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The features of nanosized Zn1-xCdxSe films deposited on porous Si

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ABSTRACT

In this work the results on the investigation of the precularity near the solar spectrum region, of Zn1-xCdxSe nanoparticles, nanofilms, nanoscale heterojunction prepared on Si substrates by precipitation from aqueous solutions are presented. The temperature dependence of dark and light conductivity, spectrum of primary and impurity photoconductivity are investigated. The obtained results show that when controlling ionic composition and heat-treatment (HT) conditions, one can purposely control the properties of Zn1-xCdxSe ($0 \le x \le 0.5$) films, achieve the appropriate degree of compensation of different recombination levels and traps attributed to intrinsic defects or impurities, which result in high level of photoelectrical parameters near the IR region. Just after deposition the photoconductivity spectrum maximum of $Cd_{1-x}Z_{nx}Se$ ($0 \le x \le 0.5$) films is observed at $\chi 1=0.485 \div 0.545 \mu m$ versus the film composition.

KEYWORDS chemical bath deposition, nanoparticle, nanoscale p-n heterojunction.

Introduction

Among the many different methods available to deposit films of semiconductors, chemical bath deposition (CBD) must rank as conceptually the simplest. CBD refers to depositions from solution (usually aqueous) where the required deposit is both chemically generated and deposited in the same bath. Thus, deposition from a supersaturated solution or spin coating from a colloidal sol are not included under the aegis of CBD: in both cases, the layer material must be pre-prepared. Neither is sol–gel layer formation, although it could be reasonably argued that the cross-linking which occurs during the process constitutes a chemical reaction. Successive ion layer adsorption and reaction (SILAR) is a related technique, where a substrate is first dipped in an ionic solution of one component, rinsed, then dipped in a solution of the second component and rinsed; this ideally results in a single monolayer of the desired compound. Liquid phase deposition (LPD) is a specific subset of CBD often used for acidic oxides. In spite of it being so simple, it is one of the least known. If scientists or engineers in general would be asked to name some semiconductor film deposition methods, evaporation, chemical vapour deposition, sputtering, may be even electrodeposition, would be the most obvious techniques that would spring to mind: CBD would probably be well down the list (with the obvious exception of those who work with the method). A part of the reason (probably not the main part, which remains non-obvious) is the many different terms used to denote CBD: chemical solution deposition (used to be more popular, but a consensus is beginning to appear favoring CBD), chemical deposition (when it is clear that chemical vapour deposition—a very different technique—is not meant) and liquid phase deposition (used for certain oxide depositions). [1,2].

The last decade sharply increased, the interest to nano-objects with the most distinguishes features. It related with the unique properties of particles with this sizes which differ them from according macro phase. The investigation of the properties of nanoparticles is one of the main aims of the novel directions of physical chemistry. Developing of this direction is closely connected with the simple and accessible methods of synthesis, which allow preparing of nanoparticles with the simulated size and rather narrow separation on sizes. The reverse micro emulsion systems are thermodynamically sustainable double phase systems, that consist of polar phase micro drops, separated in nonpolar ambient. Surface-active materials (SAM) are used for stabilization of the systems like this. It makes possible caring out chemical reactions among materials in polar phase and forming hard-solved compounds. The advantage of this preparing method of nanoparticles is relatively simplicity and also possibilities of simultaneous synthesis and stabilization of prepared particles.

The obtained results show that when controlling ionic composition and HT conditions, one can control properties of the Zn1-xCdxSe films. Furthermore, the above films are nearly similar in their main photoelectric properties and parameters to such model crystals as CdS and ZnS, to allow for the effect of sticking centers, conditioned polycrystalline structure. Since the Zn1-xCdxSe films can be used as photodetectors of the near IR region. To determine the general regularities and characteristic of recombination and electron-molecular processes, determinant high sensitivity in IR region, versus the composition and heat-treatment (HT) conditions, the photoelectrical properties of Zn1-xCdxSe ($0 \le x \le 0.4$) films deposited from the solution is the purpose of present investigations[3-5].

