

COOLING-STIMULATED REBUILDING PROCESS IN CdS

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ABSTRACT

Most processes of defect structure rearrangement in semiconductors due to influence of external factors have thermoactivation nature. The others can be related to athermic processes. However, some effects (conductivity layer formation and electron emission from surface) on the basic faces of CdS single crystals were found under cooling process. These effects can not be explain by present theories.

Our researches of dependence between the electron emission intensity with (0001)-face CdS crystals and the influence of external factors (external electric field directed along to surface, temperature of previous annealing) enabled to propose a mechanism of process conductive layer formation. It consists in rebuilding as minimum two metastable defects with different activation energies of electron desorption into vacuum.

INTRODUCTION

CdS singlecrystals are one of the modeling semiconductors. Reseaching of that material has been started in the 60-th years of last century. The high photosensitivity and the radiative recombination ability of CdS single crystals allow to use those widely in the optoelectronics as basic elements in radiation sources and receivers products. But some problems of stability parameters of devices on the base CdS are not determinated up to now, because that semiconductor crystals have the metastable defects. Evolution of such defects modifies the properties and characteristics of devices on cadmium sulphide base. That's why establishment of mechanisms of defects reconstruction processes and factors which stimulate them in CdS crystals surface layer still remains actual problem.

EXPERIMENTAL RESULTS AND DISCUSSION

The Institute for Semiconductor Physics National Academy of sciences of Ukraine researchers discovered an effect named Anomalous Temperature Dependence of Conductivity (ATDC) [1]. It was observed in pure and alloyed CdS, CdSe crystals and their films. The effect appears in anomalous growth on a few orders of dependence of the dark current on the (0001)-face at crystals cooling from 300 to 77 K instead of classic exponential decrease. Typical temperature dependence of the dark conductivity (I_d) on the (0001)- and (000 $\bar{1}$)-face of CdS high-resistance crystals at cooling and heating in temperatures diapason 4,2-450 K is shown on Fig. 1.

The deviation of classic value conductivity revealed in other crystals too:

- the conductivity of InSb, InAs crystals decrease at the cooling but its stabilized and remains invariable at the defined temperature value [2];
- in some p-type crystals under cooling action is observed a conductivity type inversion;
- the effect p-channels forming on surface of Ge crystals revealed at low temperatures in vacuum. The conductivity of that channels is on a little orders higher by volumetric [3, 4].

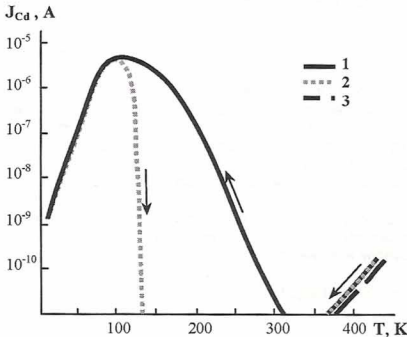


Figure 1. Temperature dependence of the dark current on the (0001)-face continuous and dot line) and (000 $\bar{1}$)-face (dash line) of CdS crystals at cooling (1,3) and heating (2,3).

The ATDC effect does not observe on freshly cleaved crystals surface. After sample has been cleaved it is necessary some time (Δt) for effect appearance which is inversely proportional to the temperature of cleaved crystals. The conductive surface layer forming on (0001)-face of CdS crystal and dark current saturation becomes during a few minutes after crystals cleaving at the room temperature. Analogic process continued during a several tens of minutes (~ 40 min) at the temperature of liquid nitrogen. Ambient atmosphere (air, oxygen, rare gas) did not have any influence on time value Δt .

In our laboratory was discovered the effect of electron emission into vacuum out of basal face of CdS single crystals during cooling from $T=300$ to 80 K without any surface excitation [5]. As in ATDC case for this effect appearance is necessary some delay after crystals cleaving. Established that of emitted electrons energy is 2-6 eV for (0001)- and 30-50 for (000 $\bar{1}$)-face of crystals. But electrons emission from S-face is observed only into first a few minutes sample heating above liquid nitrogen temperature point, and their flux density is much lesser than similar Cd-face.

It's known, that the CdS crystals have piezo- and pyroelectric properties. A maximum electric intensity value at the CdS cooling from 300 to 80 K reaches $\sim 10^5$ V/cm. That's why energy of emitted from surface electrons suppose to be

at few tens eV range which was observed for $(000\bar{1})$ -face crystal. The electrons emission effect from Cd-face still remain unsolved. By authors [6] established similar effect low temperature electron output from CdSse microcrystal into silicate glass matrix under illumination.

