D_2 appears at low temperature, at the same energy as D_1 in undoped samples.

In compensated chlorine doped material a donor level at 28 meV below the conduction band has already been determined by a time of flight technique [11]. This level can be associated with transition D_2 observed at 1.563 eV at 77 K. The shift of this level with decreasing temperature, which can be easily observed with high field spectra, corresponds to the bandgap temperature dependence. The D_2 transition can then be related to the presence of a residual group III impurity, similar to D_1 .

Since the shift of the peak C_2 is proportional to the field, the zero field transition energy can be found by extrapolation to be 1.463 eV. The ground state level of this transition is currently attributed to an acceptor complex which consists of a cadmium vacancy and a chlorine atom on the nearest tellurium site. The final state is thought to be a shallow donor state [12]. This complex center plays a dominant role in self compensating donors and deserves more detailed study.

1.2 LINEAR DICHROISM EFFECTS. — The electric field induces dichroism in the absorption which can be used to get information about the symmetry of complexes. Figure 3 is an example of such behavior. When the electric field is applied along the $(\bar{1}10)$ direction, and the incident light is coming along the (111) , the sign of the C_2 peak is opposite, depend

FIG. 2. — Dependence of the E. A. spectra on temperature for chlorine doped CdTe ($E = 1000$ V/cm).

FIG. 3. — Linear dichroism induced by the electric field peak ($E = 400$ V/cm).

ing on whether the light is polarized parallel or perpendicular to the electric field. Figure 4 shows that when the field is increased, a new narrow oscillation emerges from the broad C_2 peak.

FIG. 4. — Dependence of the E. A. spectrum ($E // P$) on increasing electric fields (Sample thickness = 1.5 mm).

Let us assume that the acceptor complexes are oriented along (111)'s as is expected for a group VII donor-cadmium vacancy association. In our sample configuration only two sets of equivalent dipoles have an electric moment modulated by the field, if the electric dipole is taken to exist along the defect axis.

To a first approximation, absorption of light is proportional to the square of the scalar product between the polarization vector $\mathbf{P}$ and the electric moment $\mathbf{D}$:

$$\alpha \simeq (\mathbf{P} \times \mathbf{D})^2.$$

The expression for the electroabsorption can be decomposed into two parts :

$$\Delta\alpha \simeq \sum (\mathbf{P} \times \mathbf{D}) (\mathbf{P} \times \Delta\mathbf{D}) + (\mathbf{P} \times \Delta\mathbf{D})^2.$$

Because of the existence of an equal number of defect dipoles oriented in opposite directions, the first term disappears upon summation. If we assume that the perturbation of electric moment is of the form :

$$\Delta\mathbf{D} = A\mathbf{D}$$

i. e., parallel to the electric moment, the second part of $\Delta\alpha$ is proportional to the square of the cosine of the angle between the polarization vector and the electric moment of the dipoles.

This gives the theoretical variation of $\Delta\alpha$ with the polarization angle δ referred to the field direction shown by the dotted line in figure 5. The experimental signal shows a quite different behavior. The amplitude at the maximum is phase shifted with respect to the theoretical curve, and there is a sign inversion during half of the period. To come to more definite conclusions, this type of experiment has to be made on crystals of different orientations. However, it seems that the symmetry of the complex C_2 could be less simple than usually considered. On the other hand, electric birefringence effects could play an important role as demonstrated in CuCl by Daunois and Deiss [13].

FIG. 5. — Comparison between theoretical variation (dotted line) and experimental measurements (solid line) of E. A. signal with respect to polarization orientation (referred to electric field direction).

2. Conclusion. — The results presented in this paper show that differential electroabsorption is a sensitive technique to detect localized levels in high resistivity semiconductors or insulators.

For chlorine compensated CdTe, electroabsorption spectra display transitions associated with the electronic levels which dominate the self compensation process : a donor level at $E_c - 28$ meV and an acceptor level at $E_v + 130$ meV.

Transitions originating from the last level exhibit a strong linear dichroism effect which cannot be simply interpreted with the usual assumption of (111) oriented acceptor complexes.

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