

Influence of the grain boundary on band-tail parameter in polycrystalline CdTe films

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The experimental evidence of the grain boundary influence on disorder and therefore on band-tail parameter in polycrystalline CdTe films is presented. A linear behavior of the band-tail parameter obtained from absorption spectra at room temperature, as a function of the reciprocal of the grain size was found. The study of the full width at half maximum of x-ray diffraction peak showed a similar behavior, which indicates that the disorder increases as grain size diminishes. The theoretical analysis justifies that the behavior is ruled by the contribution of the grain boundary traps. Both results constitute experimental evidences of the grain boundary disorder, which was quantified, and demonstrate that it is caused by the grain boundary and the trap distribution.

1. Introduction

The grain boundary of polycrystalline semiconductors plays an important role for technical applications. It is closely related with electrical and optical properties due to the presence of surface traps [1,2]. The determination of the trap concentration and its dependence on morphological and structural characteristics from optical measurements is an important profit, which made has application in the quality control and performance of optoelectronic devices. On the other hand, the existence of disorder in semiconductors leads to potential fluctuations, and therefore the band-tail parameter E_0 of the absorption profiles varies [3]. The grain surface traps, which catch carriers and ionize, produce such an effect, and consequently a dependence of E_0 on grain size must be expected.

In this paper, we report the linear dependence of the band-tail parameter on reciprocal of the grain size in polycrystalline non-doped CdTe films. Additionally a similar behavior of the width of x-ray peaks of the samples was found. From the experimental band-tail parameters the trap concentration in the grain surface was calculated and the strain was numerically evaluated

2. Experiment

Non-intentionally-doped polycrystalline CdTe films were grown on Corning 7059 glass substrates by close-spaced vapor transport combined with free evaporation (CSVT-FE) technique [4]. The samples were grown for 5 min at constant source temperature (600 °C). The substrate temperature was changed between 200 and 450°C in order

to vary the grain size. The sample thickness ranged between 5 μm for samples with grain radius of around 1 μm and 120 μm for the sample with grain radius of around 60 μm . The grain sizes were measured from the micrographies obtained with scanning electron microscopy technique (SEM). The SEM equipment was a JEOL JSM-35C. X-ray diffraction measurements were performed with a Siemens D5000 diffractometer with Cu $K\alpha$ radiation operating at 40 kV and 35 mA. The absorption spectra were obtained with an optical system, with a Lomo MDR-23 monochromator and a FEU-62 photomultiplier in its outlet. The signal was received and processed with a SR-510 lock-in amplifier coupled to a computer.

3. Results and Discussion

The band-tail parameter values E_0 were obtained from the exponential region below the band-gap energy of absorption spectra at 300 K. The absorption spectra were corrected by subtraction of the scattering attenuation to the total absorption [5]

For the sake of simplicity, the grain radius values, R , were assumed as an average grain size in each sample and ranged between 1 and 60 μm .

In Fig. 1 it can be seen an evident linear behavior of E_0 with the reciprocal of R . By the least square method we calculated, from experimental data, that $E_0 = 21.18 \text{ meV} + 121.84 \text{ meV} \cdot \mu\text{m} R^{-1}$. Taking into account that the band-tail parameter is a sum of contributions [3], we can anticipate that the grain boundary is a source of disorder that contributes to E_0 , and specifically to the disorder term E_{0x} [3]. Then:

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$$E_0 = \text{constant} + E_{0,GB} \quad (1)$$

at constant temperature. $E_{0,GB}$ is the contribution of the grain boundary to the band-tail parameter.

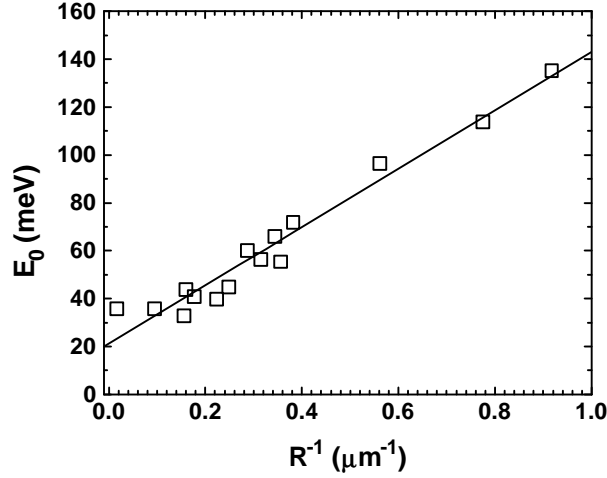


Fig. 1.- Behavior of E_0 as a function of the reciprocal of R .