Experiment

The formation of the surface complex compounds take an important role in the processes of separation and purifying of liquid mixture, chromatography, catalysis, also in formation of nucleation centers and subsequent growth of semiconductor films. The most interesting issue for theory and application of the deposition of chalcogenide metals films is content analysis and sustainability of metal complexes on the surface of porous Si. It promoted by their developed surface and high absorption. The preparation of scientific bases of the hydro chemical method of synthesis of the metal selenides films is also actual. These films can be used in optoelectronics as a functional material, sensor techniques, solar cells and nonorganic sorbents.

The materials showed below are the main reactive materials for preparing selenurea complexes from sulfide phase of zinc and cadmium on the surface of porous Si also in nitric acid solution: zinc chloride $ZnCl_2$, $Cd(NO_3)_2 \cdot 4H_2O$, selenurea $CSe(NH_2)_2$, 25 % aqueous solution of ammonia $NH_3 \cdot H_2O$. Initial solutions have been prepared with concentration 0.1-0.5M in distilled water. The ph of solutions were measured by the ph-meter ph -340 with accuracy ± 0.01 unit. The porous Si with 20x15 size and 1 mm thickness was used as a substrate. In all cases, the films of solid solutions on the porous Si differ

with the high content of cadmium selenide in crystal lattice.

Therefore increasing of the $CdCl_2$ concentration in reaction will cause to increasing of CdSe nucleus on the substrate, sequentially increase the CdSe portion in content of film. The increasing of specific surface of the substrate in case of porous glass cause to that, colloidal particles of variable content metal selenides, which had been fallen into pores, cannot increase during crystallization and form metastable structure with higher level of supersaturation for displaced component and correspondingly higher portion of CdSe in content of solid solution.

On glass ceramic substrate, where above described process can't be realized, the crystal phase of solid solution less rich with cadmium and CdSe portion in solid solution is considerable low. The obtained difference very important and demonstrate the impact of substrate to crystalline structure and content of displaced solid solution, first as the result of ambient changing for the film growth on substrates with various nature.

The nanofilms composition (0≤x≤0.4) was changed by partial substitution of the thiourea and was controlled by chemical, spectral and X-ray phase analyses. XRD pattern of Zn1-xCdxSe thin films were using in fig.1a,b. The spectral dependence of optical transmittance of Zn1-xCdxSe films were using in fig.2. A part of films was subjected to heat-treatment in the air at temperatures of 400-5000C for 0-30 min.

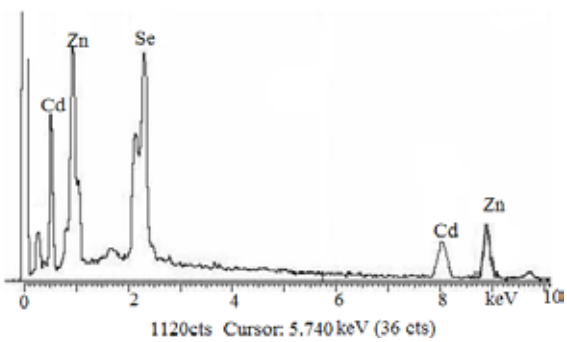


Fig.1. XRD pattern of Zn1-xCdxSe thin films.

The temperature dependence of dark (σdk) and light conductivity (σph), the spectrum and optical quenching of photoconductivity (σoq), the current-illumination characteristics, thermostimulated conductivity in the range of 80-400K has investigated. According to thermopower measurements, the films were n-type. The dark conductivity of Zn1-x CdxSe films was found to vary with x, from 10-4 to 10-5 S/cm. The ratio of photocurrent to the dark current reached 102 to 103. The carrier concentration determined from Hall measurements was 3-5x1014 cm-3 and 1016cm-3 for the films with x=0 and x=0.3, respectively.

