Photoconductivity of CdS–CdSe granular films: influence of microstructure

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Abstract
We study experimentally the photoresistance of CdS–CdSe sintered granular films obtained by the screen printing method. We mostly focus on the dependences of photoresistance on film’s microstructure, which varies with changing heat-treatment conditions. The minimum photoresistance is found for samples with compact packing of individual grains, which nevertheless are separated by gaps. Such a microstructure is typical for films heat-treated during an optimal time of 30 min at a temperature of 823 K. In order to understand whether the dominant mechanism of charge transfer is identical with the one in monocrystals, we perform temperature measurements of photoresistance. Corresponding curves have the same nonmonotonic shape as in CdSe monocrystals. Namely, photoresistance first increases with the growth of temperature, and then starts to decrease. Thus we conclude that the basic mechanism is also the same, as in monocrystals, and it is based on two types of centers in the forbidden gap. We suggest that the optimal heat-treatment time depends on two competing mechanisms: improvement of film’s connectivity and its oxidation. Photoresistance is also measured in vacuum and in helium atmosphere, which suppress oxygen and water absorption/chemisorption at intergrain boundaries. We demonstrate that this suppression decreases photoresistance, especially at high temperatures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Materials with granular structure are widely used in modern electronics and radio engineering. These materials can be fabricated either by the traditional screen printing method known for a long time or by using new technologies, such as the direct formation of electronic devices by printers and opal crystal creation by concretion of spherical microparticles from water dredges. Modern technologies enable one to fabricate much more pure and reproducible samples compared to the old ones. As a rule, by using these methods, materials with granular or polycrystalline internal structure are obtained. In general, it is not always clear \textit{a priori} how granularity affects various electrophysical characteristics of a material [1]. Therefore, electronic and optical properties of granular semiconductors attract a lot of attention now.

Films made of CdS and CdSe are known for their high photoconductivity and photosensitivity. Photoreistors based on these materials are widely used in applications such as photodetectors and optical couplers [2–5]. The investigations of photoconducting CdSe and CdS systems have a long history, see e.g. [6, 7]. It was realized long time ago that a model with the single type of recombination centers cannot account for various electronic properties of CdSe and CdS crystals, such as superlinearity of photoresistance, infrared and thermal quenching [7]. Instead a model based on two types of states in the forbidden gap was proposed [7] (see also [8], where even two more kinds of centers were introduced). It was demonstrated [6, 7, 9] that photosensitivity of CdSe monocrystals can be as high as $10^6$–$10^8$. The granular structure of thin films made of CdSe or CdS makes the physics of these systems even more complicated [1, 6, 10–13] due to
possible formation of space-charged regions inside individual crystallites and at boundaries.

In the recent paper [14] some of us studied the influence of heat-treatment conditions for CdS$_{1-x}$Se$_x$ granular films, obtained by the screen printing method, on their photoresistance. It was found that there is some optimal time for the sample's heat treatment (at a fixed temperature of heat treatment), for which the photoresistance is minimized. The light-to-dark current ratio for these films can be as large as $10^9$. This fact, together with the simple and low-cost method of film's fabrication, makes them quite attractive for technological applications. The characteristic feature of optimally prepared films is that neighboring grains, from which they are built, fit each other on large contact areas.

At the same time, long time of heat-treatment results in the recrystallization of grains and disappearance of spaces between them, so that the film's connectivity is significantly improved compared to optimally prepared films. From these studies, it has remained unclear whether the leading mechanism of charge transfer under the illumination is associated with intergrain boundaries or it is identical with that for monocrystals of the same chemical composition. It is also not evident why almost total disappearance of gaps between grains is accompanied by the increase of photoresistance, while it is expectable that gaps prevent grain-to-grain charge transfer.

The main goal of the present paper is to understand if the leading mechanism of charge transfer in these films is different from the one in crystals. For simplicity, we here restrict ourselves to CdS$_{0.2}$Se$_{0.8}$ films only. In addition to the visual analysis of SEM images of film's microstructure, we perform AFM studies of intergrain boundaries. We also measure the temperature dependences of photoresistance and compare the character of these quite nontrivial dependences with the ones for monocrystals, which are known from the literature. Additionally, we perform measurements in vacuum, as well as in the atmosphere of helium, which suppresses oxygen and water absorption/chemisorption at grain boundaries, and compare the obtained results with the ones for the atmosphere of air. These measurements indicate that surfaces indeed play some role in the charge transfer under the illumination, since absorbed oxygen and water increase photoresistance.

