

Correlation between electro-physical characteristics and elastic properties of cadmium selenide films

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Received 22 September 2003, revised 25 September 2003, accepted 20 November 2003

Published online 13 February 2004

PACS 61.50.Ks, 71.61.Ga

A number of anomalous electrophysical and photoelectrical properties of polycrystalline CdSe was investigated. This data analysis gave the possibility to state that the anomalous dependencies are conditioned by structural transformations in double phased cadmium selenide. It was established, that these electro-physical phenomena are determined by the structural parameter – Δr_m – β -CdSe phase inclusion radius change in the α -CdSe phase matrix. The anomalous properties nature is chemical bonds destruction at the nanoscale boundary between two phases of CdSe.

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1 Introduction Anomalous dark current temperature dependence (ADCTD), described as non-Arrhenius reversible temperature dependence of the current, has been often observed in polymorphic polycrystalline CdSe (see e.g., Refs. [1–3] and references therein). It has been suggested that the ADCTD originates from the structural changes in the system during thermal treatments. We used X-ray diffraction (XRD) analysis, electrical potential distribution and the temperature dependent measurements of the dark (the equilibrium state) conductivity and mobility in the temperature interval of 140–240 K, complemented by model calculation to verify such an assumption.

So far as the ADCTD is the structural phenomenon which may be registered by two-three orders of the current's magnitude it may have varied applications, e.g. elastic tensions sensors, units for the bending strength measurements, and so on.

2 Experimental results The polycrystalline CdSe layers used in this study were obtained by the thermal deposition of CdSe in vacuum on glass substrates. Immediately after the layer preparation, XRD measurements were performed. They have shown a full set of reflections ((101), (102), (103), (202), (203)) that correspond to hexagonal α -CdSe; therefore we conclude that as-grown samples consist, for the most part, of hexagonal α -CdSe phase. However, the reflections (642) corresponding to small quantities of cubic β -CdSe crystals were also registered. It was achieved by the regulation of the substrate temperature in the variable interval of (623–723) K.

Then, the layers were subjected to several cooling-heating cycles in the temperature interval 140–300 K, and the XRD measurements were again performed. As a result of the cooling-heating procedure, the intensity of the (642) reflection of the CdSe cubic phase ($d = 0.811 \text{ \AA}$) increased by an order of magnitude compared with that in as-grown layers. Moreover, the reflections (553) and (731) of the cubic phase appeared in XRD spectrum. Therefore, it is apparent that, after several cooling-heating cycles, the fraction of the CdSe cubic phase in the layers is dramatically increased.

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During such thermo-cycling the layers undergo the effects of the elastic tension due to the differences in the thermal expansion coefficients of the layers, $\alpha_L = 11.25 \text{ deg}^{-1}$, and the glass substrate, $\alpha_g = 0.256 \text{ deg}^{-1}$. The analysis [4] showed that the tension can achieve 10^7 Pa and it could be a source of energy for the structural transformations in the layer. The elastic deformations may influence $\beta\text{-CdSe} \rightarrow \alpha\text{-CdSe}$ structural transformation.

Thus, after the termocycling treatment the XRD analysis showed the structural $\alpha\text{-CdSe} \rightarrow \beta\text{-CdSe}$ transition, and calorimetric measurements showed the endothermic effect in the same temperature interval – 180 K.

Figure 1a shows the dark current as a function of temperature in the temperature intervals where thermo-cycling has been performed. Such a behavior is known as ADCTD. We note that the ADCTD effect was studied also by the Hall-effect [5], and it was established, that the anomalous current dependence appears due to the electrons concentration component, but not due to the mobility one. The analysis of non uniform potential distribution along the layer showed the presence of intergrain boundaries and their correlation with the ADCTD phenomena [5].

