

A. FEDOTOV*, A. MAZANIK, S. MANEGO, M. TARASIK,
YU. TROFIMOV, A. ULYASHIN and A. YANCHENKO

*Dark I–V characteristics of CdS_xSe_{1-x}
microcrystalline films*

ABSTRACT

The electrical properties of microcrystalline CdS_xSe_{1-x} films ($0.5 < x < 1.0$) manufactured by the improved RF sputtering technology under influence of hydrogen plasma treatment and following annealing in different regimes are described. It was exhibited that incorporation of hydrogen from plasma produced drastic changes which occurred in the dark I–V characteristics and resistivity of the films. Dark conductance revealed increasing under hydrogenation and a long-time relaxation (decrease) with time for low temperature hydrogenation. The nonmonotonic influence of the film dimensions on dark conductance and I–V characteristics is shown, which is differentiated for as-received and hydrogenated films and depends on regimes of hydrogen plasma treatment. Such behaviour is associated with transformation of potential relief of hydrogenated films.

* Corresponding author. Tel. 375-17-2265212, 375-17-2277495; fax: 375-17-2016001
E-mail address: fedotov@phys.bsu.unibel.by (A. Fedotov). Belarusian State University,
F. Skaryna Pr. 4, 220050 Minsk, Belarus.

1. INTRODUCTION

$\text{CdS}_x\text{Se}_{1-x}$ films are being studied with renewed interest owing to their use in optoelectronic devices and potential application in solar cell structures [1]. However, the reproducibility of photoelectric and other properties of $\text{CdS}_x\text{Se}_{1-x}$ thin films is rather sensitive to the technology of their manufacturing. This is due to polycrystalline structure, native defects in the grain bulk and surface contamination of the films [2,3].

To prepare $\text{CdS}_x\text{Se}_{1-x}$ thin films with the desired photoelectronic properties, usually different doping techniques are used [1,2]. At the same time, new techniques such as plasma hydrogenation and ion implantation of hydrogen, which are applied in a large scale in semiconductor devices technology, have been less studied with respect to II–VI compounds, especially $\text{CdS}_x\text{Se}_{1-x}$ films [4]. Among other factors which determine necessity of hydrogenation, the polycrystalline structure of the films is of prime importance due to the influence of extended defects (grain boundaries, dislocations, precipitates, fluctuations of composition, etc.) and native defects in the grain bulk. Passivation of these defects and possible doping effects under hydrogen treatment of $\text{CdS}_x\text{Se}_{1-x}$ films can significantly change their electric properties [4]. However, if for such semiconductors as silicon and III–V compounds, the processes proceeding under hydrogenation have been clarified to a large degree [5,6], for II–VI compounds they have not been adequately investigated.

The main purpose of this work was to investigate the effect of hydrogen plasma treatment and following annealing on dark electric properties of microcrystalline $\text{CdS}_x\text{Se}_{1-x}$ films. This was done with two aims: (a) to improve control over the dark properties of these compounds; (b) to study possible influence of the intensity of electric field and dimensions of the samples on the carrier transport in microcrystalline $\text{CdS}_x\text{Se}_{1-x}$ films before and after hydrogenation. Incorporation of hydrogen from plasma

produced somewhat unexpected results, since drastic changes occurred in the dark response of the films.

2. TECHNOLOGY OF FILM PREPARATION

A triode system of sputtering with additional RF bias is more preferable for manufacturing of II–VI films. Triode system provides sufficient velocity of deposition (0.05–0.1 $\mu\text{m}/\text{min}$) at the least specific power on target (of the order of 1 W/cm^2). An extent of contamination by foreign gas impurities, which depends on the relation of operating pressure to the film deposition rate is much smaller for layers produced in such a system.

The quality of targets is the main factor which controls properties of films in many respects. In this connection, targets should offer mechanical strength, homogeneity in composition and density. Preparation of the films with uniform thickness and homogeneous properties over the area on substrates of large dimensions necessitates the use of targets with 100 mm diameters and upwards. To prevent overheating of the target during sputtering, we used special construction and method of production of the cathode unit. With this goal we used cold molding of targets from high-purity powders of II–VI materials and special powders with good electrical and thermal conductance. It made possible to produce double-layered monolithic targets (shaped as planar discs) without application of organic binders or conductive adhesives to create good contact and attach the target to cathode.

