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THIN FILM CdS/PbS SOLAR CELL BY LOW TEMPERATURE CHEMICAL BATH DEPOSITION AND SILVER DOPING OF THE WINDOW LAYER

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The effects of incorporation of Ag nanoparticles into "glass/ITO/CdS/PbS/conductive layer" thin film solar cell fabricated by economic low temperature method were studied. The n-CdS/p-PbS heterojunction for thin film solar cells was prepared via chemical bath deposition (CBD), varying factors like temperature, deposition time and pH of the solutions. A cadmium sulfide (CdS) window layer was deposited over indium tin oxide (ITO) covered glass substrate. Once the deposition method was optimized, nanoparticles of silver (Ag) were incorporated into CdS films via two different methods: Electrophoretic Deposition (EDP) and Ion Exchange Process using a solution of $AgNO_3$, in both cases trying to modify the surface of the film, expecting to improve scattering properties and the overall solar cell performance. The lead sulfide (PbS) absorber layer was grown on ITO/CdS to fabricate a p–n junction. Expected improvements were achieved, Ag nanoparticles incorporation did improve solar cell efficiency. Obtained solar cells are photosensitive in a large spectral range from all visible to, specially, near infrared regions.

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Keywords: Thin film solar cell, Silver nanoparticles, CdS/PbS heterojunction, Chemical bath deposition.

1. Introduction

Nowadays the extensive use of energy has created a necessity for renewable energy power sources, which triggered the development of photovoltaic solar cell devices industry and technology. One of the most important problems is the production cost, for what the thin film technology has been identified as a viable solution [1]. There is a wide variety of deposition methods that permit the synthesis of semiconductor thin films. One of these methods – Chemical Bath Deposition (CBD), which is known for its use of low temperatures, simplicity and inexpensiveness – is a technique that has been widely applied to the fabrication of thin films for photovoltaic applications [2,3]. One material commonly used in solar cells as the front transparent contact is indium tin oxide (ITO) thin film – a transparent conductive oxide with a band gap between 3.5 and 4.3 eV and resistivity around 9.36×10^{-5} Ω cm, which shows high transmission in the visible and near–IR regions of the spectrum [6, 7]. Currently it is widely used in solar cells, batteries, liquid crystal displays, and in flat panel displays. The high conductivity of ITO is due to the contribution of substitutional Sn and Oxygen vacancies [8, 9].

As active layers in solar cells, several materials have been used, for example CdS, which is frequently selected as a window layer, is a wide band gap (2.42 eV) II–VI semiconducting material [10]. A thin film of this material can be deposited by a variety of methods, being CBD one of the simplest and less expensive ones [8]. Nevertheless, widely used CBD methods frequently employed complexing agents like ammonia additionally to special heat treatment in post growing steps, until recent achievements [13, 14] of cleaner processes. This, ammonia free, low temperature CBD alternative was used as a starting point for present work.

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To complement a P-N junction PbS is used, this material is an important binary IV-VI semiconductor with a direct narrow optical energy gap (0.41 eV at 300 K) and relatively large excitation Bohr radius (18 nm) [11].

Recently, a tendency appeared to interpret nanoparticles as quantum dot sensitization for solar cells [4,5]. In the present work, CdS/PbS solar cells have been fabricated and some of them doped with Ag nanoparticles by two methods, electrodeposition and ion-exchange. A comparative study of the developed solar cells was performed with and without nanoparticle-doping by both methods involved, highlighting how this modifies the properties of the device.

2. Experimental procedure

Thin films used for this research (CdS and PbS layers) were fabricated by low temperature chemical bath deposition method without ammonia as complexing agent, using conducting ITO/glass commercial substrates. The total structure of the fabricated solar cell device used in this work was as follows: glass/ITO/CdS/PbS/graphite (Fig. 1).

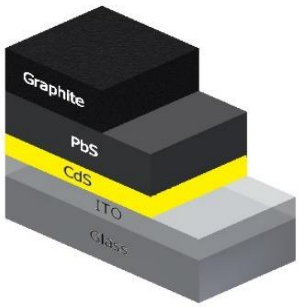

Fig. 1 Structure of the "glass/ITO/CdS/PbS/Graphite" solar cell.

