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Injection Spectroscopy of Deep Traps in Nanostructured Films of Cadmium Sulfide

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Nanocrystallin CdS films with controlled stoichiometry deposited by CSVS were investigated by method of the current-voltage characteristics in ITO/CdS /In structures. It was shown that in the case of cadmium excess (S <Cd) charge flow mechanism both in the dark and under illumination is determined by bimolecular recombination in the material. In the case of excess sulfur (S>Cd) charge flow mechanism is determined by monomolecular recombination. In the band gap of CdS with excess of cadmium there was detected localized states with energy E_t = 0.514 ± 0.026 eV, while in the material with Excess sulfur there are two localized states with energy E_{t1} = 0.514 ± 0.026 eV and E_{t2} = 0.700 ± 0.026 eV. Full concentration of localized states is more than $2 \cdot 10^{21}$ m^{-3} – $5 \cdot 10^{22}$ m^{-3}. Dependence of injection in parameters and nature of injection in the structures based on nanostructured CdS films on their stoichiometry was determined.

Keywords: CdS film,Nanostructured layer, Current-voltage characteristic, Differential approach, Injection spectroscopy, Trap

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1. INTRODUCTION

Recently CdS films have been intensively investigated due to the possibility of using it as base layers of photo- and gas sensors, thin films transistors, vidicons, LEDs, electrochemical cells, electroluminescent devices, window layers of high efficiency solar cells on the base of absorbing layers of CdTe, $CuInSe_2$ (CIS), $CuIn_{1-x}Ga_xSe_2$ (CIGS), $Cu_2ZnSnSe_4$ (CZTSe) and others [1-2].

For practical use in micro-and optoelectronics, solar energy CdS films require optimization of their optical and electrical characteristics which determined by the ensemble of intrinsic point defects and uncontrollable impurities [3]. If these defects are charged, they form traps and recombination localized states (LS) in band gap (BG). The need of focused control of such properties led to considerable interest of researchers to studying the defect structure of CdS and determining its impact on the physical characteristics of the material. At the same time, despite the large number of works devoted to this issue, the energy spectrum of LS in CdS BG remains insufficiently explored, first of all, it refers to film samples obtained by different techniques of condensation in vacuum.

The method based on the analysis of steady-state current-voltage characteristics (CVC) in regime of space charge limited currents (SCLC) [4-5] is one of the most suitable methods of studying of LS in semiconductors such as CdS. It combines the simplicity of the experimental equipment and their high sensitivity to low concentrations [4-5].

This method in various modifications [6-8] is widely used for determined parameters of traps in a large group of wide semiconductors and dielectrics. However, in classic form, CVC SCLC method has several disadvantages that lead to a significant reduction of informativeness and some incorrectness of obtained results [9].

That is why in some studies [10-12] there were provided approaches that can rid disadvantages of existing method of analysis of CVC SCLC and receive the most detailed information about LS in the range of wide BG material directly from the experimental CVCs by their differential processing (injection spectroscopy (IS) method), i.e. by solving the inverse problem of research. Differential approach gives also the possibility to determine the charge flow mechanism in multilayer structures by analyzing the CVC [13-15].

This paper presents the results of calculation of LS parameters in nanocrystalline CdS films depending on the stoichiometry and conditions of obtaining samples using the low-temperature approximation of differential approach, as well as the results of the charge flow mechanism.

2. EXPERIMENTAL DETAILS

CdS films were prepared by vacuum evaporation of the CdS powder of semiconductor-quality purity by vacuum evaporation of the semiconductor-quality purity by close-spaced vacuum sublimation (CSVS) at substrate temperature of T_s = 600-640 °C and evaporator temperature of T_e = 720-750 °C. To control the stoichiometry of layers during the process of deposition there was co-evaporation of sulfur at temperatures T_{eS} = 60-200 °C. The deposition was performed onto glass substrate covered by conductive ITO underlayer. Peculiarities of the films obtained have been described in detail

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in [16]. In contact layer (area ~ 0.02 cm^2) was obtained by vacuum evaporation. This material allows to realize the injection of charge carriers into CdS layer.

Surface morphology and stoichiometry of the films obtained were studied using electron microscope Hitachi S-806 and Superprobe-733 JEOL, respectively.

Dark and light quasi steady-state CVCs in forward and reverse directions were measured at room temperature by the standard automated tester 14 TKS-100 (Russia). The voltage was changed step by step with the period of 160 ms, and current measurement was carried out at 90 ms after supplying voltage. Measuring the light CVC was carried out using white light from a halogen lamp with intensity of ~30 W/m^2.