For formulating $E_{0,GB}$ we considered that the grain boundary of polycrystalline semiconductors is a bidimensional (2D) amorphous layer between the grains [6] with traps, which tend to catch carriers and ionize [7]. The free carriers screen the Coulomb field of the ionized traps, which modifies the carrier distribution in the surroundings. Assuming spherical symmetry in the grains, from the Poisson's equation [7], the potential $V(r)$ can be found to be [8,9]:

$$V(r) = V_0 \exp\left(-\frac{R-r}{L_D}\right) \quad (2)$$

where V_0 is the potential in the grain surface, r is the distance from the grain center, R the grain radius, and $L_D = (\epsilon_s kT/e^2 N)^{1/2}$ the Debye length. N is the free carrier concentration, k the Boltzmann constant, e the electron charge, and ϵ_s the static dielectric constant.

Deriving Eq. (2) it is possible to find the electric field, as:

$$F(r) = F_s \exp\left(-\frac{R-r}{L_D}\right) \quad (3)$$

where $F_s = -V_0/L_D$ is the field at the grain boundary. From the electroneutrality condition in the grain boundary it follows:

$$F_s = \frac{eQ_t}{2e_s} = \frac{en'L_D}{e_s} \quad (4)$$

where Q_t is the grain surface charge density, which is

independent of the grain size [8]. n' is the difference of carrier concentration between center and surface of the grain.

By comparing the expressions of the potential variance given by the Halperin-Lax model [3,10] with Eqs. (3) and (4) and assuming $N=n'$ and $L=L_D$, it is possible to obtain an expression that relates the electric field induced by the charge distribution with the variance of the potential:

$$\mathbf{x} = \frac{2p^2 Z_t^2 e^3}{e_s} F \quad (5)$$

where, Z_t is the trap ionization.

As the electric field varies spatially, we took the average field $F = \langle F_{GB} \rangle = \int_0^R F(r) dr / R \cong F_s L_D / R$, and therefore the corresponding tail parameter is:

$$E_{0,GB} = \frac{4p^2 e^4 Z_t^2 m^* L_D^3 Q_t}{9\sqrt{3} e_s^2 \eta^2} R^{-1} \quad (6)$$

Hence, for $N=10^{16} \text{ cm}^{-3}$ and $Z_t=1$ we calculated that $Q_t = 1.15 \times 10^{11} \text{ cm}^{-2}$ from the slope of experimental E_0 dependence on R^{-1} and Eq. (6). This result agrees with $Q_t \cong 7 \times 10^{11} \text{ cm}^{-2}$ reported in electrodeposited CdTe with a grain size of $0.3 \mu\text{m}$ [12].

By considering that the bulk defects also act as charged centers which trap carriers, we can similarly obtain the contribution of the bulk defects to E_0 :

$$E_{0,def} = \frac{8p^2 e^4 Z_t^2 m^* L_D^3 N_d}{9\sqrt{3} e_s^2 \eta^2} \quad (7)$$

where N_d is the bulk defect concentration.

The structural disorder contribution to the tail parameter is [3]:

$$E_{0Y} = \frac{3}{8} Y k \theta_D \quad (8)$$

where Y describes the lattice strain throughout E_{0Y} and its weight on potential fluctuations in the bulk, and θ_D is the Debye temperature. Y is considered associated to internal strain and elastic properties, and it is influenced by the lattice structure distortion.

These results can be introduced in the model of Ref. [3]:

$$E_0 = E_{0I} + E_{0,GB} + E_{0,def} + E_{0Y} \quad (9)$$

where E_{0I} is the sum of the contributions to the band-tail parameter given by carrier-impurity and carrier-phonon interactions, and depends on temperature and carrier concentration. From the formulation of the model we calculated the interactive contributions to the band tail, considering $T = 300 \text{ K}$ and the carrier concentration $p =$

10^{16} cm^{-3} , and was found to be $E_{0I}=6.5 \text{ meV}$ in CdTe. Taking $N_d=10^{14} \text{ cm}^{-3}$ given in polycrystalline CdTe [13], it is possible to obtain that $E_{0,def}=10.3 \text{ meV}$ from Eq. (7). Then $E_{0Y} = 4.5 \text{ meV}$ and from Eq. (8) it can be found that $Y= 0.93$, which is consequent with those values found in amorphous SiH ($Y=2.1$) [14].