The correlation both effects: electrons emission and ATDC at cooling was established (the same Cd-face of crystal, temperatures range and value Δt). Both these effects can not be explain by existent theories. In our laboratory were made some additional researches for elucidation mechanism of crystals defect structure rearrangement on $(000\bar{1})$ -face surface layer at the cooling.

High- ($n_e < 10^{10} \text{cm}^{-3}$) and low-resistance ($n_e \sim 10^{14} \text{cm}^{-3}$) CdS crystals were studied. The crystals were synthesized in the Institute for Semiconductor Physics, National Academy of sciences of Ukraine. The oriented experimental samples cut out of a single crystal boule were cleaved perpendicularly to C axis, thus allowing to obtain S $(000\bar{1})$ and Cd $(000\bar{1})$ -surfaces Fig. 2). Then the sample were placed into a vacuum cryostat ($p \sim 10^{-5} \text{Pa}$) allowing to study the electron emission and conductivity in the temperature range from 80 to 500 K. The energy distribution of emitted electrons was examined using the stopping potential method, a БЭУ-6 was used to record the flow [7].

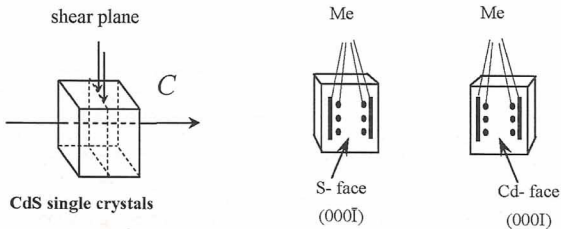


Figure 2. The experimental samples with the metal contacts on the basal faces.

The obtained results have shown that electrons emission intensity depends on crystals conductivity value (Fig. 3). The increasing of crystal specific resistance leads to decreasing of emitted electrons stream during cooling or heating process. Only in the case of low-resistance crystals (40 Ohm-cm) was observed precise low-temperature maximum at $T=130 \text{K}$.

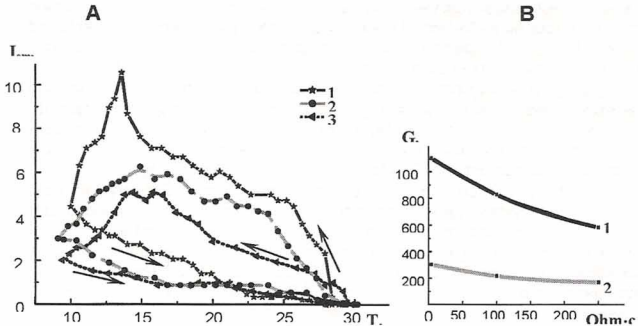


Figure 3. The influence of specific resistance of CdS crystals on electron emission intensity (A) and electron stream (B) from (0001)-face at cooling:

A: 1 – $\rho=40$ Ohm-cm, 2 – $\rho=1000$ Ohm-cm, 3 – $\rho=2500$ Ohm-cm;
 B: 1' – cooling, 2' – heating.

Electrons emission intensity depends on samples cooling rate (Fig. 4). Augmentation of examples cooling speed in 2 times in the temperature range from 180 to 270 K intensity leads to increase value of electrons emission into 4-5 times (Fig. 4). Sharp deceleration examples cooling below $T=180$ K (curve 2' on Fig. 4) does not bring to the decrease of electrons stream respectively (curve 2 on Fig. 4) but is observed stabilization of this value. When cooling process of CdS crystal was stopped and constant temperature value of sample was supported we observed a slow isothermal decrease electrons emission intensity from (0001)-face. At a fixed sample temperature the decreasing of electron stream intensity $I(t)$ is an exponent. Since the temperature value exposition of samples was raising the relaxation speed of emissive dependence was increasing as well. The corresponding dependence are shown on Fig. 5. They characterize different speed of relaxation processes, which are associated with defects structure rearrangement. Only sample heating over $T=350$ K after full isothermal relaxation of electrons emission leads to full restore of the crystals emissive properties.