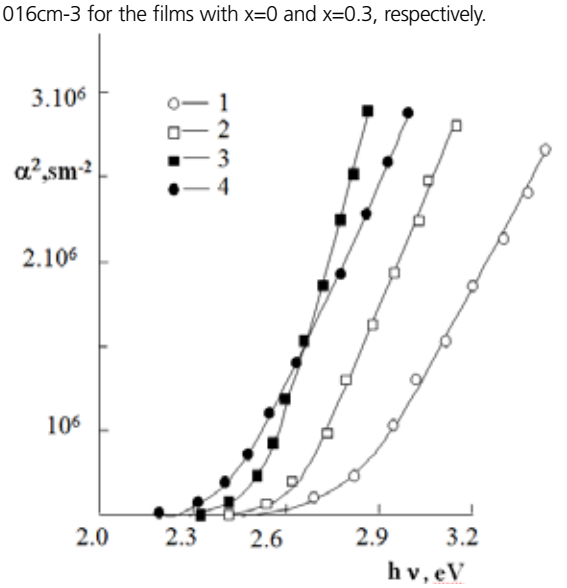


Fig. 2. The spectral dependence of optical transmittance of Zn1-x CdxSe films.

Just after deposition the above films are characterized by long-term relaxation photoeffects. Subsequent to heat-treatment, the considerable changes in photoelectric (PE) properties versus the composition, temperature and annealing time (τa) are observed. The dependence of conductivity as a function of time (τ0) has nonmonotonically character, i.e. with low τa , the conductivity of films increases and achieves a maximum value exceeding the initial one by more than four orders of magnitude. The further increase of annealing time up to 15min leads to a sharp decrease of conductivity. The σc(τa) dependence has an extremum character, i.e. primarily it increases at annealing times to 15min, then (t≥15 min) a slow decay is observed. With increasing annealing temperature and x, a shift of the above dependence extremums toward the lower times takes place. Photoconductivity spectrum maximum of Zn1-xCdxSe (0≤x≤0.4) films is observed at 0.485-0.545μm versus the composition (Figure 3, curves 1-4). Subsequent to heat treatment, the photoconductivity spectrum considerable widens and the peaks at (0.58-0.70) μm and (0.90-1.13) μm appear. With increasing time, to 4≤τa≤15min, the intensities of additional maximum increases and intensity of principal maximum decreases.. The Zn1-xCdxSe (0≤x≤0.4) films after the heat treatment at 5000C for 5-10min exhibit high sensitivity (σph/σdk= 104 to 105) over a wide spectral range (Fig.4, curve 4).

The photosensitivity in near IR region is comparable with proper photoconductivity. But with increasing temperature from nitrogen to room, the photosensitivity stays constant. At low temperatures the Zn1-xCdxSe (x=0.2) films have a complex spectrum of the impurity photoeffects, i.e. a superposition of several bands with 0.60μm, 0.64μm and 0.69μm maximums attributed to impurity and defect centres.

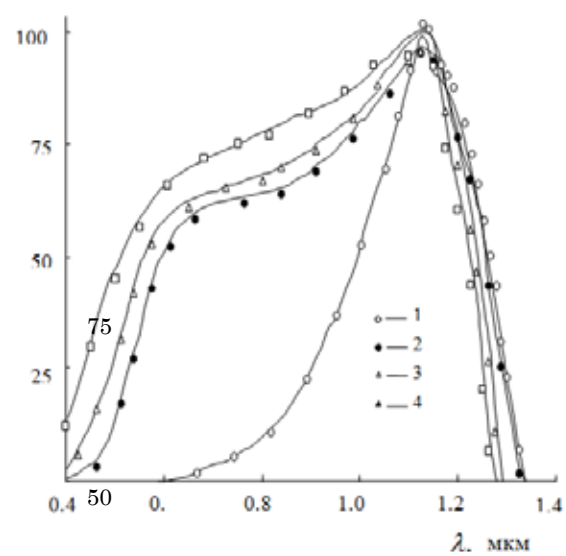


Fig.3. The photoconductivity spectrum of p-Si (1) and p-Si-Zn1-xCdxSe (0≤x≤0.4) structures, versus x; 2-(0.1), 3- (0.2), 4- (0.4).