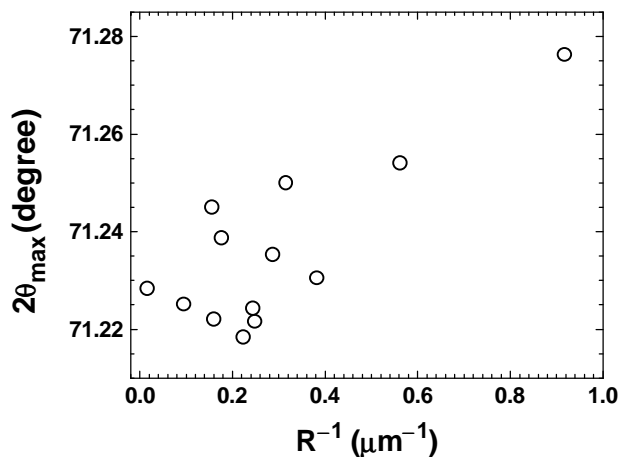


Fig. 2.- Plot of the [422] plane peak angle as a function of R^{-1} .

An additional analysis of the x-ray pattern lines of the samples was made. In a polycrystalline materials there exists interactions between grains, which produce structural deformations. The strain varies from a grain to another or from one part of a grain to another part, on a microscopic scale. This strain manifests in the angle position and the half width at half maximum (FWHM) of x-ray pattern peaks. That analysis was carried out on the CdTe [422] x-ray peak of our samples. This high angle diffraction peak was chosen to show clearly the changes of the lattice spacing [15]. In Fig. 2 it is shown the angle position of the [422] x-ray peak as a function of the reciprocal of the grain radius. No tendency was considered because of the data dispersion. The average angle value was $2\theta_{av}=(71.25 \pm 0.01)^\circ$, and the average lattice constant is $a=(0.648 \pm 0.002) \text{ nm}$. This value coincides with that of monocrystalline CdTe [16], however, the data deviation indicates that some strain, either compressive or tensile, is present [17], and it is related with the amorphous glass substrate and the growth technique characteristics.

The fractional variation of the plane spacing it is given by the expression [11]:

$$\frac{\Delta d}{d} = \frac{\Delta 2q - \Delta 2q_0}{2} \cot q \quad (10)$$

where $\Delta 2\theta$ is the measured FWHM, and $\Delta 2\theta_0$ is the instrument FWHM of the line, and θ the line angle.

From the [422] x-ray peak and the FWHM we evaluated Eq. (10). Fig. 3 shows the dependence of $\Delta d/d$ in the [422] plane vs. R^{-1} . By the least square method we calculated that the behavior follows the expression $\Delta d/d = 5.936 \times 10^{-4} + 0.00124 \mu\text{m}^{-1} R^{-1}$. The line intercept $\Delta d_0/d =$

5.936×10^{-4} is a base value for a supposedly monocrystalline CdTe ($R=\infty$) plus the instrument FWHM. This values is a constant, and it is related with the grain bulk disorder. The increase of $\Delta d/d$ respect to the base value indicate an increase of the lattice distortion in the grain bulk region nearby the boundary.

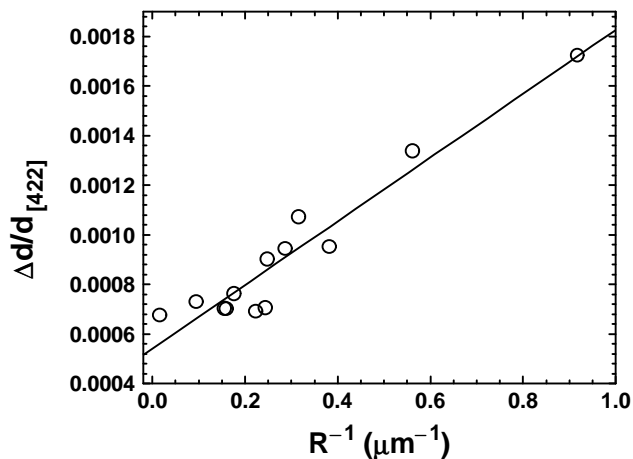


Fig. 3.- Behavior of the FWHM of the [422] line as a function of the reciprocal of R.

The dependence of $\Delta d/d$ as a function of R^{-1} is similar to that of E_0 . The premise of the 2D boundary is not consequent with these results, which establish that the grain boundary is a thin tridimensional layer in the grain edge and the inter-grain regions. Hence the boundary region must be expected to has a gradual disordering with a maximum just in the grain boundary, and in the same way the traps are distributed. Thus the main disorder source is the grain boundary, but the major influence arises from grain region nearby the boundary.

Therefore, a comparison between the band-tail parameter and the fractional strain can define the nature of the disorder.

4. Conclusion

We obtained a linear dependence of the band tail parameter of absorption spectra and the FWHM of x-ray diffraction on reciprocal of the grain size of CdTe polycrystalline samples, which had not been reported and constitute experimental evidence of the influence of the grain boundary on disorder. From a theoretical analysis the trap density was calculated. The results indicate that the disorder and trap distribution is gradual with a maximum in the grain boundary and diminish toward the grain inside part.

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