The films were deposited onto insulating substrates (fused silica, aluminium oxide ceramics, sapphire, oxidized single-crystalline silicon, glass, etc.) [7]. To improve adhesion of films and substrates the underlayer of Ta_2O_5 deposited (0.03 to 0.05 μm by thickness) on substrates was used.

We used a triode ion-plasma DC sputtering system with an additional RF-biasing with 13.56 MHz for II-VI films deposition. Density of ion current was between 0.2 and 0.35 mA/cm², bias voltage was 2 to 4 kV for the target-substrate gap of 50 mm. When using plasma-creating gas argon of high purity (99.995 vol. %) and its pressure 1.4 to 2.6 Pa and the foregoing conditions, rates of film deposition were about 0.03–0.06 μm/min. The target and substrate temperatures were stabilized at 150–200°C and 160–380°C, respectively. In such sputtering conditions the films of II–VI with thickness from 0.4 to 2.0 μm were deposited.

As-received films are characterized by the quasi-amorphous structure and very low photosensitivity. For activation of their photoresponse, the films were recrystallized and doped in special activating powder mixtures (charge) over the temperature range 390–430°C. In the elaboration of photosensitivity activation process in powder mixtures the following requirements have to be taken into account:

- material of powder charge should be of high chemical stability and inactivity to the film material;
- the major material of charge (powder matrix) should be uniformly saturated by dopants and fluxes at elevated temperatures and then reproducibly loose the doping microquantities of alloying composition required for the film;
- the charge should have minimal absorption of moisture to prevent the creation of HCl vapors due to interaction of water with copper and cadmium chlorides; exposure of the film material by these vapors makes it more porous and thin;
- particles of powder charge should have rounded or oval shape for their good mixing and their easy removal from the film surface after activation process (the lack of sintering effect);
- the charge material should have enhanced thermal conductivity that improves homogeneity of thermal fields in the charge bulk; the last is important for uniform doping and recrystallization.

As has been shown, the charge based on high purity TiO_2 features all these properties. The above-mentioned improved technology makes possible to prepare high-quality photo-sensitive II–VI films and their solid solutions and also photoresistive structures on their basis.

3. EXPERIMENTAL

In our experiments the n-type films 1 μm thick were deposited onto substrates of aluminium oxide ceramics using described above technology [7]. As-received $\text{CdS}_x\text{Se}_{1-x}$ films with $0.2 < x < 1.0$ were characterized by the quasi-amorphous structure with grain sizes of about 10–30 nm, very low photosensitivity and very high dark resistivity (more than $10^{14} \Omega\cdot\text{cm}$ for low-doped films with $x < 0.5$). After activation heat treatment, the recrystallized films exhibited polycrystalline structures with the mean grain sizes around 1–3 μm (see Fig. 1). Note that grain sizes correlate with the duration of recrystallization process: the longer duration, the greater is a grain size.

Recrystallized films were subjected to hydrogen plasma treatment and following annealing. Activated, hydrogenated and annealed films were subjected to measurements of dark Hall effect, current-voltage (I–V) characteristics and equilibrium resistivity at room temperatures. Hydrogenation of the samples studied was carried out in a reactive ion etching system (RIES) with hydrogen plasma. An exposure to atomic hydrogen in RIES was with the electrode voltage of 330 V and current density of $56 \mu\text{A}/\text{cm}^2$ at 20–120°C in a sample holder for 5–50 minutes.

