보론 도핑된 CdS 박막의 구조적 및 광학적 특성

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Effects of Boron Doping on the Structural and Optical Properties of CdS Thin Films

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요 약

보론 도핑된 CdS 박막을 chemical bath deposition법으로 증착하고, 도핑농도에 따른 박막의 구조적, 광학적 특성을 조사하였다. 보론 도핑된 CdS 박막은 XRD 분석 결과 (002)면 방향으로 강한 우선성장 방위를 가지며 육방정(hexagonal) 구조로 성장하였다. 보론 도핑에 관계없이 모든 시편은 2.3 eV(녹색 발광) 및 1.6 eV(적색 발광) 부근에서 PL peak을 가지며, 도핑 농도가 증가함에 따라 피크 세기는 감소하였다. 보론 도핑에 따라 CdS 박막의 가시광 영역에서의 광투과율은 향상되었고, 밴드 갭은 증가하였다.

ABSTRACT

Boron-doped CdS thin films were chemically deposited onto glass substrates. X-ray diffraction (XRD), photoluminescence (PL), and Raman techniques were used to evaluate the quality of B-doped CdS films. XRD results have confirmed that B-doped CdS films has a hexagonal structure with a preferential orientation of the (002) plane. The PL spectra for all samples consists of two prominent broad bands around 2.3 eV (green emission) and 1.6 eV (red emission) and the higher doping concentrations gradually decreased the green emission and red emission. Raman analysis has shown that undoped films have structure superior to those of B-doped CdS films. Boron doping into CdS films improved the optical transmittance and increased the optical band gap.

I. Introduction

The two basic requirement of the CdS film in this heterojunction solar cell application are low electrical resistivity and high optical transparency. Specifically for optimum photovoltaic conversion efficiency it is necessary that the CdS films have resistivity of the order of 10^{-1} Ω-cm or less and transmit more than 80% of the solar photons with energy greater than the band gap of CdS.

Various deposition techniques have been applied to deposit CdS films such as: thermal evaporation, metal organic chemical vapor deposition(MOCVD),

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laser ablation, chemical bath deposition(CBD), electrochemical deposition, and rf sputtering. Among these methods, chemical bath deposition yields stable, uniform, adherent films with good reproducibility by a relatively simpler process [1]. Even though resistivity and optical transmittance strongly depend on preparation conditions, undoped CdS films prepared by the chemical deposition generally show high electrical resistivity due to near stoichiometric composition. Failure to make these films n-type limited their utilization as a window material in most heterojunction devices. In the past, efforts have been made to increase CdS film conductivity by doping with the impurity such as indium [2-4]. However, the incorporation of indium into CdS is unlikely because of the facts that the solubility of $In(OH)_3$ in water is only 2.2×10^{-9} mol/liter at 20°C and that unlike $Cd(OH)_2$, $In(OH)_3$ is insoluble in ammonia [5].

In this article, different concentrations of n-type CdS thin films were deposited with intentional boron doping by CBD technique. The effect of doping on the structural and the optical properties are studied to evaluate proper doping level for good quality films.

II. Experimental

The CdS films were prepared using aqueous solutions of cadmium acetate (0.025 M), ammonium acetate (0.1 M), ammonia (35%), and thiourea (0.05 M). Films were deposited on corning 7059 glass using an optimized solution temperature of 75 °C, a pH of 11 and a deposition time of 40 min. Boron doped CdS films were deposited by adding boric acid (H_3BO_3) as a dopant source to the solution. The ratio of boric acid to cadmium acetate ($CdAc_2$) was varied from 0 to 0.1. Details of the CBD process used in this work have been already described in a previous work [6].

The crystal structure of CdS films was determined by X-ray diffractometry. Grain size and microstructure of the films were observed using a scanning electron microscope (SEM). Photoluminescence (PL) spectra were recorded with the excitation wavelength of 488 nm using Ar laser in the range of 350-900 nm at the room temperature. The Raman spectra of the CdS samples were recorded in a Laser-Raman spectrometer built around a double grating monochromator (SPEX 14018). An argon laser, lasing at 488 nm wavelength with 50 mW power was used as the source.