3. THEORETICAL PART

Recognition of charge flow mechanism in the samples was carried out by the method of differential processing of CVC, developed in the works [10-17]. This method allows us to determine distinction between concomitant and competing charge-flow mechanisms in the structures and allocate high field processes among them. It is possible by joint analysis of $j - U$, $\eta - U$ and $d(\ln\eta)/d(\ln U) - U$ dependencies, where j is the current density; U is the applied voltage and $\eta = d(\ln j)/d(\ln U)$

$$\left(\eta = \frac{d(\ln j)}{d(\ln U)},\ \eta' = \frac{d^2(\ln j)}{d(\ln U)^2},\ \eta'' = \frac{d^3(\ln j)}{d(\ln U)^3}\right)$$

The IS method was used only for the processing of CVC in the SCLC regime. The basic ratio of IS method derived in [10-12] is the following:

$$n_{fL} = \frac{\eta}{2\eta - 1}\frac{jL}{e\mu U}, \quad (1)$$

$$n_{sL} = \frac{\rho_L}{e} = \frac{2\eta - 1}{\eta}\frac{\eta - 1}{\eta}\left[1 - \frac{\eta'}{\eta(2\eta - 1)(\eta - 1)}\right]\frac{\varepsilon\varepsilon_0 U}{eL^2}, \quad (2)$$

where e is the electron charge; μ is the mobility of charge carriers; L is the sample thickness; ε_0 is dielectric constant; ε is the dielectric permittivity of the material; n_{fL} is the concentration of free charge carriers at the anode (later the index L in the ratio will be not used); n_{sL} is the actual concentration of carriers captured by local states near anode; ρ_L is the space charge density at anode responsible for limiting the current through the sample.

Using the well known relation between the concentration of free carriers and the position of the Fermi level, it is easy to write an equation to determine the energy scale of the LS study

$$E_F = kT\ln\frac{N_{c(\upsilon)}e\mu}{L} + kT\ln\frac{j}{U} + kT\ln\frac{\eta}{2\eta - 1}, \quad (3)$$

where E_F is the position of the quasi Fermi level for injection; k is the Boltzmann constant; T is the temperature; $N_{c(\upsilon)}$ is free effective density of states in the conduction (valence) band.

Distribution function of carriers localized at deep centers, is obtained by differentiation of (2) for the energy

$$\frac{dn_s}{dE_F} = \frac{1}{kT}\frac{2\eta - 1}{\eta}\left\{1 + \frac{3(\eta - 1)\eta\eta' - \eta\eta'' + 3\eta'^2}{\eta^2\left[(2\eta - 1)(\eta - 1) - \eta'/2\right]}\right\}\frac{\varepsilon\varepsilon_0}{eL^2}U. \quad (4)$$

The distribution function of LS density for the energy $h(E) = dN_t/dE$ at low-temperature approximation is thought to coincide the function that describes the distribution of localized carriers. However, this leads to errors during playback the shape of distributions of traps and determining their depth (E_t) and concentration (N_t) [9, 12, 17].

At a high temperature approximation function $h(E)$ can be found from the convolution:

$$\frac{dn_s}{dE_f} = \int_E h(E)\frac{df(E - E_f)}{d(E - E_f)}dE, \quad (5)$$

where $f(E - E_F)$ is the Fermi-Dirac function.

The joint solving of equations (3), (4) and (5) allows to find $h(E)$ function in BG of material directly from the experimental CVC SCLC measured at arbitrary temperature. For this purpose it is necessary to define three derivatives at each point of CVC in log-log scale.

Mathematically, the task is reduced to the construction of cubic spline that approximates the experimental data. Then the cubic spline is differentiated in nodes and finally $h(E)$ function is found from the convolution (5).

Physically, the ability to scan the energy distribution of traps at the injection of charge carriers from the contact was caused by the following. With the increasing of applied voltage the quasi Fermi level moves in BG of the material and it occurs the filling of LS by free carriers and changing of the conductivity of the structure. Since there is a correlation between the values that can be experimentally measured (j, U), and those that characterize the distribution of traps, (E_F, ρ), thus each point CVC carrying an information about corresponding section of the energy spectrum of LS.

In this paper, in order to determine parameters of LS in CdS films the low-temperature approximation of IS method was used. In this case, the Fermi-Dirac statistics in (5) replaced by the Heaviside function. In order to calculate the energy levels of traps in BG and its concentration the methods proposed in [11, 18] was used. Obtained results are verified by solving the direct problem of the experiment and building CVC SCLC by the known parameters of LS. Coincidence of form of input and reconstructed CVC was indicating about the accuracy of determining of the parameters of deep traps in the material [17].