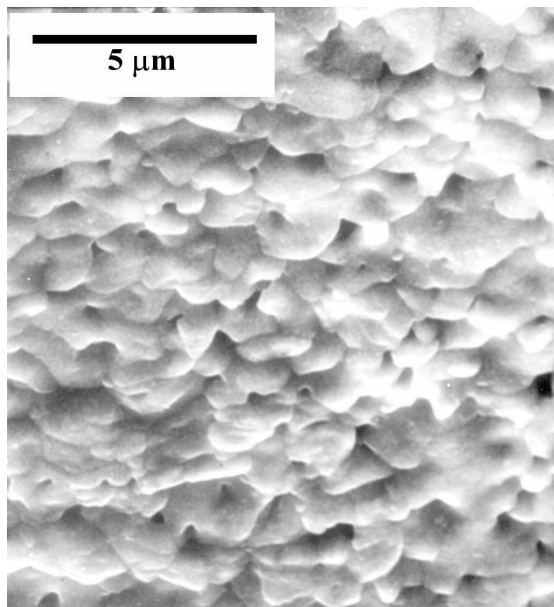


Fig. 1. Microstructure of recrystallized (activated) $\text{CdS}_x\text{Se}_{1-x}$ films

We used different geometry of the film samples when measuring their electric properties: rectangular (for Hall and resistivity measurements), spiral-like, snake-like, step-type pyramid, etc.

4. RESULTS AND DISCUSSION

According to Hall and resistance measurements in activated samples studied concentration of free carriers was about 10^{16} cm^{-3} and dark resistivities in the range 10^6 – $10^8 \Omega\text{-cm}$ that were dependent on composition of the films and regimes of sputtering and activation heat treatment. Our measurements have also shown that for activated and unhydrogenated films I–V characteristics can be changed from a linear-like I~V to the squared-like I~V². It is seen in Figure 2 for two samples of low-resistive CdS films.

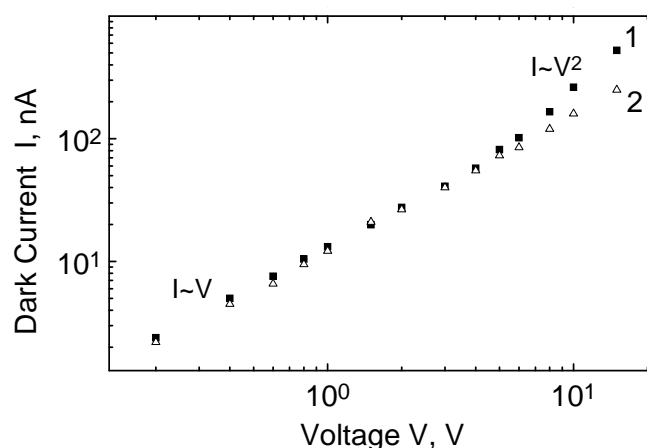


Fig. 2. Dark I–V characteristics for two rectangular samples of low-resistive CdS films measured at 295 K before hydrogenation

Hydrogen plasma treatment introduces modification in the electrical properties of films. As is seen from Figure 3, the films exhibit a great increase in the dark conductance (by 4–7 orders) after hydrogenation. This effect correlated with the initial film resistance: the initial resistance of the film is higher, the effect of resistance lowering under hydrogen irradiation is higher. It should be noted that the observed changes in dark resistance may be scattered from sample to sample for every set of films, although they depend on stoichiometric composition within certain limits. Transformation of dark I–V characteristics of low-resistive CdS films with rectangular geometry 20mm·2mm·0.001mm under hydrogenation is shown in Figure 4. As is seen, the films hydrogenated at room temperatures revealed a long-time relaxation of dark conductance resulting in its degradation (decrease) with time. Figure 5 shows that characteristic times of relaxation ranged up to 500–600 hours.

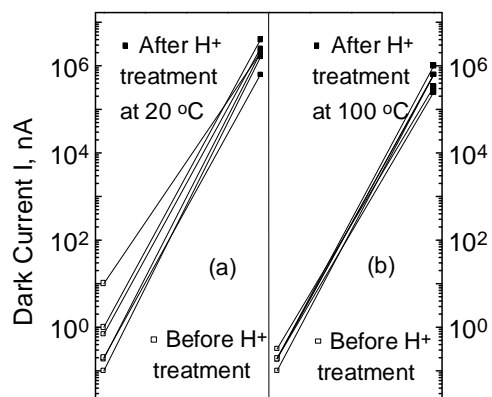


Fig. 3. Room temperature dark current (for $V = 1$ V) of $\text{CdS}_x\text{Se}_{1-x}$ films before (left part) and after (right part) hydrogen plasma treatment for 5 min at 20°C (a) and 100°C (b)