The conductive glass/ITO commercial substrates, which have around 20 nm of thickness (ITO) and a sheet resistance of 70-100 Ω/sq, were cleaned prior to the deposition by the method described by Junfeng Han et al [15]. Initially, they were immersed for 20 min in isopropanol; thereafter, for 20 min in acetone; and lastly, for 10 min in deionized water. They were dried with nitrogen to eliminate any remaining humidity. Acid based drying method, presented by Obaid et al in [16] was also tested, but was finally discarded, as it consumes about 10 nm of ITO – near half in our case. However, the method can be successfully used with thicker substrates.

For the deposition of CdS thin films, the reacting solution was prepared by mixing 7.5 ml of $CdCl_2$ (Cadmium chloride) at 0.05M; 7.5 ml $C_6H_5O_7Na_3$ (Sodium citrate) at 0.5M; 2.5 ml of KOH (Potassium hydroxide) at 0.5M; 3.75 ml of $CS(NH_2)_2$ (Thiourea) at 0.5M; 2.5 ml of buffer pH10 and 26.25 ml of deionized water. The substrates were positioned (inclined) on the baker during the deposition time which was 7.5 hrs at 30° C divided in 3 episodes of 2.5 hrs each. The best film adherence was obtained at mentioned temperature, while the best growing was observed during the first 2.5 hrs of deposition.

High electric resistivity of CdS films limits its performance in photovoltaic devices [17]. However, optoelectronic properties of semiconductor thin films, such as CdS, can be influenced by doping [12, 18]. Several metals have been used for doping CdS films showing increase in conductivity [19, 20]. In this context silver is acting as acceptor dopant which enhances transport properties of II-VI semiconductor films [12].

The obtained CdS films were immersed in two different solutions. The first one consisted of $AgNO_3$ solution using a concentration of 0.002M where the CdS films were immersed during 1 min for doping. The second solution consisted of Ag nanoparticles (NP) solution with a concentration of 0.002M where the films were immersed during 2 minutes using electrodeposition at voltage of 0.7 V and 50 μs high/low pulse sequence.

For the deposition of PbS the chemical solution contained 2.5 ml of $Pb(C_2H_3O_2)_2$ (Lead (II) acetate) at 0.5M; 2.5 ml of NaOH (Sodium hydroxide); 3 ml of $CS(NH_2)_2$ (Thiourea) at 1M; and 2 ml of $C_6H_{15}NO_3$ (Trietanolamine) at 1M; the total volume of the deposition solution was made equal to 50 cm^3 by addition of deionized water. The films were deposited also by a CBD method, first at 70 °C on the CdS/ITO/substrates for 6 hrs (in 3 sets of 2 hours each) obtaining thicknesses between 500 and 1500 nm in order to cover the reported thicknesses of 900 to 1400 nm [16]. Later, the temperature was lowered to 30 °C because at 70 °C CdS layer was beginning to detach. Also, the process was performed in darkness, as the involved reaction is affected by light.

Once the P-N union was fabricated, to complete the solar cell, a layer of conducting material was printed over PbS film. There were three different materials used for contact: graphite paste and silver paste applied by hand, and aluminum applied by sputtering with and without additional chrome layer which improves adherence, however, the performance of the used materials was similar. Thought, graphite paste contact showed improvement after adding one fifth part of graphite powder to it followed by thermal treatment of 6 hours at 60 °C which leads to liquid evaporation and better adherence.

3. Results and discussion

3.1 Analysis of CdS films

The fabricated thin films were subjected to series of analysis. Transmittance analysis showed changes within doped samples; however, the edge of absorption remained at 500 nm corresponding to the band structure of CdS.

After being doped, the films showed reduction of the transmission spectrum in the 300 to 600 nm region because of the plasmonic excitation introduced by Ag particles [12]. The highest transmittance was found in the films doped with silver nitrate reaching 80% for the wavelengths around 700 nm (fig. 2).

Band gap values were extrapolated from the graph (fig. 2, insert) as a function of the energy of the incident photon at the particular point where the value of the function increments abruptly. Before doping the value of the band gap was 2.42 eV. For the film doped with Ag NP band gap value maintained similar at 2.39 eV while the sample doped with Ag nitrate showed a decrement to 2.33 eV which can be attributed to the insertion of free electrons inside the system.

