DARK I-V CHARACTERISTICS OF HYDROGENATED MICROCRYSTALLINE CdS FILMS

A.Fedotov[1], S.Manego[2], A.Mazanik[1], L.Survilo[2], M.Tarasik[1], Yu.Trofimov[2], A.Ulyashin[3], A.Yanchenko[1]

[1] *Belarusian State University, F.Skaryna av. 4, 220050 Minsk, Belarus,*
e-mail: fedotov@phys.bsu.unibel.by
[2] *Institute of Electronics, National Academy of Sciences, 220090 Minsk, Belarus*
[3] *Belarusian State Polytechnical Academy, 220027 Minsk, Belarus*

The electrical properties of micro-crystalline CdS-CdSe films manufactured by the improved RF sputtering technology are described. The nonmonotonic influence of the film dimensions on dark conductance and current-voltage characteristics is shown, which is differentiated for as-received and hydrogenated films and depends on regimes of hydrogen plasma treatment. Such behavior is associated with transformation of potential relief of hydrogenated films.

Introduction

CdS films are being studied with renewed interest owing to their use in optoelectronic devices and potential application as window layer in solar cell structures like CdS/CdTe, CdS/CuInSe$_2$ [1]. However, the reproducibility of photoelectric and other properties of CdS-CdSe 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 CdS thin films with the desired photoelectronic properties, usually different doping techniques are used, including ion implantation of hydrogen [1,2,4]. Among other factors which determine necessity of hydrogenation, the polycrystalline structure of the films is of prime importance due to the influence of grain boundaries, other extended defects (dislocations, precipitates, etc.) and native defects in the grain bulk. Passivation of these defect under hydrogen treatment of semiconductors can significantly change their electric and photoelectric properties [4].

The main purpose of this work was to investigate the effect of hydrogen plasma treatment on dark I-V characteristics of microcrystalline CdS films. This was done with the aim to improve control over the dark properties of these compounds. The second goal of the study was to detect possible influence of the intensity of electric field and dimensions of the samples on the carrier transport in microcrystalline CdS films.

Experimental

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 ($0.05 - 0.1$ µm/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 more less 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 spe-
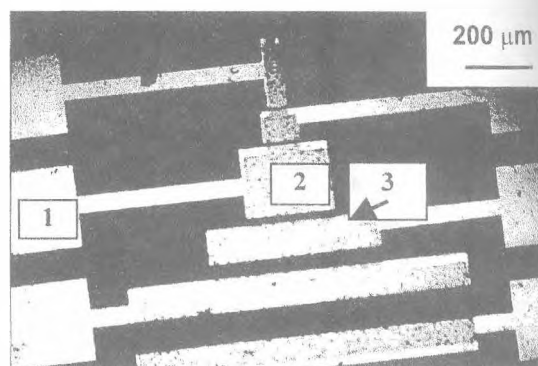

Fig.1. Piramid-like samples of CdS films: 1 – indium probes; 2 – CdS film; 3 – 20 µm portion for measurements

cial 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 1 µm thick films were deposited onto insulating substrates (aluminium oxide ceramics). We used a triode ion-plasma DC sputtering system with an additional RF-biasing with 13.56 MHz [5]. Density of ion current was between 0.2 and 0.35 mA/cm^2, bias voltage was 2 to 4 kV for the target-substrate gap of 50 mm. When using of 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 were deposited with thicknesses from 0.4 to 2.0 µm were received. To improve adhesion of films and substrates the under-

...al Ta_2O_5 deposited (0.03 to 0.05 μm by thick-...) on substrates was used.

As-received films are characterized by the quasi-amorphous structure with grain sizes of about 10-30 nm and very low photosensitivity. For activation of their photoresponse, the films were recrystallized and doped in special activating powder mixture based on high purity TiO_2. After activation heat treatment, the recrystallized films became polycrystalline with the mean dimensions of grains around 1-3 μm. Note that grain sizes correlate with the duration of recrystallization process: the longer duration, the greater is a grain size. Activated and hydrogenated films were subjected to measurements of Hall effect, dark current-voltage characteristics at room temperature.

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 300 V and current density of 56 μA/cm² at 20 -120°C in a sample holder for 5 -50 minutes.

We used different geometry of the film samples. Taking into account a relatively large-grained structure of the films studied after recristallization procedure (their micro-crystallinity), 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 a step-type pyramid were carried out. As is seen from Fig 1, 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 on one substrate of such pyramids were manufactured during one technological process. Such geometry of samples provided a possibility to make electrical measurements (in particular, dark and light current-voltage 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.

Results and Discussion

In the samples studied concentration of free carriers (electrons) was about 10^{16} cm⁻³. Such activated films of CdS exhibited dark resistivities in the range 10^6-10^8 Ω·cm that were dependent on regimes of sputtering and activational heat treatment. Hydrogen plasma treatment introduces modification in the electrical properties of films. The most interesting effect is a great increase in the dark conductance (by 4-7 orders) after hydrogenation of the films that correlates with the initial film resistance: the initial resistance of the film is higher, so the effect of resistance lowering under irradiation is higher. It should be noted that the observed changes of properties may be scattered from sample to sample for every set of films.