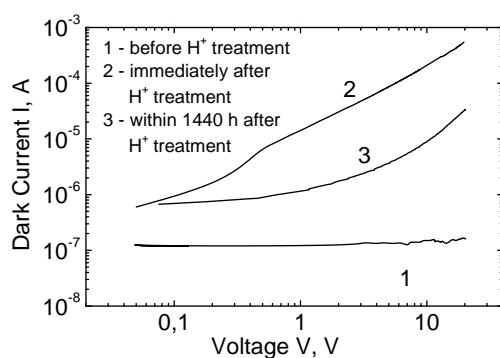


Fig. 4. Room temperature dark I–V characteristics of rectangular CdS films before (1) and after (2, 3) hydrogen plasma treatment for 5 min at 20°C

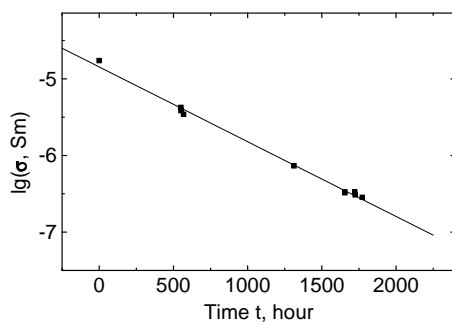


Fig. 5. Long-time relaxation of dark conductance for rectangular CdS films after hydro-generation for 5 min at 20°C

Our investigations have shown that annealing of $\text{CdS}_x\text{Se}_{1-x}$ films hydrogenated at room temperatures results in recovery of their properties to more resistive state, i.e. the changes introduced by the atomic hydrogen incorporation were removed. This annealing passes through two stages. A significant increase and then decrease of dark conductance (Fig. 6) in limits of one order and a drop of photosensitivity were observed during heat treatment even at the temperatures $\sim 60\text{--}100^\circ\text{C}$. Nearly total restoration of dark conductance to its initial state takes place after annealing at temperatures higher than 200°C .

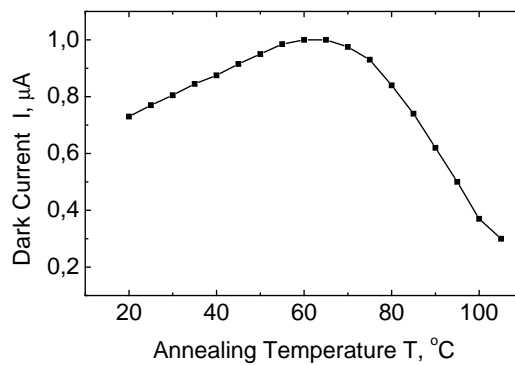


Fig. 6. Dark current at $V = 1\text{ V}$ vs. annealing temperature at heating with the velocity $10^\circ\text{C}/\text{min}$ for $\text{CdS}_{0.2}\text{Se}_{0.8}$ film hydrogenated for 10 min at 20°C

Taking into account a relatively large-grained structure of the films studied after recrystallization procedure (their microcrystallinity), it was expected that μm scale sample dimensions (more precisely, gaps x between current probes) would influence the electric characteristics of the films. To this end, special experiments on the samples in the shape of step-type pyramids were carried out. As is seen from Figure 7, steps of such pyramids had different lengths and widths so that every portion between electric probes on steps should be characterized by the same equilibrium resistance (at bias voltage close to zero), as we expected. Several

tens of such pyramids on one substrate were manufactured during one technological process. Such geometry of samples provided a possibility to make measurements of I–V characteristics for 6 portions with different lengths on a single sample. The values of gaps x between ohmic electrical probes produced by evaporation of indium were equal to 5, 10, 20, 50, 100 and 200 μm , respectively.