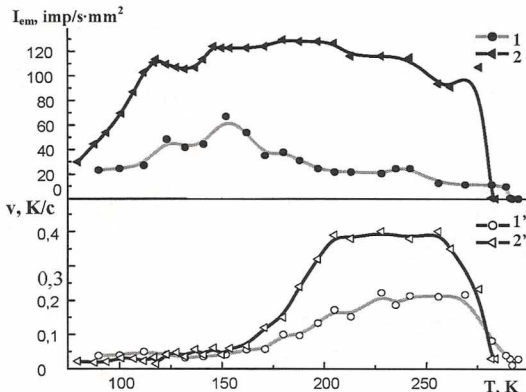


Figure 4. Dependence of electron emission intensity (1, 2) on cooling rate (1', 2' respectively) for high-resistance ($\rho=2500$ Ohm-cm) CdS crystals.

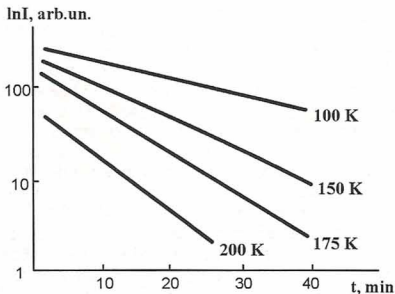


Figure 5. The isothermic relaxation of electron emission amplitude from Cd-face at the different fixed temperature values of CdS crystals.

To establish nature of processes which leads to low-temperature electrons emission effect the influence of vacuum thermal crystals annealing was researched. After observation of electron emission effect at cooling from room temperature the sample was annealed at $T=420$ K during 20 min. It was discovered, that the electrons emission effect from (0001)-face crystal take place from the beginning moment of cooling process from $T=420$ K as in case when

cooling starts at room temperature (Fig. 6). Maximum emission intensity value in both cases reaches in temperature span $T=130\pm 250$ K (see Fig. 6).

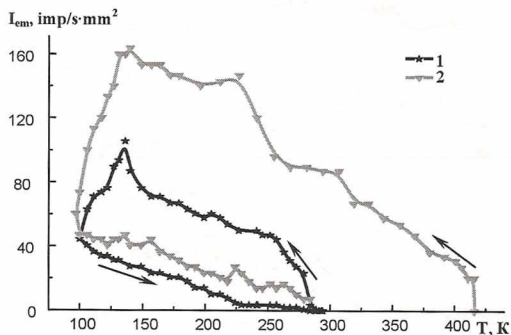


Figure 6. Electron emission intensity from (0001)-face of low-resistance ($\rho=40$ Ohm-cm) CdS crystals before (1) and after (2) high-temperature annealing ($T=420$ K, $t=20$ min).

The annealing temperature increasing up to $T=550$ K stimulates the emissive processes from Cd-face of crystal. But substantial decreasing of electrons emitted stream was recorded at annealing temperatures higher than $T=550$ K. The mass-spectrometer measurements of thermal desorption components from CdS crystals showed that emission into vacuum of cadmium atoms begins at the temperature higher than $T=550$ K. Most likely it was Cd_i internodular atoms which are shallow donor centres in crystal.

An external electric field impressed along emitting face of crystal has an influence on electron emission dependence. Received dependence is presented on Fig. 7. Impressed electric field strength less than $E=1,5$ V/cm to low-resistance ($\rho=40$ Ohm-cm) and $E=5$ V/cm to high-resistance ($\rho=2500$ Ohm-cm) crystals leads to increasing of electrons emitted stream at the simples cooling. The changes in form of emissive dependence spectrums were observed also. Impressed electric field strength stimulates high-temperature electrons emission in the region 175-300 K. At the increasing of electric field strength to $E=3,0$ V/cm for low-resistance and to $E=10$ V/cm for high-resistance CdS crystals emission intensity from (0001)-face decrease to initial level (electrons emission intensity without impressing electric field).

Established that equilibrium free carriers concentration of high-resistance CdS crystals at $T=300$ K is very low ($n_e < 10^8$ cm⁻³). During cooling process in (0001)-face surface is forming a conductivity layer up to 500Å thickness with carriers concentration $n_{e \text{ surf}} \sim 10^{12}$ cm⁻² at $T=100$ K. The additional free electrons can appear by thermal or field ionization of local donor centres. But in these crystals in equilibrium conditions the electrons are located