The results of measurements of dark current-voltage characteristics for recrystallized CdS films manufactured in the pyramid-like geometry are given in Fig.2. It 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 as-received 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. 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 srongly scattered from pyramid to pyramid (sometimes by 1-2 orders), although the conductance of the longest 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.2).
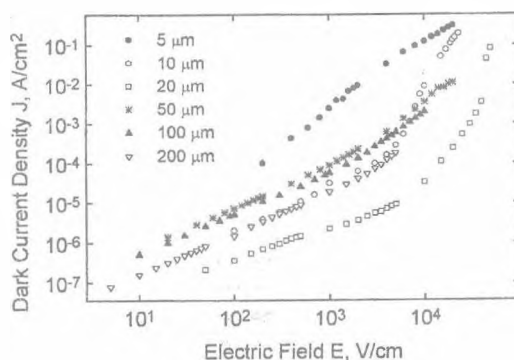

Fig.2. J-E dependences for as-received piramid-like samples

Treatment by hydrogen plasma at the temperatures 40-120°C during 5 min results in a sharp (by 2-4 orders) increase of pyramid portions conductance, that is strongly dependent on the gap and treatment temperature. In particular, for 40°C and 5 μm gap J-E becomes linear. At the same time, J-E curves for other gaps are clastered 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.
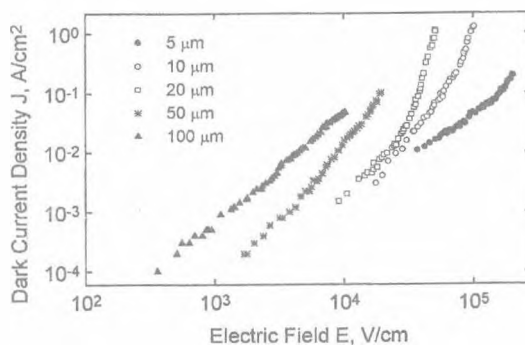

Fig.3. J-E dependences for hydrogenated (120°C, 5 min) piramid-like samples

A completely different situation hydrogenating at higher temperatures 120°C). As is seen from Fig.3, dark

the shortest gaps becomes lower than for the longest ones and J-E curves itselves come apart, although the power law is conserved for E < 10⁴ V/cm.

The conducted study shows that microcrystalline films of CdS 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 enriched by the compound components. Such approach implies that the observed changes in properties of CdS 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 CdS 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 [6,7] with the films heat treated in molecular hydrogen. We believe that both the 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 μm) and more long (≥10 μm) gaps of pyramids in the original state. In particular, non-monotonic behavior of curves in Fig.4 and great scattering of conductance for the 5 μm gaps between electric probes in different pyramides may be connected with accidental (and non-reproducible fr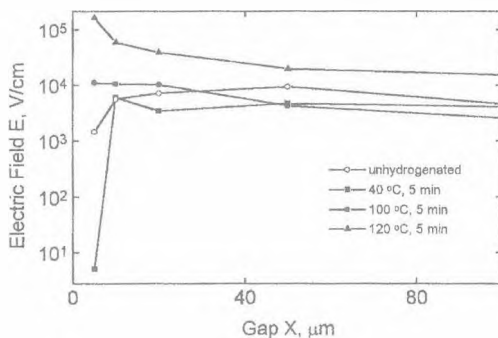om sample to sample) amounts of grains with dimensions d = 1-3 μm which are fitted in the gap x = 5 μ Actually, the situation with d ~ x results in accide changes of the intergrain barriers (their heights areas) crossed by the carriers when they are mov between electric probes. At the same time, any p tion with x >> d represents a very complicated (b microscopically more homogeneous) percola system involving current routes both along an across intergrain barriers and in the grain bulk. As seen from Fig.4, the conductance in such a syste has more weak dependence on the value of gap x.

To interpret the obtained results, it is necessar to resolve the question concerning a possible role the air components (oxygen, nitrogen, etc.) in th effects observed. At their adsorbtion on the surface of films the probability is increased that the character of these effects will be "surface" but not the "bulk". T clarify this question we have made special experiments on etching of as-received activated films and pre-hydrogenated films in argon plasma in RIES. These experiments with argon etching of CdS films provided a convincing demonstration that the observed increase of 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.

Conclusion

The recrystallized CdS_xSe_{1-x} films prepared by the RF-sputtering method are characterized by the microcrystalline structure and display effect of the film dimensions on the dark conductance and J-E characteristics for as-received and hydrogenated films. The most interesting effect is a great increase in the conductance of activated films, both in the dark and in the light, after hydrogenation and its correlation with the initial resistance. This effect has 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 native defects in the bulk.

Fig.4. E-x dependences for as-received (for J = 0.001 A/cm²) and hydrogenated (for J = 0.1 A/cm²) piramid-like samples

References

1. *Sanchez A., Sebastian P.J., Gomez-Daza O.* // Semicond. Sci. Technology. - 1995. - V. 10. - P. 87.
2. *Mahdjoubi L., Hadjzoubir N., Benmalek M.* // Thin Solid Films. - 1998. - V. 156. - P. 121.
3. *Bube R.H.* Photoconductivity of Solids. - New York Wiley, 1960.
4. *Estreiher S.K.* // Materials Science Forum. 1994. -- V 148-149. - P. 349.
5. *Giro A.M., Goncharova O.V., Kourmashev V.I. et al.* In: New Materials for Thin Film Electron Devices. - Minsk Nauka i Technika, 1994. - P. 131.
6. *Martinuzzi S., Cabane-Bronty F., Qualid J., Mostaven A., Granier J.L.* // Proc. of Int. Photovoltaic Solar Energy Confer. -Luxemburg, 1977. - P. 587.
7. *Bongnot J., Perotin M., Sirkes M., Savelli M.* // Proc. o 12-th IEEE Photovoltaic Specialists Confer. - Baton Rouge 1976. - P. 519.