We finally make a conclusion that the leading mechanism of charge transfer in the systems studied is most probably the same as in monocrystals, while the existence of the optimal heat-treatment time is due to the competition between the oxidation of grain boundaries during their heat treatment, which suppresses charge transfer, and improvement of film's connectivity, which facilitates this process.

The paper is organized as follows. Section 2 deals with the sample characterization. In section 3, we describe our experimental setup. In section 4, we present the results for the measurements of photoresistance and discuss them. We conclude in section 5.

2. Sample characterization

We used CdS and CdSe powders as initial components for the paste, from which samples are then fabricated. The initial powders of CdS and CdSe were milled together. The prepared CdS–CdSe powder and the coupler were mixed in a special barrel in order to obtain the paste. Propylene glycol was used as a coupler. Through a stencil, this paste was deposited on the pyroceramics substrate and then seasoned at room temperature for 0.5 h. After that, samples were dried for 1 h at a temperature of 373 K in order to remove the coupler. This raw material, represented by a film of 15–20 mkm thickness, was heat-treated in the stove with a quasi-free air access through the untight cup of the crucible. The time of heat treatment for different samples varied from 5 to 90 min, and the temperature—from 773 K to 873 K. Finally, samples were washed out in a bidistilled water and dried at room temperature.

During the heat-treatment process, small particles of the powder corresponding to different chemical compositions, CdS or CdSe, merge into grains, each grain containing a large number of initial particles. As we found, these grains consist of a solid CdS–CdSe solution. In order to prove the fact that the solid solution is indeed formed, we performed x-ray analysis of fabricated films. The typical measured XRD patterns for samples are presented in figure 1. Positions of narrow peaks on XRD patterns do correspond to the solid solution. The shift in the positions of these peaks depends on the ratio of initial components (CdS and CdSe). Note that a trace quantity of oxide CdSO$_3$ was also detected in our samples.

The microstructure of the obtained samples was studied by SEM. We found that the microstructure is highly sensitive to the heat-treatment conditions. The analysis of SEM images showed us that heat treatment increases grain sizes due to their merging. This process is naturally accompanied by the growth of contact areas between neighboring grains and thus to the better fitting between them: grains become more compactly packed. If the heat-treatment time is long enough, samples begin to recrystallize and intergrain boundaries disappear.
Figure 2. Micrographs of granular CdS$_{0.8}$Se$_{0.2}$ films fabricated with different times of heat treatment at a fixed temperature of 823 K: 5 min (a), 30 min (b), 60 min (c).

Typical SEM images for CdS$_{0.2}$Se$_{0.8}$ films, which were heat-treated at a temperature of 823 K, are presented in figure 2. Figures 2(a)–(c) correspond to films which were heat-treated for 5, 30 and 60 min, respectively. We found that the average grain size was around 3–12 μm in all these cases with the tendency of this size to increase upon the prolongation of the heat-treatment time, as clearly seen from figure 2. By its structure, the film in figure 2(a) resembles a sand: relatively large spaces exist between neighboring grains, these grains being connected to each other only by rather small areas on their surfaces due to the rounded shape of grains. At the same time, spacings between grains in figure 2(c) seem to disappear; many of them now reduce to grooves. Figure 2(b) corresponds to the intermediate heat-treatment time, which leads to a compact packing of grains; nevertheless, narrow, long and deep gaps between them still exist. Images of higher resolution, compared to the ones presented here, support these conclusions.

In order to demonstrate the tendency of the growth of the average grain size with the increase of annealing time, we have taken 24 samples, which were heat-treated at the same temperature of 823 K, but during different times. Then, we extracted the average grain size for each sample by performing the visual analysis of SEM images of these samples, each image containing around 40–50 grains. The size of each grain was taken as an average between its dimensions in the directions, where the grain has smallest and largest dimensions. Our results are presented in figure 3, where each dot corresponds to the particular sample, while the solid curve gives the interpolation for the average grain size. It is clearly seen from figure 3 that the increase of annealing time indeed...
leads to the growth of grains. This growth is however quite nonlinear with respect to the heat-treatment time. Initially, heat treatment leads to the rapid increase of the average grain size and then this size tends to stabilize.