In the solar cell of CdTe, the lattice mismatch between n-Si and p-CdTe and the low bandgap of $Zn_{1-x}Cd_xSe$ window layer are known to have some drawback on cell performance. Using higher bandgap materials like ZnSe or $Zn_{1-x}Cd_xSe$ as a heterojunction partner to CdTe can improve the window bandgap, but the lattice mismatch of these materials is worse than that of CdS. Trading off the latter mismatch for the higher bandgap may not be the solution, for the loss in cell performance due to lattice mismatch outweighs the gain due to the increase in window bandgap.

A more homogeneous Zn1-xCdxSe film is obtained at low process-

ing temperature if the stacked layers are thin. Of great importance is that the grown structure is almost homogenized in the chemical bath at the temperature below 900C. The homogenization of our structure is achieved by annealing at 4000C, the temperature generally used for processing solar cells. The low processing temperature developed here in the fabrication of Zn1-xCdxSe means that the proposed Zn1-xCdxSe/CdSe solar cell window could be grown at temperatures that will not damage the glass or the underlying transparent conducting oxide generally used as substrate in solar cells. The structures are Si/ Zn1-xCdxSe/contact, type 1 n-Si/ Zn1-xCdxSe and type (Figure 4a, curves 1-3) 2 p-Si/Zn1-xCdxSe (Figure 4b, curves 1-3) . In type 1 Zn1-xCdxSe/ CdTe window, a 0.15μm-thick ZnCdSe film was first deposited on Si substrate. This was then dipped in CdCl2 methanol solution for about 30 s to improve the conductivity, then dried with an infrared lamp, and then rinsed in the deionized water. This was followed by an additional deposition of 0.05μm CdSe thin film to complete the window fabrication. In type 2 p-Si/Zn1-xCdxSe window, a 150 nm thick CdTe film, sandwiched between two 40 nm-thick ZnSe films, was first deposited by CBD on Si substrate. The sample was then annealed in CdCl2/Ar ambient at 4000C for 15 min. The window fabrication was completed by the deposition of an additional 0.035μm-thick CdSe film. In the following order, Si/Zn1-xCdxSe structure have 75% or slightly higher quantum efficiency in the 450–850 nm wavelength region. We note that the structure with the Zn1-xCdxSe layer generally has better short wavelength response, as expected.

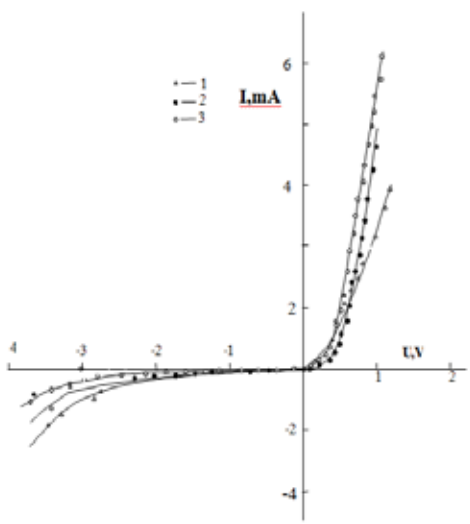


Figure 4a. VAX of n-Si-Zn1-xCdxSe (0≤x≤0.4) structures, versus x; 2-(0.1), 3- (0.2), 4- (0.4).

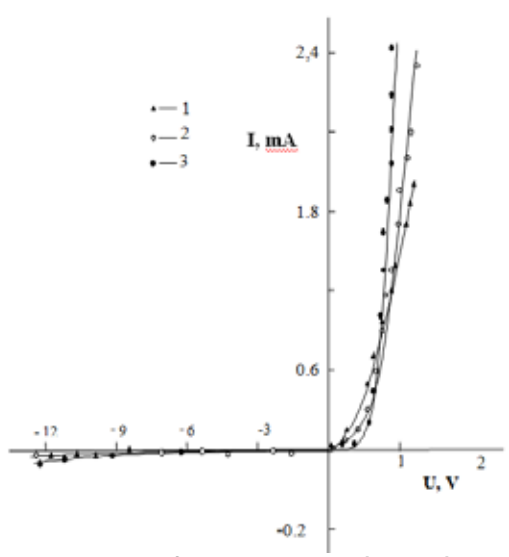


Figure 4b. VAX of p-Si-Zn1-xCdxSe (0≤x≤0.4) structures, versus x; 2-(0.1), 3- (0.2), 4- (0.4).