III. Results and Discussion

Fig. 1 shows typical XRD patterns of B-doped CdS films on glass substrate. From the pattern, it is clear that the films are polycrystalline in nature. All peaks from the diffraction patterns were found to be characteristic for pure CdS, suggesting that incorporation of B in the films does not imply changes in the crystal structure of CdS. The films exhibit three peaks related to (002), (110), (112) plane of hexagonal phase and show strong preferential orientation of (002) plane which has the lowest surface energy in the wurtzite structure. It is known [7,8] that CdS structure has a stable hexagonal phase and a metastable cubic phase, but for solar cell applications, hexagonal structured films are preferable [9]. Despite of showing higher lattice mismatch with $CuInSe_2$ by hexagonal CdS (1.2%) compared to that of cubic CdS (0.7%), hexagonal structure is more useful due to the stability [10]. However, several other authors [7,11] classified the structure of as-grown CBD-CdS film from a basic aqueous bath as cubic structure. Further,

they report that the transition from this metastable phase to the stable hexagonal phase occurs around 300 ℃.
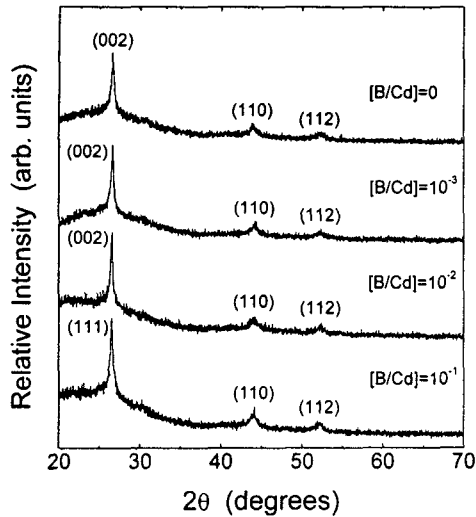

Fig. 1 X-ray diffraction patterns of CdS films with various [B/Cd] ratios.

Fig. 2 shows the PL spectra at room temperature for CdS films with different boric acid concentrations. The PL spectra for all samples consists of two prominent broad bands around 2.3 eV and 1.6 eV. In polycrystalline systems the PL emission lines are not sharp peaks but are broad bands because of the presence of many recombination sites; the grains will have different impurity concentrations, surface areas and defect types and concentration (e.g. stacking faults). Hence the individual PL emission lines will have a range of energies and form a broad band. For undoped CdS films, the maximum PL intensity was observed. As the boric acid concentration increased, the intensity decreased together with a broadening of the FWHM (full width half maximum) of each band.
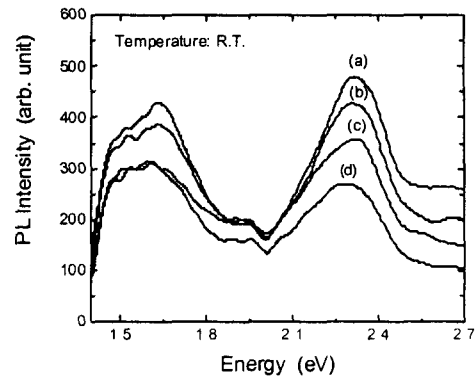

Fig. 2. PL spectra of CdS thin films at room temperature: (a) undoped film, (b) [B/Cd]=10^{-2}, (c) [B/Cd]=3×10^{-2}, (d) [B/Cd]=10^{-1}.

The green emission (GE) bands corresponding to a 2.3 eV were attributed in the literature to the transition of sulfur vacancy (VS) to the valence band and the donor acceptor pairs recombination [12,13]. Since the energy separation between green band (2.32 eV) and the band to band transition (2.45 eV at RT) is about 0.13 eV, this probably excludes the possibility of the recombination of free electron with holes localized at VCd and/or IS. Low doping concentration of boron may have resulted in an increase of interstitial Cd and interstitial S concentrations. Higher concentrations gradually decreased the green emission. It appears that doping with boron may play the role of filling the Cd-vacancy and neutralizing the S-vacancy. For the red emission (RE) band centered at around 1.6 eV, the trend is similar to that of the GE band. The RE band has been ascribed to surface states, in particular, Cd-vacancies [14]. The intensity of RE band decreases with as evidenced in Fig. 2. This fact is caused by the decreasing of surface Cd-vacancies density because of filling boron atoms.

Fig. 3 shows the typical Raman spectra of B-doped CdS thin films. A Lorentzian line shape is

fitted to the Raman spectrum from which the peak position and FWHM have been obtained. It is well known that Raman scattering spectra can give useful information about the crystalline of the film by evaluating the spectral peak position and the spectral width of the Raman spectra. Each spectrum has two peaks. The first peak is a 1LO (longitudinal optical) phonon peak and the other is 2LO. These Raman spectra are essentially independent of the boric acid concentration. For completeness, Table 1 shows the comparison in wavenumber of LO modes of our films with those of single-crystal [15] CdS and pulsed laser-evaporated [16] (PLE) CdS thin films. Here, the wavenumbers of LO modes of our films, like those of PLE CdS films, shifted to lower values compared to single-crystal LO modes. These shifts is attributed to the effect caused by the grain size [17,18], i.e., the effect of dimensions on the vibrational properties in small crystalline.

