Journal of Luminescence 142 (2013) 40–47

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Temperature dependence of the photoluminescence spectra of CdS: In thin films prepared by the spray pyrolysis technique

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ARTICLE INFO

Article history:
Received 24 June 2012
Received in revised form
18 January 2013
Accepted 25 March 2013
Available online 2 April 2013

Keywords:
Cadmium sulfide
Photoluminescence
Temperature dependence
Spray pyrolysis
Heterojunction solar cells

ABSTRACT

Indium doped cadmium sulfide thin films (CdS:In) are prepared by the spray pyrolysis technique on glass substrates using a home-made spraying system at a substrate temperature T_s=490 °C. The photoluminescence (PL) spectra are recorded at different temperatures in the range 24–160 K. Two broad peaks were observed; a strong one in the visible region centered on E≈2.0 eV and a weak one in the infrared region centered on E≈1.06 eV. The first one is deconvoluted into two Gaussian peaks corresponding to the yellow and red bands, and the second one is deconvoluted into one Gaussian peak corresponding to the infrared band. A strong quenching of the PL intensity with temperature is observed after T=60 K for the yellow and infrared bands and after T=90 K for the red band. The activation energy E_a was estimated by using the Arrhenius plot for the different bands. The estimated values for the three bands lie in the range E_a≈23.4–27.3 meV. The peak positions of the yellow and red bands are red-shifted after T=90 K, while the peak position of the infrared band is blue shifted in the whole temperature range. The full width at half maximum (FWHM) for the three bands increases with temperature. According to these findings the three bands are explained in terms of bound excitons.

1. Introduction

Cadmium sulfide (CdS) is an important semiconductor with direct band gap of 2.48 eV which falls in the visible spectrum region at room temperature [1]. Because of this CdS material is an interesting material which can be applied to optoelectronic devices [2]. CdS thin films are of practical interest for photoconductors, solar cells, laser materials, and nonlinear integrated optical devices [1,3]. In particular, thin films of n-type CdS are widely used as window layer in heterojunction solar cells [4,5]. Several methods have been used to get n-type CdS thin films, such as: doping with indium [5–8] or silver [9], or varying the concentrations of the reagents in the precursor solution [3].

Different techniques exist to obtain CdS thin films, like rf sputtering [1], close spaced vapor transport (CSVT) [4], chemical bath deposition (CBD) [10], close-spaced sublimation (CSS) [10], pulsed laser deposition (PLD) [5,11], and spray pyrolysis (SP) [6–8,12]. However, the SP technique is a very low cost and simple technique that enables intentional doping and getting large area and uniform thin films.

The crystalline quality of the semiconductor film can be analyzed by means of photoluminescence (PL), which is a very sensitive and non-destructive optical technique [4]. PL can also provide information about impurity and defect centers which act as recombination centers for charge carriers which also reduce the PV conversion efficiency [10]. For the window layers in solar cells such as CdS, PL probes optically active recombination centers. Some of these will contribute to losses in photocurrent of solar cell devices due to optical absorption in the CdS window layer. So, the intensive study of the photoluminescence of CdS -bulk and thin films- is very important for the use of this material in solar cells and in opto-electronic devices.

The photoluminescence of CdS single crystals and thin films was extensively studied, but the temperature dependence of the photoluminescence of this material still needs more research. Jeong and Yu [2] studied the temperature dependence of the free excitons in the CdS single crystal. Aguilar-Hernández et al. [4] reported temperature dependence measurements of PL on CdS films prepared by the CSVT technique. Agata et al. [13] investigated the temperature dependence of photoluminescence spectra of CdS microcrystals prepared by the gas evaporation technique. Ullrich et al. [14] had experimentally and theoretically investigated the temperature dependence (4–300 K) of the photoluminescence properties of thin CdS films on glass formed by laser ablation. According to our knowledge just Feldman et al. [12] studied in 1980 the PL-spectra of spray-pyrolyzed CdS thin films at T=77 K and room temperature and compared them with those of amorphous silicon, and just Perna et al. [5] investigated the

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http://dx.doi.org/10.1016/j.jlumin.2013.03.033

temperature dependence of the PL spectra of CdS:In thin films prepared by pulsed laser deposition in the temperature range 10–300 K. So there is a lack of experimental work on the PL-temperature dependence of CdS:In thin films prepared by different techniques especially those prepared by the SP technique. Hence, this is the first study on the temperature dependence of the PL spectra for spray-deposited CdS:In thin films.

In this work we investigated the temperature dependence of the intensity, positions and full width at half maximum (FWHM) of the yellow, red and infrared bands in the PL spectra of spray-deposited CdS:In thin films. The temperature dependence of the spectroscopic positions of the yellow and red bands is found to be in accordance with the relation between bandgap energy and temperature, while that of the infrared band is slightly blue shifted. The FWHM is found to increase with temperature in accordance with that of the excitonic peaks. The activation energies of these bands are estimated by using the Arrhenius plot.

2. Experimental part

The films are prepared as described elsewhere [6–8,15,16] by SP technique on glass substrates that are (6 cm × 2.6 cm × 0.1 cm) at a substrate temperature of 490 °C. Approximately a stoichiometric solution of thiourea ($(NH_2)_2CS$) and cadmium chloride ($CdCl_2 \cdot H_2O$) in distilled water with indium chloride ($InCl_3$) as the doping source is used. The ratio of the ions' concentrations $[In^{+3}]/[Cd^{+2}]$ in the sprayed solution is 10^{-4}.