Discussion of results

The interpretation of experimental results becomes complicated due to a simultaneous occurrence of several processes (evaporation, generation and transformation of intrinsic defects) in films at the heat treatment. The kinetics of every process has a complicated character5. The dependence observed in photoelectric properties of films point out the changes of concentration of defects of donor and (or) acceptor character due to film annealing. The decreases of film photosensitivity at low annealing times (τa) indicate the increase in concentration of fast-recombination centres (s-centres), i.e. the increase of the recombination flux (gs), and hence the decrease in the life of electrons takes place. The measurements of the current-illumination characteristics of samples show that at low annealing times the decrease in hole concentration on the slow recombination centres (r - centres) is observed. This fact can be attributed either to increase of compensating shallow donor concentration or decrease of the r-centre concentration. A simultaneous increase in concentration of shallow donor centres responsibly for increase of dark conductivity and the fact recombination centres causing the decrease of photosensitivity allows to assume that the s-centres are the complexes consisting of shallow donors[7].

The change observed at $\tau_a \geq 5$ min can be explained when the anion and the cation vacancies diffusing into the volume are formed on their surfaces. Due to heavy evaporation of metal at initial stages of annealing, the near-surface region is mainly enriched by cadmium and sulfur vacancies playing the role of slow recombination centres. Their diffusion to the volume leads to increase of photosensitivity and to decrease of dark conductivity. In this case, the complexes of cadmium, sulfur and selenium vacancies, i.e. the recombination r-centres, are formed. The decrease of photoconductivity of annealing times τa>15-20 min is attributed to a single electron-molecular mechanism considering the initial state of film surface as were as local and collective phenomena at chemisorption. At initial state of annealing the increase of surface potential barrier due to chemisorption leads to increase of film sensitivity due to slow recombination. When the recombination controlled by the r-centres, the increase in their occupancy by holes due to chemisorption results in decrease of the lifetime of photoholes, i.e. the photoconductivity decreases. In this case, with increasing sulfur concentration in films the effect of oxygen becomes lower.

The experiments carried out shown that there are no difference in kinetics of photocurrent reduction under illumination with the wavelengths corresponding to the both quenching maximum and this testifying their relations to one type of recombination centres.

The curve of photocurrent reduction is characterized only by the time of that recombination centre where the electrons from v-band are transferred by impurity light.

The obtained results show that when controlling ionic composition and heat treatment conditions, one can control the properties of Zn1-xCdxSe (0≤x≤0.4) films, achieve the appropriate degree of compensation of recombination levels and traps attributed to intrinsic defects or impurities. In this way model crystals, as CdSe and ZnSe, can explain the main photoelectrical properties and parameters of Zn1-xCdxSe (0≤x≤0.4) films.

Conclusion

The $Zn_{1-x}Cd_xSe$ (0≤x≤0,4) films deposited from solution the sensitivity condition of these films have been determined. The obtained results show that when controlling ionic composition and HT conditions, one can control the properties of $Zn_{1-x}Cd_xSe$ (0≤x≤0,4) films.

Furthermore, the above films are nearly electron similar on their main photoelectric properties and parameters to such model crystals as CdSe and ZnSe. The recombination schemes and electron transitions in $Zn_{1-x}Cd_xSe$ (0≤x≤0,4) films and A^2B^6 crystals are identical. Not only a chemical composition but also a degree of crystallization are not determining, and the difference in photoelectric properties is attributed to the nature and the concentration distribution of recombination centres and trapping levels.

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