only on deep centres and thermal excitation energy is evidently insufficient. That's why in our opinion the thermal ionization mechanism does not work. The ionization of deep electron trapping sites by pyroelectric field ($E_{\max}=7 \times 10^4$ V/cm at $T=80$ K) is impossible too. Because of that we think the low-resistance layer formation on Cd-face after crystal's cleaving associated with the processes where electronic and ionic subsystem of crystal take active part. It known that CdS crystals were characterized by high concentration of Cd superstoichiometric composition. Migration of shallow donors (Cd_i) to (0001)-face and their localization in surface layer on defect places (at the dislocations, at a Shottky defect points) with formation of clusters and microstructures takes place after crystal's cleaving at band bending field. Especially since the possibility of moving and generation of dislocations in CdS crystals was observed at the low temperature not less than $T=1.8$ K [8]. Obviously, that Cd_i internodular atoms which are localized on structural defects form the metastable centres. In the cooling process these centres are transforming whit free electrons releasing.

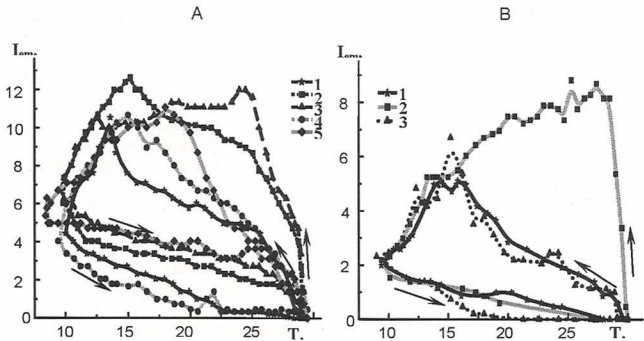


Figure 7. Dependence of electron emission intensity from (0001)-face of low-resistance (A) and high-resistance (B) CdS crystals on electric field intensity directed along surface
 A ($\rho=40$ Ohm-cm): 1 – $E=0$ V/cm, 2 – $E=0,75$ V/cm, 3 – $E=1,5$ V/cm, 4 – $E=2,25$ V/cm, 5 – $E=3,0$ V/cm;
 B ($\rho=2500$ Ohm-cm): 1' – $E=0$ V/cm; 2' – $E=5$ V/cm; 3' – $E=10$ V/cm.

A high-temperature annealing causes diffusion of Cd internodular atoms from crystal volume to surface and growth of their concentration near surface layer. However at the annealing temperature $T_a > 550$ K established cadmium atoms emission into vacuum from CdS crystals. At the same time intensity of emitting electrons stream was decreasing. It confirms our hypothesis that source of free electrons at samples cooling is defects structure rearrangement by near-surface Cd_i atoms participation.

CONCLUSIONS

1. The process of conductive layer formation at the cooling of CdS crystals consist in rebuilding of Cd_i-containing metastable defects.
2. The appearance of pirofield leads to electron emission from near-surface layer of (0001)-face into vacuum and determines energy of emitting electrons.
3. The values of piroelectric field intensity and annealing temperature influence on the effect of electron generation in near-surface layer of (0001)-face CdS crystals.
4. Taking into account the dependence of electron emission intensity from (0001)-face of CdS crystals on electric field intensity directed along surface we propose a mechanism of rebuilding process. It consists in rearrangement at least two metastable defects with different activation energies of electron desorption into vacuum.

REFERENCES

1. Korsunskaya N.E., Markevich I.V., Shulga E.P., Sheinkman M.K. *Semicond.Sci.Technol.* **7**, 92 (1992).
2. Balagurov L.A., Borkovskaya O.Yu., Dmitruk N.L. at al. *Fiz. I Tekhn. Polupr.* **10**, 1108 (1976).
3. Vul B.M., Zavaritskaya E.I., Sokol E.G. *Pisma v JETF.* **30**, 517 (1979).
4. Abessonova L.N., Dobrovolskij V.N., Zharkih Yu.S. // *Ukr.Fiz.Zhurn.* **24**, 409 (1979).
5. Pavlyk B.V., Cybulyak B.Z., Goryn` Ya.M., Kozak I.V. *Func. Mat.* **6**, 83 (1999).
6. A.M.Turkhin, M.N.Tolstoj, L.B.Glebov, V.L.Savelev *Phys.Stat.Sol.* **99**, 155 (1980).
7. Matulskij V.B., Pavlyk B.V., Tyutko I.O. *PTE*, **3**, 47 (1991).
8. Salkov E.A., Tarbayev G.A., Shepelskyj G.A. *Ukr.Fiz.Zhurn.* **26**, 1570 (1981).