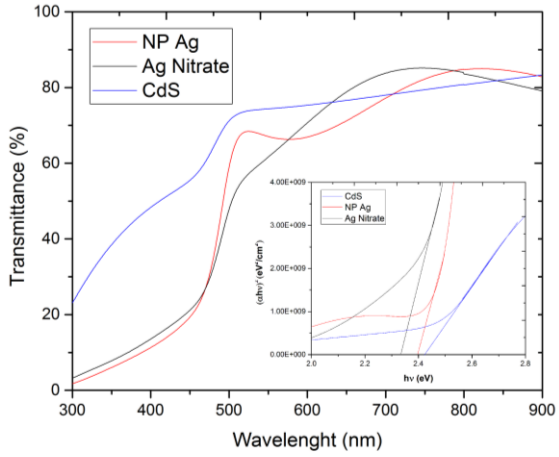

Fig. 2. Transmission spectra and linear approximation for gap energy calculation of CdS films.

X-Ray analysis (fig. 3) showed cubic and hexagonal phase conservation. However, the peaks intensity of doped CdS is lower showing that incorporation of small quantities of silver doesn't imply changes of the crystalline structure of the synthetized films.

XPS analysis of the surface evidentiates the presence of silver on the surface in both cases (fig. 4) based on the intensities of the peaks of each element: Cd3d, S2p and Ag3d, normalizing for spectrometer's sensitivity. High concentration of silver in the film doped by ionic exchange is suggesting a ternary material. However, X-Ray analysis did not show the presence of other phases than CdS.

Morphologic analysis, on the other hand, showed a notorious increase of roughness in CdS films after doping. The measurements were taken within 2x2 μm areas, where a root mean square values (RMS) were taken on each surface. Histograms (fig. 5) show the roughness distribution. It can be seen that silver doped films have grains of greater height. In case of Ag nitrate doping the grains are also less polidispersed. This behavior can be attributed to the silver forming additional structures during the doping process where a part of the silver is dispersed over the surface.

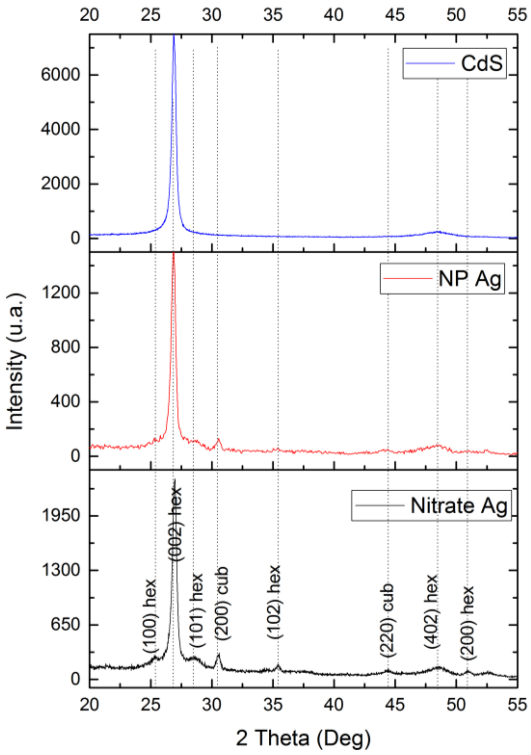

Fig. 3. X-Ray spectra of the CdS films without and with Ag NP and nitrate doping.

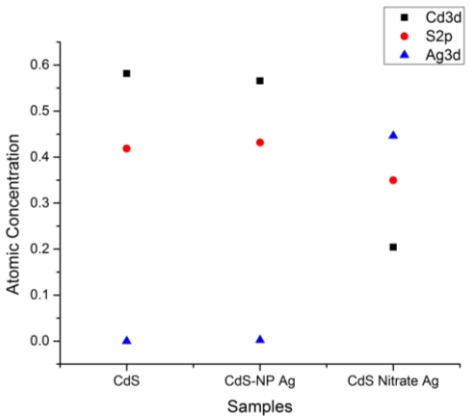

Fig. 4. Atomic concentrations of CdS films before and after doping.