4. RESULTS AND DISCUSSION

Electron microscope images of surface of CdS films are presented in Fig. 1. As we expected layers were continuous and had finely dispersed nanocrystalline structure (Fig. 1a). Further deposition led to form nanorods on the surface of CdS films (Fig. 1b). Data of element composition studying proves that layers obtained at T_{eS} <80 °C contain the excess of cadmium (Cd > S by 3-5%), and at T_{eS} >120 °C there is the excess of sulfur (Cd < S by 2-3%).

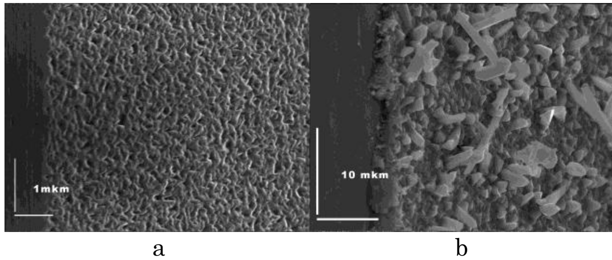

Fig. 1 – SEM images of CdS film surface: short- (a) and long-term growth phase (b)

Fig. 2a displays dark and light CVC (in forward and reverse bias) of ITO/CdS/In multilayer structure, where CdS films have excess of cadmium (Cd > S by 3-5%). in Fig. 2b shows the forward and reverse CVC curves of ITO/CdS/In multilayer structure with excess of sulfur (Cd < S by 2-3%). The analysis of CVCs indicates that the resistivity ITO/CdS/In is equal about ($5 \cdot 10^6$-10^7) Ohm·cm. Fig. 2 shows that the high content of sulfur in CdS film leads to increase the photoconductivity of the structure. Conductivity of illuminated material increases almost about three orders of magnitude at the excess of sulfur (Fig. 2b), whereas at the deficiency of sulfur increase of photoconductivity i only about one order in magnitude. The shortage of cadmium was found to reduce the dark conductivity of the structure by two orders of magnitude.

Several almost linear sections with different slope were observed in the dark CVC of the structure ("+" ITO) both with excess and deficiency of sulfur at the region of high applied bias. Usually the areas with dependence of current on voltage with type: $I \sim U$, $I \sim U^{1,5\text{-}2}$, $I \sim U^{3\text{-}4}$ were allocated. In some cases, after super linear behavior there was quadratic one.

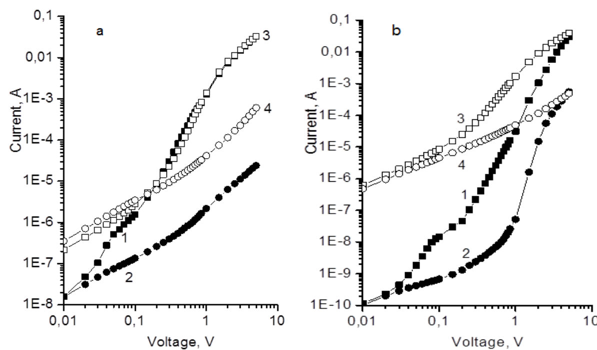

Fig. 2 – CVCs of ITO / CdS / In multilayer structures: a) case with the excess of cadmium (Cd>S by 3-5%); b) case with the excess of sulfur (Cd<S by 2-3%); 1.3 - "+" ITO, 2, 4 - "+" In. Full symbols correspond to dark current, open ones correspond to light current under illumination of white light from a halogen lamp with intensity of ~30 W/m²

It should be noted that the features of CVC can be seen at $\eta - \log U$ dependences which allows to reveal the fine structure of CVC. Each point of the graph determines the angle of the current-voltage curve in a log-log scale. $\eta - \log U$ dependence were obtained by finding the derivative at each experimental point of CVC SCLC. As already mentioned, mathematically task was to build a cubic smoothing spline that approximates the experimental data and its differentiation in nodes. The results of the differential processing of dark and light CVCs are shown in Fig. 3 a–d and 3 e–h respectively.

Differential analysis of CVC slope (Fig. 3 c, d) [13-15] revealed two mechanisms in the nature of injected carriers: in the case of excess of cadmium ($S<Cd$) there is a bimolecular recombination in the material in the dark and under illumination, and it provides a differential slope of the CVC η =1.5. In case of sulfur excess ($S > Cd$) the principal mechanism of charge flow is monomolecular recombination, namely it provides a differential slope of current-voltage curves η = 2.