We also used a semicontact AFM with thin cantilevers of whisker type in order to study in more detail the structure and geometry of boundaries between grains. The typical radius of curvature for the whisker was 10 nm and the typical height was 1 μm. Figures 4(a) and (b) show the AFM images for the structure and profiles of typical grain boundaries in samples, which were previously studied by SEM and which were fabricated during the 30 and 60 min of heat treatment, respectively, at the same temperature of 823 K. The microrelief of samples, obtained by 5 min of heat treatment, cannot be investigated using this experimental approach, since the surface landscape is very nonuniform in this case, which prevents the use of a whisker.

It is seen from figure 3 that our expectations, obtained from the visual analysis of SEM images, are basically correct: samples, which were sintered during an intermediate time, contain narrow gaps, which do not disappear completely during the fabrication process. These gaps become more and more narrow when moving away from the film surface toward its interior regions. Spacings between grains in films, which were heat-treated for a long time, tend to disappear and they shrink into grooves on the film surface, see figure 4(b), which shows such a groove separating two regions of the grain with different growth orientations.

3. Experimental setup

The experimental setup allowed us to study film’s specific resistance by spreading resistance method. For measurements of the resistance, we used indium contacts, which were prepared by the transfer of melted indium from a Teflon plate under the pressure applied. The obtained contacts have a square shape with 1 mm on side. The distance between contacts is also 1 mm. Samples were placed in an isolated chamber that allows us to study the influence of various gaseous atmospheres (at pressures close to the atmospheric pressure) and of vacuum. It was also possible to use streams of gases for the same purposes. An incandescent lamp served as a source of light. By changing the distance between the lamp and the film, we tuned the intensity of light, which illuminated the samples. The film’s resistance was measured under the illumination up to 10^4 lux and at the temperature varying from room temperature to 420 K.

The samples were placed on the stage, which was heated resistively. Thermocouple was positioned inside the stage close to its surface, on which the sample was situated. During the measurements, the temperature was changing smoothly and nearly linear in time, with the rate of 1–1.5 K min⁻¹. In order to control the accuracy of our measurements of temperature, we have used an additional thermocouple, which was placed on the top of the sample. The difference between the temperatures was within 0.1 K.
4. Results and discussion

4.1. Photoresistance versus temperature

As was shown in [14], the lowest photoresistance at room temperature was achieved for films, which were heat-treated during an intermediate time, nearly 30 min, at a heat-treatment temperature of 823 K. By photoresistance we mean the sample’s resistance under the illumination. In this paper, we focus on the temperature dependences of photoresistance $R(T)$ for samples characterized by different heat-treatment parameters. We expect that these dependences can shed some light on the leading mechanism of charge transfer. In total, for $R(T)$ measurements we used more than 30 samples. The results were reproducible: for instance, for the photoresistance maximum, the difference between different trials was within 5%.

Figure 5 gives typical temperature dependences for the fixed illumination of 100 lux. It is clearly seen from this figure that the shape of all these curves is rather peculiar: they consist of two segments demonstrating opposite tendencies. At low temperatures, resistance grows with the increase of temperature, while at high temperatures it decreases. The first type of behavior is quite unusual for conventional semiconductors and insulators (and common for metals), where charge transfer occurs by the simple thermal activation of carriers through the forbidden gap. However, similar temperature dependences of photoresistance were found in CdSe monocrystals [6] with the ‘anomalous’ part of the $R(T)$ curve being localized in nearly the same range of temperatures.

The non-monotonic behavior of $R(T)$ in CdSe monocrystals is explained by the presence of centers in the forbidden gap belonging to two different classes [6, 7]. These centers differ from each other by the fact that centers of the first class have comparable capture cross sections for both the free electrons and holes, while, for the centers of the second class, capture cross section for holes is much larger. The latter centers thus sensitize the photoconductor. By tuning light intensity or temperature, one moves steady-state Fermi levels and changes the number of centers contributing to the recombination. This gives rise to the superlinearity, as well as to the non-monotonic dependence of photoresistance on temperature. Since a quite peculiar temperature dependence of photoresistance found in our granular films is similar to that in monocrystals [6], it is reasonable to suggest that the leading mechanism of charge transfer under an illumination is unique both in our samples and in monocrystals, while the influence of internal boundaries is a less important factor. This factor, however, is not negligible because it can provide an additional decrease of photoresistance up to one order of magnitude in a certain range of temperatures by varying annealing conditions, as seen from figure 5 (compare, for instance, curves 1 and 3 near the temperature of 100 °C).