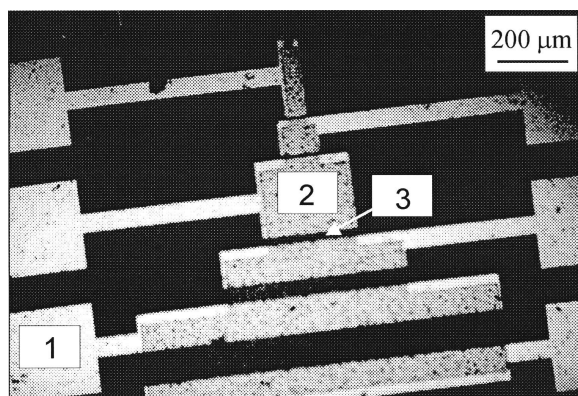


Fig. 7. Pyramid-like samples of CdS films: 1 – indium probes; 2 – CdS film; 3 – 20 μm interprobe portion for I–V measurements

The results of measurements of dark I–V characteristics for recrystallized CdS films manufactured in the pyramid-like geometry are given in Figures 8–11. Figure 8 shows dark I–Vs presented in J – E scale (J is current density and E is intensity of electric field between two current probes) for the initial films. As is seen, for $E < 10^3$ V/cm they are characterized by the power law $J \sim E^n$, where an exponent n is distinguished for different interprobe gaps. Note that these distinctions are associated not only with n and the shape of J – E curves but also with the values of current densities reached at a certain constant field (see Fig. 11 below). The lowest equilibrium conductivity is characteristic of the shortest 5 μm gaps. Note that conductance values for the 5 μm gap between electric probes were strongly scattered from pyramid to pyramid (sometimes by 1–2 orders), although the conductance of the 50 to 200 μm gaps scattered

within 10-30 %. Moreover, the 5 μm gap is characterized by squared-like J - E characteristics while portions with longer gaps are characterized by linearity of J - E (see Fig. 8).

Treatment in hydrogen plasma at the temperature 40°C during 5 min results in a sharp (by 2–4 orders) increase in pyramid portions conductance (Fig. 9), that is strongly dependent on the gap. In particular, for 5 μm gap J - E becomes linear. At the same time, J - E curves for other gaps are clustered in the narrow region of E and J , being transformed from linear (for the initial state) to the root-like ones with $n = 0.5$ after hydrogenation.

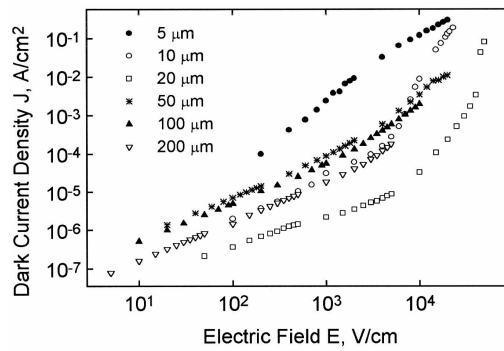


Fig. 8. J - E dependences for recrystallized CdS pyramid-like samples

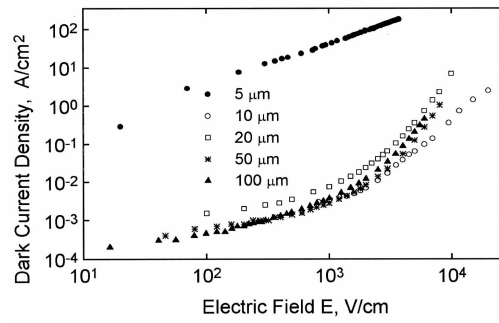


Fig. 9: J - E dependences for hydrogenated (40°C, 5 min) CdS pyramid-like samples

A completely different situation occurs when hydrogenating at higher temperatures (100 to 120°C). As is seen from Figure 10, dark conductance of the shortest gaps becomes lower than for the longest ones (as differentiated from Fig. 8), and J - E curves themselves come apart, although the power law is conserved for $E < 10^4$ V/cm. More distinct difference in the influence of hydrogenation temperature on the dark conductance of pyramid-like samples is shown in Figure 11, where the dependence of the electric field needed for reaching of a particular current density on the value of gap between probes is presented. These dependences were produced by section of J - E curves along the current density axes.

To interpret the obtained results, it is necessary to resolve the question concerning a possible role of the air components (oxygen, nitrogen, etc.) in the effects observed. At their adsorption on the surface of films the probability is increased that the character of these effects will be “surface” but not the “bulk”. To clarify this question we have made special experiments on etching of as-received activated films and pre-hydrogenated films in argon plasma in RIES with the electrode voltage of 1000 V and current density of 300 $\mu\text{A}/\text{cm}^2$ at 20°C for 10 minutes.