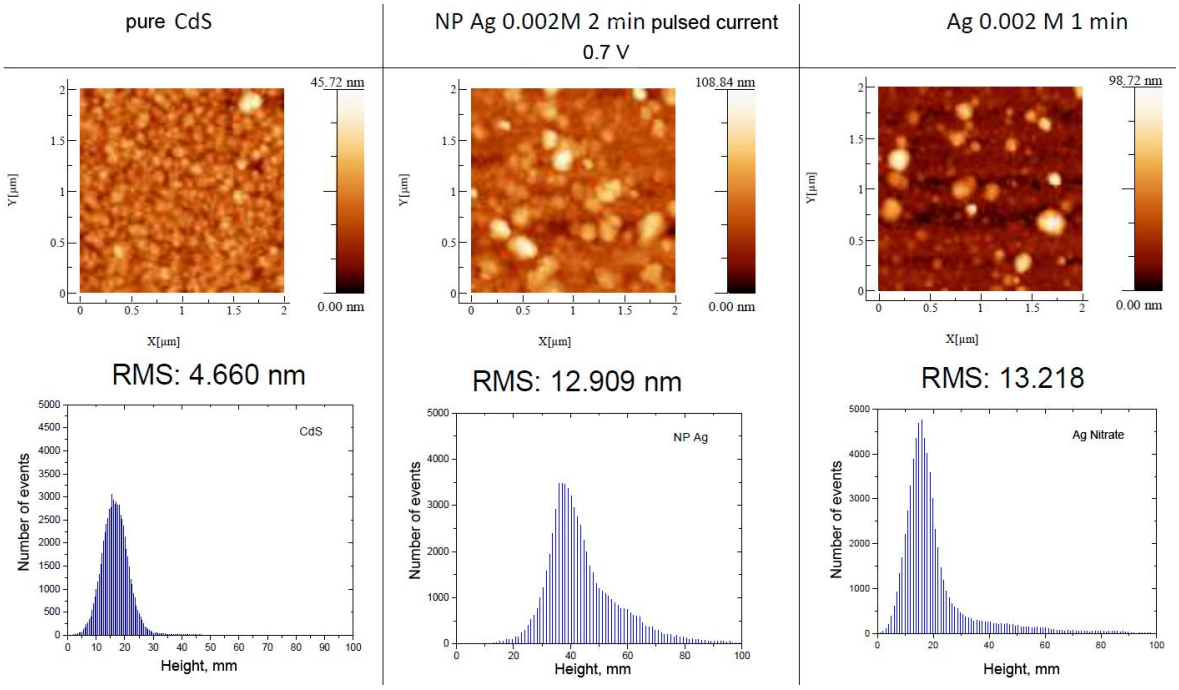

Fig. 5. AFM images, RMS values and histograms of CdS films, doped and pure.

3.2 Analysis of PbS films

Transmittance spectrum of the next, absorber layer PbS thin film, was measured in the 400-2000 nm range at room temperature (fig. 6). It can be seen how the film darkens from 1 to 3 deposition iterations of consecutive CBD, being 3D thickness of up to 1500 nm. Also, it can be seen as the bandgap slightly drifts for different thickness of the film, being equal to 0.68 eV for (1500 nm thickness achieved with 3 consecutive depositions.

It can be noted that PbS films are of highly absorbent nature for wavelengths below 800 nm. XRay analysis showed well defined peaks which indicate good crystallinity of the films. Also, no phase transformation or oxidation was detected. The good quality of the films specially matters taking into consideration low temperature ammonia free process.

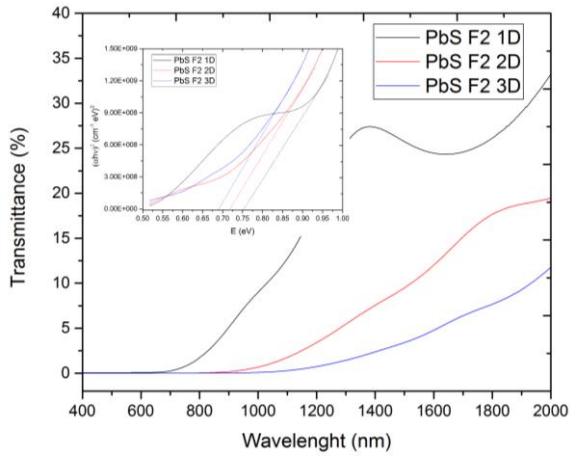

Fig. 6. Transmittance and bandgap of the PbS films with 1, 2 and 3 deposition iterations.