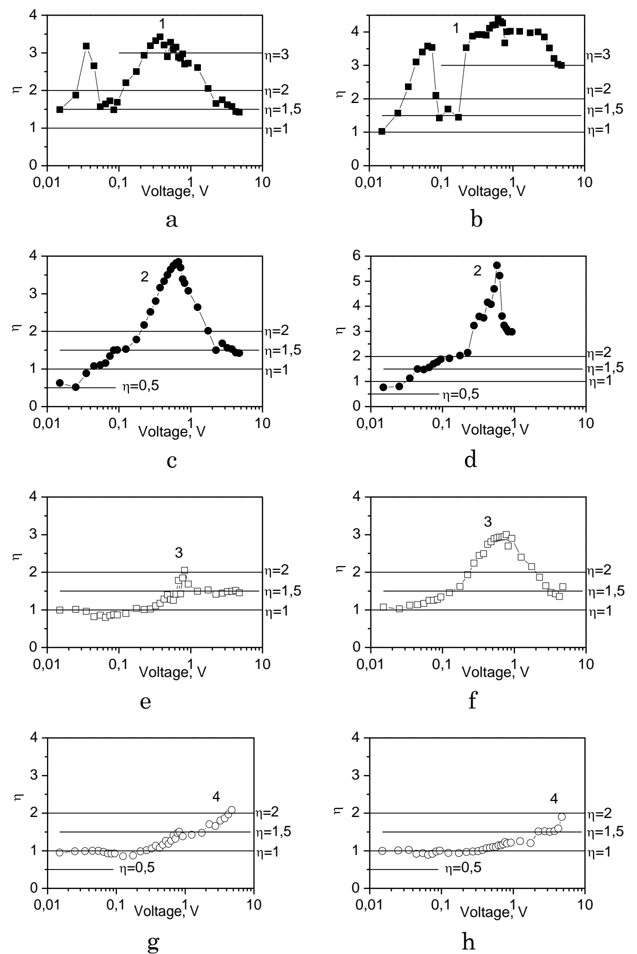

Fig. 2 – Differential slope α of CVCs: a, c, e, g films with the excess of cadmium; b, d, f, h films with the excess of sulfur; 1,3 - "+" ITO, 2, 4 - «+» In; full symbols (a-d) correspond to dark currents, open ones (e-h) correspond to currents under white light illumination

In all cases, there are jumps of current that characterized for SCLC. Mathematical processing of the corresponding curves gives the possibility to construct dependences $n_s - E_F$ (a) and $dn_s/dE_F - E_F$ (Fig. 4) and to determine the E_t, N_t values of traps which are presented in the wide BG material.

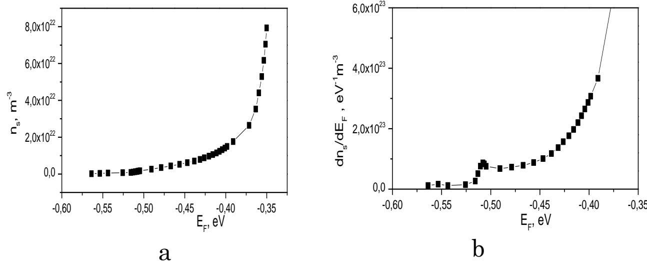

Fig. 4 – Typical differential curves $n_s - E_F$ (a) and $dn_s/dE_F - E_F$ (b), obtained as a result of processing the CVC SCLC, which allowed to determine the parameters of traps in the material

It was found that CdS with excess of cadmium characterized by LS with energy $E_t = 0.514 \pm 0.026$ eV. While in the material with excess of sulfur there were existed two LS in BG with energy of $E_{t1} = 0.514 \pm 0.026$ eV and $E_{t2} = 0.700 \pm 0.026$ eV. Concentration of refill charge carriers on these LS was varied from $2 \cdot 10^{21}$ m^{-3} to $5 \cdot 10^{22}$ m^{-3}. Respectively, the full concentration N_t of these LS is more than determined values.

Thus it was determined dependence of injection parameters and nature of injection in the structures based on nanostructured CdS films on their stoichiometry.

5. CONCLUSIONS

Nanocrystalline textured films of CdS with regulated stoichiometry deposited by CSVS method were investigated. The CdS layers obtained at T_{eS} < 80 °C was found to contain the excess of cadmium (Cd>S by 3-5%), whereas the CdS layers obtained at T_{eS} >120 °C contain the excess of sulfur (Cd<S by 2-3%). It was shown that in the case of excess of cadmium (S < Cd) charge flow mechanism in the structure ITO/CdS/In was determined by bimolecular recombination both in the dark and under illumination. In the case of sulfur excess main mechanism of charge flow was monomolecular recombination. There were determined LS with energy of $E_t = 0.514 \pm 0.026$ eV in CdS with excess of cadmium and with excess of sulfur - $E_{t1} = 0.514 \pm 0.026$ eV and $E_{t2} = 0.700 \pm 0.026$ eV by IS method.

Full concentration of localized states is more than $2 \cdot 10^{21}$ m^{-3} - $5 \cdot 10^{22}$ m^{-3}. Dependence of injection parameters and nature of injection in the structures based on nanostructured CdS films on their stoichiometry was determined.

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