The PL spectra are recorded at different temperatures in the range 24–160 K by a system which consists of an Air Product He cryostat DISPLEX DE-202 capable of cooling down to 10 K, where the Ar ion laser of wavelength 488 nm is used as an excitation source. The laser power is 9 mW and the diameter of the laser beam on the sample is about 2 mm. The PL signal is collected by a multi-channel optical spectrometer which hosts two gratings. The first grating has a range 640–1280 nm and the second grating has a range 190–860 nm. The spectrometer resolution (FWHM) ranges from 0.3 to 10 nm depending on the recorded region and the grating.

The films' thickness is estimated by comparing the films with a standard one of known thickness by using the transmittance at a certain wavelength and Lambert law of absorption. The values of the films' thickness are about 0.5 μm.

3. Results and discussion

Fig. 1 displays the PL spectra of an as-deposited CdS:In thin film at six different temperatures varying from 24 K to 160 K. In Fig. 1a the part of the PL spectrum in the energy range 1.7–2.4 eV is shown, where the measurements are taken by the second grating. A strong broad peak centered on ~2.0 eV is seen in this figure which consists of the red band and the yellow band. In (b) the part of the PL spectrum in the energy range 0.9–1.7 eV is shown, where the measurements are recorded by using the first grating. In this figure the PL-spectrum consists of the tail of the red band and an infrared asymmetric emission centered at about 1.06 eV. To show the effect of temperature on this emission, it was plotted alone in Fig. 1c with expanded scales for more clarity. As the figure shows, the intensity of the whole PL spectrum is decreasing with temperature. By comparing these results with those of other authors, it is found that the broad peak was observed by a number of authors such as [4,11,17,18]. Perna et al. [11] observed it at $T=30$ K and found that it was rapidly quenched with increasing temperature. Mandal et al. [17] observed the broad emission of undoped CdS films at about 570 nm (≈2.18 eV) and for Cu doped CdS films its center was shifted toward longer wavelengths. Chamarro et al. [18] observed the room temperature PL spectrum of Mn doped CdS nanocrystals and found that it is dominated by a yellow band peaking at 2.13 eV characteristic of Mn^{2+}. At lower energy, they [18] observed a broad tail which exists around 1.77 eV. For the undoped sample the emission that they [18] got consists of a very broad band centered at about 1.95 eV and a small and narrower shoulder at 2.55 eV.

As Fig. 1 shows, the temperature dependence of the PL spectra of CdS:In thin films is quite evident, where the intensity of the whole PL spectrum decreases with temperature, which means that PL efficiency damps with temperature. The damping of the PL efficiency is likely due to the temperature increase of non-radiative recombination channels, which are in competition with radiative transitions. The decrease of the integral PL intensity with temperature due to the thermal quenching is represented by the relation [19]

$$I(T) = \frac{I_0}{[1 + A\exp(-E_a/kT)]} \quad (1)$$

where I_0 is the peak intensity at temperature $T=0$ K, A is a parameter, k is Boltzmann's constant, and E_a is the activation energy in the thermal quenching process. The significance of E_a comes from the fact that with the use of it one can determine the energy levels inside the bandgap of the semiconductor, which is the ultimate point to be reached.

The decrease in the PL intensity with temperature was recorded by different authors such as [5,12,20]. Feldman et al. [12] explained the decrease in the PL intensity with temperature by saying that: "Normally, the same intergranular region that contains luminescence sites would also contain nonradiative sites. At higher temperatures, the trapped electrons can be thermally excited into these nonradiative sites and the photoluminescence intensity would be strongly reduced". On the other hand, other authors found that the PL intensity of some bands increases with temperature. Aguilar-Hernández et al. [4] found that the intensity of the red band increases with temperature. For polycrystalline CdS thin films deposited by the gradient recrystallization and growth (GREG) technique Albor-Aguilera et al. [21] found that the intensity of the bands in the 2.04–2.11 eV range increases with temperature, while that of the excitonic peak decreases with temperature.

To explore this temperature dependence of the present data the broad peak in Fig. 1a is fitted to two Gaussian peaks corresponding to the yellow and red bands, while the peak in the infrared region shown in Fig. 1b and c is fitted to one Gaussian peak. The fits are performed for all values of temperature under study and they are displayed in Figs. 2 and 3. The fit parameters for the three bands at the different temperatures are inserted in Tables 1–3.

Fig. 4 depicts the relation between the integrated area under each of the three Gaussian peaks obtained from the fits and temperature. As the figure shows, the behavior of the intensity with temperature approximately seems to be the same for all bands, where a strong decrease occurs after a certain temperature ($T=60$ K for the yellow and infrared bands and $T=90$ K for the red band). The decrease in the intensity with temperature is due to thermal ionization of the involved levels. Or in other words, the damping of the PL efficiency of all bands is likely due to the temperature increase of non-radiative recombination channels, which are in competition with radiative transitions. It is noticed that the intensities of the yellow and infrared bands have stronger temperature dependence than the intensity of the red band. For the increase in temperature from 24 K to 160 K, the integrated area (Integrated intensity) under the yellow band is reduced by a factor of about 5.8 and the integrated area under the infrared band is reduced by a factor of 5.9, while that under the red band is