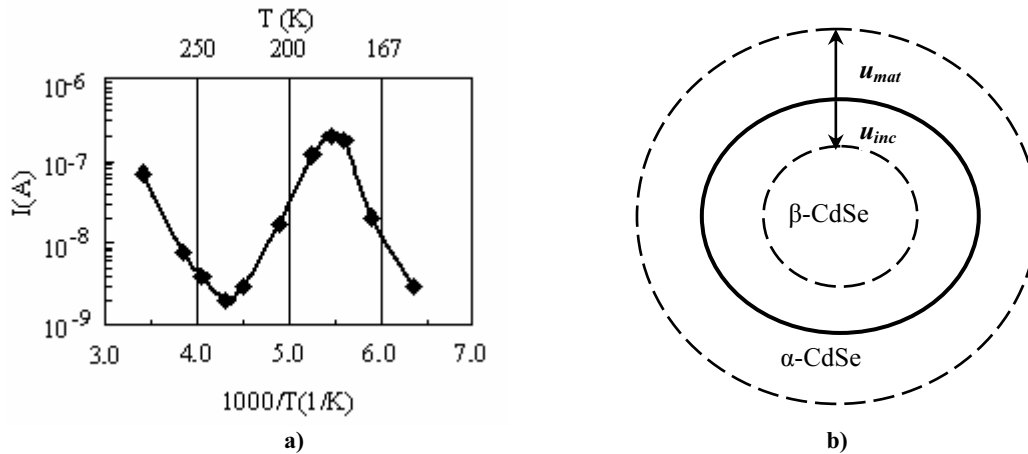


Fig. 1 Principal characteristics of the ADCTD phenomenon: a) temperature dependence of dark current measured during thermocycling procedure (160–270 K); b) schematic picture of the investigated object: matrix- $\alpha\text{-CdSe}$ and inclusion $\beta\text{-CdSe}$ border.

Thus, in the next section it will discuss these phenomena using both the electrophysical and structural data and the elements of elasticity theory.

3 Discussion To interpret the experimental data, we model our system as $\alpha\text{-CdSe}$ matrix, containing the inclusion (nucleus) of another (foreign) crystal phase, e.g. $\beta\text{-CdSe}$. In Fig. 1(b) it is schematically shown that the foreign inclusion creates elastic tensions the “matrix-inclusion” border.

If the inclusion is removed from the matrix, then its outer border will move outward by u_{inc} . At the same time, the matrix inner border will move inside by u_{mat} . Thus, in order to restore the initial conditions, it is necessary to compress the inclusion, by the value u_{inc} and to expand the matrix by u_{mat} . Thus,

$$u_{mat} \neq u_{inc} \rightarrow u_{mat} - u_{inc} = u_o \neq 0 \tag{1}$$

In other words, we have a contact model of two structurally different substances, $\alpha\text{-CdSe}$ and $\beta\text{-CdSe}$, with their individual elastic parameters. Note, we shall use only normal component of elastic forces in further discussions. It is important to realize that this model works (considering all experimental data) if the forces that act on different parts of the border surfaces are constant in time and are not equal: $f_{mat} = f_{inc} \neq \text{const}$ (here f_{mat} is the elastic force from the side of matrix, f_{inc} is the elastic force from the side of inclusion). Assuming that the inclusion is a sphere, the expression for the inter phases boundary tensions is given by [6]:

$$P_o = \frac{4k_{inc} \cdot \mu_{mat}}{3k_{inc} + 4\mu_{mat}} \frac{\Delta V}{V_o}, \quad (2)$$

where, V_o is the inclusion volume, ΔV is the change in the inclusion volume, k_{inc} is the modulus of dilatation for the inclusion, and μ_{mat} is the shear modulus for the matrix. Let us suppose, that the inclusion undergoes the structural transformation, when $\Delta V/V_o = 0.01$. We then, according to Eq. (2), estimate the boundary tensions $P_o \sim 10^4 \text{ kg/cm}^2 \sim 10^9 \text{ Pa}$ for the inclusion, giving the values of k_{inc} and $\mu_{mat} \sim 10^6 \text{ kg/cm}^2$. This value of boundary tension is two orders of magnitude higher than 10^7 Pa required for the transition [1] and, hence, it is enough for the initiating the new phase nucleus growth in the matrix or the $\beta\text{-CdSe} \rightarrow \alpha\text{-CdSe}$ transition. Hence, we may conclude that the inclusion size increases, with simultaneous increasing of the intergrain boundary surface. The intergrain boundary surface growth corresponds to the surface charge growth which provides the chemical bonds formation. Thermally stimulated (during cooling) structural transformations lead to the breaking of chemical bonds. Electrons, previously participating in the formation of the chemical bonds, are activated into the conduction band and give their contribution to the measured current.