We now discuss in more detail how annealing conditions affect the photoresistance. During the heat treatment, the average grain size increases, which results in the increase of contact areas between neighboring grains and thus to the improvement of the sample’s connectivity. The process of grain growth is very fast in the beginning (see figure 3) and therefore the photoresistance of the sample heat-treated during 30 min (curve 2 in figure 5) is much lower than that of a sample, heat-treated during 5 min (curve 1 in figure 5).

Moreover, heat treatment also leads to the intensive oxidation of grains surfaces, while the oxidation decreases photoconductivity. Besides, merging of grains leads to the fact that oxidized boundaries are now inside individual grains. Further increase of heat-treatment time does not result in so intensive growth of grain sizes, as seen from figure 3. The oxidation nevertheless still occurs. Moreover, oxygen can diffuse from the bulk toward boundaries. Thus, oxidation starts to lead to the increase of photoresistance with the prolongation of the heat-treatment time (curves 2 and 3 in figure 5). In other words, an optimal heat-treatment time depends on two competing mechanisms. Note that the existence of annealing temperatures, which maximize photosensitivity, was reported in [16] for CdSe thin films obtained by a chemical bath deposition technique.

Next, we discuss the position of the photoresistance maximum along the temperature axis in figure 5. It is seen from this figure that the temperature corresponding to the photoresistance maximum is dependent on the heat-treatment parameters, i.e. on microstructure. An increase of heat-treatment time first leads to the increase of temperature at which this maximum is achieved (curves 1 and 2). Such a behavior implies that the contribution of the sensitizing centers is increased at this stage, so their effect is evident at curve 2 up to higher temperatures. This can be due to improvement of crystallinity, as well as of intergrain boundaries, where various defects, which can act as centers of the first class, should be presented with higher concentration. However, further prolongation of heat-treatment time results in the opposite shift of the corresponding temperature (curves 2 and 3). This can be explained by oxidation, which favors the appearance of additional centers of the first class.

![Figure 5](https://example.com/figure5.png)
It is worth noting that the optimal heat-treatment time, which minimizes the photoresistance, is strongly dependent on the temperature at which the photoresistance is tested. While this optimal time was found to be approximately 30 min at room temperature, it shifts toward 1 h when temperature is rising up to 160 °C.

An important electrophysical characteristic of photoconductive materials is a dark resistance as a function of temperature. In figure 6, we plot the dependence of resistance without illumination on temperature for the same three samples, addressed in figure 5. We see that the logarithm of resistance depends linearly on inverse temperature, in accordance with the Arrhenius law. From the slopes of these dependences we can extract activation energies. We have found that these energies are nearly the same for all the three samples and are equal to 2.0 eV with the error ±0.1 eV. The dark resistance of optimally prepared films is the highest one, while the resistance of the sample, heat-treated during 60 min, is the lowest one. This can be understood by noting that the latter case corresponds to the very well connectivity of the sample due to merging of individual grains. At the same time, heat treatment also leads to oxidation of grain boundaries, which suppresses charge transfer over intergrain barriers. The competition between the two mechanisms, in the case of the absence of illumination, leads to the domination of the oxidation effect for the case of optimally prepared films in contrast to the resistance under the illumination.

The value of the activation energy is in agreement with the width of the forbidden gap of CdS$_{0.2}$Se$_{0.8}$ and the measured photocurrent spectra, one of which is presented in figure 7 (for the sample, heat-treated during 5 min at $T = 823$ K). Measurements were performed using a scanning spectrometer at room temperature. The spectral range was from 400 to 900 nm. The spectra were decomposed into separate lines (Gauss or Lorentz functions) with the confidence probability of 95%. The smallest discrepancy value was used as a criterion of decomposition. All the measured spectra contain three components, which correspond to energies of 2.0 eV (curve 1), 1.7 eV (curve 2) and 1.6 eV (curve 3). The first one is due to direct transitions in the forbidden gap, while the other two are linked to the transitions with participation of centers in this gap. Curve 4 in figure 7 gives the sum of the three contributions, and the dots correspond to experimental data.

Note that we have also studied the response of the sample to the rectangular illumination impulse with the amplitude of nearly 200 lux and with the width of the order of $10^{-5}$ s. We have found that the typical photoresponse time was of the order of $10^{-6}$ s.