Let us consider for a moment the dominant 1LO mode in the CdS films. The wavenumber of this mode is 300 cm^{-1} in undoped films and 298 cm^{-1} in both boron doped films, where 5 and 7 cm^{-1} are respective shifts from 305 cm^{-1} of the single-crystal CdS. The 1LO in undoped film has the least shift, indicating that this film has a better structure. The overall intensities of the peaks of undoped CdS films are weaker than those of boron doped films. Also, from the Raman spectra the full width at half maximum (FWHM) of 1LO peaks are 18, 19, and 18 cm^{-1} for undoped, [B/Cd]=10^{-2}, and [B/Cd]=10^{-1}, respectively. The values previously reported [19] for CBD-CdS film range from 20 to 30 cm^{-1}. Our values agree with the low end of this latter range, thus attesting to the quality of our films.
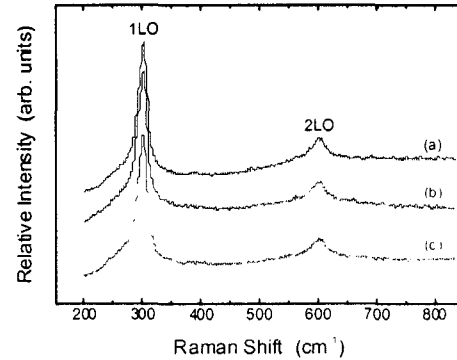

Fig. 3. Raman spectra of CdS thin films at room temperature: (a) undoped film, (b) [B/Cd]=10^{-2}, (c) [B/Cd]=10^{-1}.

Table 1. Comparison in wavenumber of LO modes of our films with those of single crystal CdS and PLE CdS thin films.

CdS type or growth method	Raman shift (cm^{-1})			
	1LO	2LO	3LO	4LO
Single crystal [7]	305	604	909	1200
PLE [9]	300	600	904	
Undoped	300	603		
[B/Cd]=10-2	298	600		
[B/Cd]=10-1	299	601		

Fig. 4 shows the optical transmittance spectra of the undoped and B doped CdS thin films. An increase in transmittance is observed for the boron doped films. It is seen that the fall of transmittance at the absorption edge is quite sharp, which is an indication of good crystallinity of the film. A shift in the absorption edge toward shorter wavelengths due to increasing carrier density was observed. It is clear that such a shift to shorter wavelengths is an advantageous feature for CdS layers applied as heterojunction window layers in solar cell because it extends the range of their spectral transmission just in the maximum of the solar emission spectrum. This shift is advantageously correlated

with high electric conductivity. For larger boron concentration more than 10^{-2}, however, the absorbtion edge is shift toward the longer wavelength region. CdS is a direct band gap material and for a direct allowed transition, the absorption coefficient (α) is related to the band gap (E_g) by the relation $\alpha \propto (h\nu - E_g)^{1/2} / h\nu$. The optical band gap can be obtained by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ versus $h\nu$ to $\alpha = 0$. The optical band gap for the undoped film is found to be 2.38 eV. The band gap values are found to be increasing with boron doping and it is found to be 2.41 eV for $[B/Cd] = 10^{-2}$. This increase of band gap may be offered based on possible decrease in the grain size of the B-doped CdS. Yu et al. [20] have observed an increase of about 0.1 eV in the band gap when the grain size decreased from 25 to 5 nm.
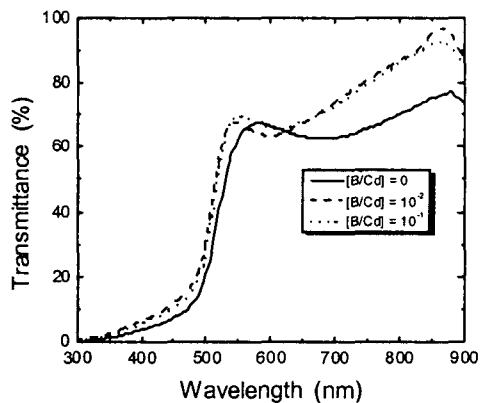

Fig. 4. Optical transmittance of CdS thin films with various [B/Cd] ratios.

IV. Conclusions

We have grown the B-doped CdS thin films by CBD technique on glass substrate. CdS thin films show a predominant hexagonal phase with small crystallites. The photoluminescence spectra show two peaks located at 2.3 eV (green emission) and 1.50 eV (red emission), respectively. Raman peaks due to CdS LO phonon shift to lower values compared to single crystal CdS. The undoped films have smaller Raman shift than those for B-doped CdS films. This is contributed by larger grain size.

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