When the sample is heated, the reversible structural transformations result in restoration of the chemical bonds, previously broken during cooling. Thus, the electrons required for the formations of these chemical bonds, are removed from the conduction band, which is registered as anomalous fall of current, giving the ADCTD.

The described situation is supported by the structural investigations of the CdSe layers. It is established that the initial ($\alpha + \beta$) CdSe structure contains the metastable nucleus of $\beta\text{-CdSe}$ phase. The temperature of 180 K, where ADCTD is registered, is the temperature of structural transition in the layers [7].

As long as we know the grain boundary tension, P_o (Eq. (2)), it is possible to determine the tension distribution in the matrix at the structural transition. For this, we shall use the equilibrium conditions for an isotropic body in the situation when the deformation is caused by the forces normal to the surface [6]. Considering Eq. (2) we obtain:

$$2(1 - \nu) \text{grad div } \vec{u} - (1 - 2\nu) \text{rot rot } \vec{u} = 0 \quad (3)$$

where ν is the Poisson's ratio, \vec{u} is the displacement. Solution of Eq. (3) without intermediate manipulations can be written as follows:

$$\sigma_{rr} = P \left(\frac{R_o}{r} \right)^3; \quad \sigma_{\varphi\varphi} = \sigma_{\theta\theta} = \frac{P}{2} \left(\frac{R_o}{r} \right)^3, \text{ where } r \geq R_o, \quad (4)$$

R_o is the radius of an inclusion. Let us try to evaluate a transition region's size for the $\beta\text{-CdSe}$ phase to $\alpha\text{-CdSe}$ transformation. Let the minimal necessary tension P_n , which initiates $\beta \rightarrow \alpha$ transition to be n times less than the grain boundary tension P_o (2) then $P_o/P_n = n$. Then for one thermocycle we obtain from Eq. (4)

$$P_n = P_o \left(\frac{R_o}{r_1} \right)^3$$

$$r_1 = R_o \sqrt[3]{n} \quad (5)$$

in general, for m -th thermocycle

$$r_m = R_o n^{\frac{m}{3}}. \quad (6)$$

Thus, it is obtained that the radius of the inclusion, r_m , will grow with the number of thermocycles.

So far, as the intergrain boundary surface $S \sim r_m^2$, and the dark current changes $\Delta I_d = I_{max} - I_{min}$, as in Fig. 1a, are conditioned by the charges changes at the inter phase surface, then

$$\Delta I_d \sim \Delta S \sim \Delta r_m^2 \sim R_o n^{\frac{2}{3}(m-1)} \left[n^{\frac{2}{3}} - 1 \right], \quad (7)$$

I_{max} – maximal value of the dark current for the curve, I_{min} – minimum value of the dark current for the same curve, Δr_m^2 – radius in square difference for two successive thermocycles. We may consider that r_m is a parameter of nonuniformity of our object and the current growth change is dependent on the structural parameter, Δr_m .

4 Conclusion In conclusion, we performed analysis of structural and electrophysical properties of two phase polycrystalline cadmium selenide. We have established that the structural transformations in this system are due to the thermo-stimulated elastic tension arising from the differences in the thermal expansion coefficients of different phases. We have also shown that the anomalous current changes (the increase with the decreasing temperature and vice versa) are due to the reversible breakage of chemical bonds at the intergrain boundary between two structural modifications of CdSe (α - and β -CdSe), which results in the activation of electrons to the conduction band. Furthermore, we have introduced the parameter of nonuniformity of a structure, r_m , and have shown that r_m is radius of the metastable β -CdSe phase; the correlation between the current change, ΔI_m and the nonuniformity parameter, Δr_m has also been obtained;

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