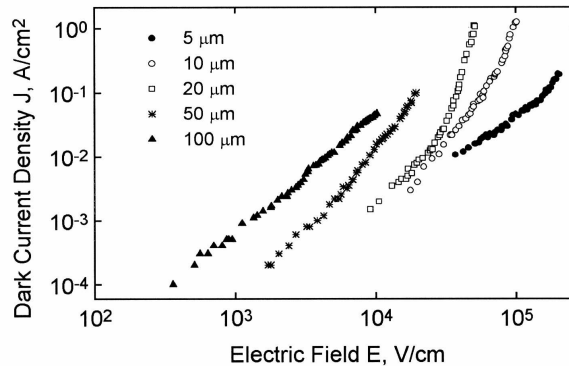


Fig. 10. J - E dependences for hydrogenated (120°C, 5 min) CdS pyramid-like samples

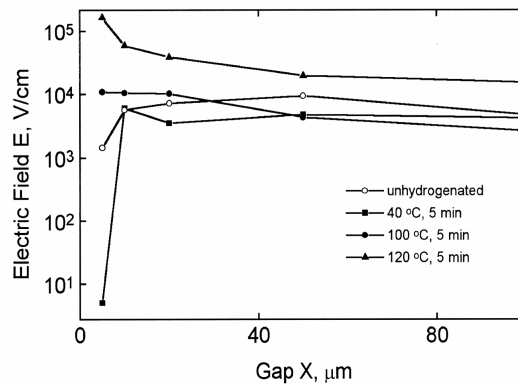


Fig. 11. E - x dependences for as-received (for $J = 0.001 \text{ A/cm}^2$) and hydrogenated (for $J = 0.1 \text{ A/cm}^2$) CdS pyramid-like samples

After argon etching of as-received activated samples I-V characteristics did not change. Argon treatment of pre-hydrogenated films results in an additional increase in dark conductance of the films although not so high as after pre-hydrogenation. This testifies that, apart from the etching effect, the change in the film properties is observed. The effect under discussion can be explained very easily. During pre-hydrogenation process atomic hydrogen H^+ diffuses in depth of the film resulting in aestivation of grain boundaries and other defects and increase in dark conductance. At the same time, a portion of H^+ may be united into molecules of H_2 (as it was observed in [9]) and accumulated near the surface of the film, taking no part in changing of the film properties. Under subsequent treatment in argon plasma argon ions break hydrogen molecules into atomic constituents which diffuse fast into the film depth, resulting in the same effect as for pre-hydrogenation.

These experiments with argon etching of CdS_xSe_{1-x} films provide a convincing demonstration that the observed increase in dark conductance under the influence of plasma hydrogenation is due to interaction of hydrogen with the films rather than to residual gases adsorbed at the surface of the films.

The conducted study shows that microcrystalline films of $\text{CdS}_x\text{Se}_{1-x}$ may be treated as microscopically inhomogeneous systems with large-scale fluctuations of the potential relief. The later is due to both native defects in the grain bulk (owing to their possible compositional inhomogeneity, the presence of extended defects, etc.) and electrically active grain boundaries. As a result, a number of mechanisms of carrier transport can be realized in such a system: zone mechanism of conductance by the grain bulk, tunnel or thermionic mechanism of conductance over the intergrain barriers and also conductance along grain boundaries and dislocations enriched by the compound components. Such approach implies that the observed changes in properties of $\text{CdS}_x\text{Se}_{1-x}$ films under the influence of hydrogen plasma treatment may be attributed to two main origins. Firstly, incorporation of hydrogen changes large-scaled potential relief due to passivation of grain boundaries. Secondly, the observed changes in the atomic-plasma treated samples can be attributed to H^+ chemical reactions. Following [2], one could assume that hydrogen removes sulfur atoms from particular sites through the formation of H_2S , resulting in an increase in the density of sulfur vacancies. The latter acting as donors in $\text{CdS}_x\text{Se}_{1-x}$ result in the resistance lowering. A similar increase in the CdS film conductance was observed in [2] with the films implanted by H^+ and in [10,11] with the films heat treated in molecular hydrogen. We believe that both above mentioned mechanisms can be present in our case.