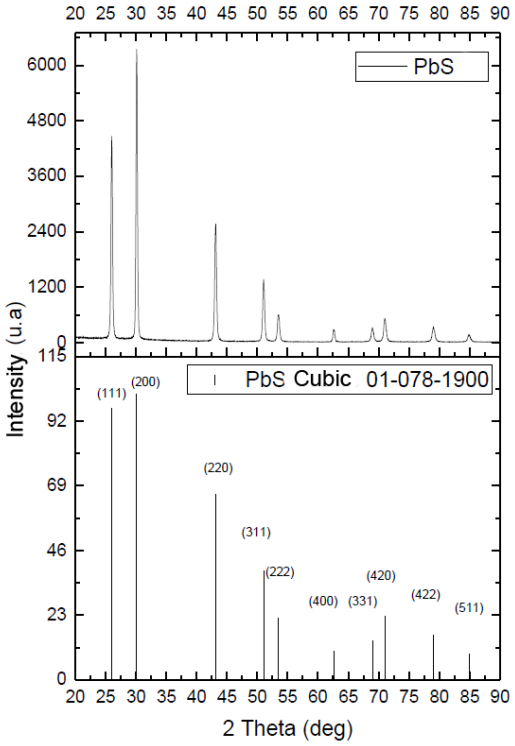

Fig. 7. XRay pattern of the PbS film.

3.3 Analysis of the solar cell

Finally, the solar cell was completed by applying posterior contact. Graphite mixture of paste and powder were selected best as the most economical option while delivering similar results as silver paste, "alumina sputtering" and "alumina with chrome" sputtering which were also tried. Current-voltage characterization of the cell is presented on fig. 8. Tungsteen-halogen irradiation was used as full spectrum sun simulator was not available at the time. However, the cell is expected to be more sensitive in red and IR region of the spectrum, while tungsten-halogen light provides needed intensity in that region. The cell was analyzed under two different intensities, as suggested in [21], which allowed calculating cell's series resistance giving it the value of 177 Ω-cm^2 , which means that no good ohmic contact was achieved. Nevertheless, it can be clearly seen that silver doping does have strong effect of photo-sensitivity of the cell. Nitrate Ag doped cells showed the strongest increase in sensitivity, especially under greater amount of irradiation. This ITO/CdS-Ag/PbS/Graphite solar cell was characterized with the following parameters: short circuit current of 85.2 mA, short circuit current density of 1.085 mA/cm^2, maximum current of 43.9 mA, open circuit voltage of 0.11 V, maximum voltage of 0.6 V, maximum power of 26.3 μW, fill factor of 28.07 % and efficiency of 0.0335%.

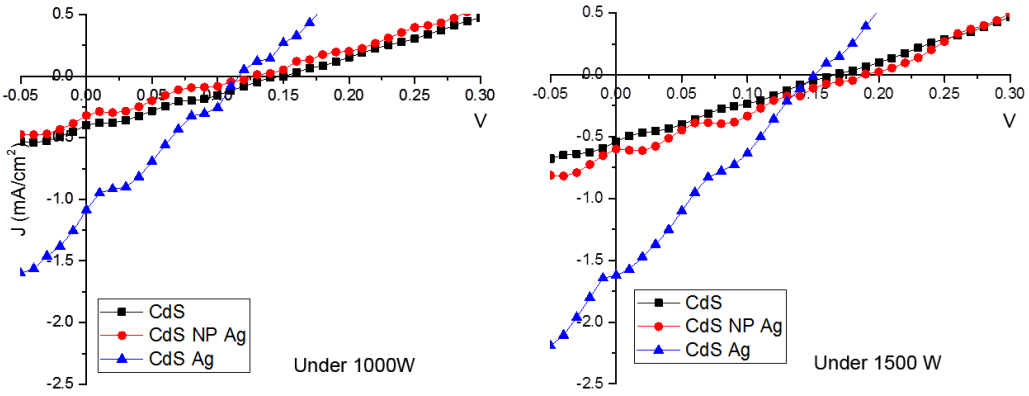

Fig. 8. Current-voltage curves for the fabricated cells under 1000 and 1500 watts of tungsten-halogen irradiation.

4. Conclusions

We have used a low temperature ammonia free chemical bath deposition technique for the preparation of thin films due to the inexpensive cost and the simplicity of the method. A solar structure with CdS and PbS as active layers were developed. The doping of the CdS layer allowed to increase the efficiency of the cells. With the studies performed it is concluded that the Ag has optical and electrical effects as seen on transmittance and efficiency of the device. Based on the results obtained we recommend to try combining CBD growing thin films with other NP and other doping techniques in order to expand this study.

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