4.2. Influence of ambient atmosphere

In order to better understand the role of oxygen and water, which are absorbed/chemiabsorbed at the surfaces, we performed experimental investigations of photoresistance in helium atmosphere, in vacuum and also in the stream of helium, after keeping samples in these environment for 1 h. These conditions diminish oxygen and water absorption at intergrain boundaries, as well as at the film’s surface. Of course, an oxide layer cannot be removed by this method, since this layer essentially appears during the heat treatment with a quasi-free air access.

Figure 8 presents the typical results for the $R(T)$ dependence at a constant illumination of 1500 lux in the atmosphere of air, helium and in the vacuum for the samples heat-treated for 30 min at a temperature of 823 K. Firstly, the shape of all these curves is not dependent on the atmosphere, which evidences that the non-monotonic $R(T)$ dependence cannot be due to oxidation/deoxidation processes during the sample’s heating/cooling: This is consistent with the supposition that the dominant mechanism of charge transfer is the same as in monocrystals. Secondly, it is seen from figure 5 that the lowest photoresistance is achieved in the vacuum, i.e. when oxygen and water absorption are suppressed, while the highest photoresistance shows up in the air atmosphere.
The influence of absorption is not very strong at low temperatures, i.e. at the ‘anomalous’ parts of $R(T)$ curves, since there absolute values of photoresistance for different curves vary only within 30%. However, at higher temperatures, when approaching the thermoactivation part of $R(T)$ curves, an atmosphere starts to play an important role. For instance, the resistance of the sample in vacuum (curve 3) is approximately two times lower than that in the air (curve 1) at $T = 130$ °C. The resistance of the sample in the helium atmosphere (curve 2) is lower than that in the air (curve 1), but is also higher than the resistance in vacuum (curve 3). This can be attributed to the weaker desorption of air and water in the helium environment compared to the vacuum.

We finally note that different studies of CdS and CdSe films performed in the past provided different results for the temperature dependence of photoresistance. For instance, in [17], where photoresistance of CdS$_{1-x}$Se$_x$ polycrystalline films was investigated, an ‘anomalous’ part of the $R(T)$ curve was not found, the whole dependence being of ‘thermoactivation’ nature. Reference [18] deals with CdSSe(Cu) in silicone resine binder layers, which also demonstrates simple monotonic behavior. At the same time, the non-monotonic $R(T)$ dependences, similar to the ones presented here, were reported in [19] for CdS$_{1-x}$Se$_x$ sintered layers and in [20] for CdSe thin films prepared by thermal vacuum evaporation.

5. Conclusions

Highly photosensitive granular CdS$_{0.2}$Se$_{0.8}$ films were fabricated by the screen printing method. X-ray analysis has shown that grains consist of a solid CdS–CdSe solution. We measured the temperature dependences of photoresistance and found that they have a peculiar non-monotonic shape, which is practically identical with that for CdSe monocrystals, known from the literature. Namely, photoresistance first increases with the increase of temperature and then it starts to decrease. We therefore conclude that, in these granular films, the leading mechanism of charge transfer under the illumination is the same as in monocrystals, i.e. based on the presence of two kinds of centers in the forbidden gap.

The influence of intergrain boundaries is however not negligible. This follows from the fact that photoresistance also depends on the film’s microstructure, which can be changed by tuning the time and temperature of heat treatment during the process of the sample’s fabrication. The longer the heat-treatment time, the larger the grains and the more compactly they are packed. The lowest photoresistance at room temperatures was found for films, heat-treated for an intermediate time, in which gaps between grains still exist. This ‘optimal’ heat-treatment time, however, strongly depends on the temperature, at which photoresistance is probed, namely it decreases with the increase of temperature. For a certain range of temperatures, one can suppress photoresistance as much as up to one order in magnitude by only varying film’s internal microstructure.

An explanation for the optimal heat-treatment time was suggested in terms of the competition between the two mechanisms: longer heat treatment improves film’s connectivity, but also results in additional oxidation. The optimal heat-treatment time thus depends on the interplay between these two factors.

To better understand the effect of grain boundaries, we performed additional measurements of photoresistance in vacuum and also in helium atmosphere, which have shown that oxygen and water absorption/chemisorption at grain boundaries increase photoresistance.

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