This approach to the films studied will also allow for an understanding of the role of grain boundaries in conductance of the pyramid-like samples and specifically to explain great differences in conductance of the shortest ($5 \mu\text{m}$) and more long ($\geq 20 \mu\text{m}$) gaps of pyramids in the original state. In particular, no monotonic behavior of curves in Figure 11 and great scattering of conductance for the $5 \mu\text{m}$ gaps between electric probes in different pyramids may be connected with accidental (and non-reproducible from sample to sample) amounts of grains with dimensions $d = 1-3 \mu\text{m}$ which are fitted in the gap $x = 5 \mu\text{m}$. Actually, the situation

with $d \sim x$ results in accidental changes of the intergrain barriers (their heights and areas) crossed by the carriers when they are moving between electric probes. At the same time, any portion with $x \gg d$ represents a very complicated (but microscopically more homogeneous) percolating system involving current routes both along and across intergrain barriers and in the grain bulk. As is seen from Figure 11, the conductance in such a system has more weak dependence on the value of gap x .

3. CONCLUSIONS

The recrystallized $\text{CdS}_x\text{Se}_{1-x}$ films prepared by the RF-sputtering method are characterized by the microcrystalline structure and high dark resistivity. Hydrogen plasma treatment introduces modification in the electrical properties of $\text{CdS}_x\text{Se}_{1-x}$ films. The most interesting effects are a great increase in the conductance of hydrogenated films which correlates with the initial resistance of as-received and activated films, a long-time relaxation of conductance of hydrogenated films, influence of the film dimensions on the dark conductance and I–V characteristics for recrystallized and hydrogenated films. These effects have been attributed to transformation of potential relief of hydrogenated films due to two probable reasons: chemical reactions of H^+ with sulfur atoms (and generation of sulfur vacancies) and passivation of grain boundaries as well as other defects in the bulk. As is shown, these effects are due to interaction of hydrogen with the films instead of influence of residual gases adsorbed at the surface of the films.

REFERENCES

- [1] Sanchez A., Sebastian P. and Gomez-Daza O.: „*Semicond. Sci. Technol.*” 1995; 10:87.
- [2] Mahdjoubi L., Hadjzoubir and Benmalek M.: „*Thin Solid Films*” 1998; 156:121.
- [3] Bube RH.: *Photoconductivity of Solids*, Wiley New York 1960.
- [4] Estreher S.K. [In:] *Hydrogen Compound Semiconductors (Materials Science Forum)*, Vols. 148–149, Edited by S.J. Pearton Trans Tech Publication, Switzerland 1994, 349.
- [5] Sopori B.L., Deng X., Benner J.P., Rohatgi A. et al.: „*Solar Energy Matter and Cells*” 1996; 41/42:159.
- [6] Nickel N.H., Jackson W.B., Johnson N.M. and Walker J.: „*Phys. Stat. Solidi*” 1997;159:65.
- [7] Giro A.M., Goncharova O.V. and Kourmashev V.I.: [In:] *New Materials for Thin Film Electron Devices* (Nauka i Technika, Minsk 1994), 131.
- [8] Rose A.: *Concepts in Photoconductivity and Allied Problems*, Academic Press, New York and London 1963.
- [9] Job R., Fahrner W.R., Ulyashin A.G., Bumai Yu.A. and Ivanov A.I.: [In:] *Gettering and Defect Engineering in Semiconductor Technology*, „*Springer Ser. Solid State Phenomena*”, 1997 Vols. 57–58, Edited by C. Claeys and J. Vanhellemont, H. Richter and M. Kittler, Scitec Publications, 91.
- [10] Martinuzzi S., Cabane-Bronty F., Qualid J., Mostaven A. and Granier J.L.: [In:] *Proc. Int. Photovoltaic Solar Energy Conf.*, Luxembourg 1977, 587.
- [11] Bongnot J., Perotin M., Sirkes M. and Savelli M.: [In:] *Proc. of 12-th IEEE Photovoltaic Specialists Conf. (Baton Rouge, LA, November 15-18, 1976)*, Baton Rouge 1976, 519.

