〈연구논문〉

Crystal Growth and Sensor Development of II-VI Compound Semiconductor : CdS

D.I. Yang, Y.J. Shin, S.Y. Lim and Y.D. Choi*

*Cheonbuk National University, *Mokwon University*
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II-VI족 화합물 반도체의 결정성장 및 센서 개발에 관한 연구

양동익 · 신영진 · 임수영 · 최용대*

전북대학교, *목원대학
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Abstract—This study deals with the crystal growth and the optical characteristics of CdS thin films activated by silver. CdS:Ag thin films were deposited by using an electron beam evaporation(EBE) technique in vacuum of 1.5×10^{-7} torr, voltage of 4 kV, current of 2.5 mA and substrate temperature of 250℃. CdS:Ag photoconductive films prepared by EBE method show high photoconductivity after annealing at about 550℃ for 0.5 h in air and Ar gas.

The grain size of CdS:Ag thin films annealed in Ar atmosphere (1 atm) was grown over 1 μm and the thickness of the films is 4~5 μm. The analysis of X-ray diffraction patterns shows that the crystal structures are hexagonal. The diffraction line by (00.2) plane can only be observed, indicating that c-axis of hexagonal grows preferentially perpendicular to the substrate. The profiles of photoluminescence spectra of CdS:Ag films show Gaussian type curves at room temperature, the maximum peak spectral sensitivity of CdS:Ag is located at the wavelength of 520 nm.

We annealed CdS:Ag thin films in air and Ar vapor in order to make the CdS photoconductors having the intensive photocurrent, the broad distribution of the photocurrent spectrum and the large value of the ratio of the photocurrent (pc) to the dark current(dc). We found that CdS:Ag thin films annealed in air atmosphere was the best one.

요 약—E-Beam 기법을 이용하여 증착시킨 Ag doped CdS 박막은 육방정계이고 공기, Ar 분위기에서 550℃로 열처리한 결과 grain size가 1 μm 정도로 성장되었고, Van Der Pauw 방법으로 구한 Hall data로부터 CdS crystal은 n형 반도체이고 상온에서의 carrier 농도는 2.7×10^{11} cm^{-3}이고 Hall mobility는 5.8×10^{2} cm^{2} V^{-1}sec^{-1} 정도임을 알 수 있었다.

CdS : Ag 박막의 PL spectra는 Gaussian curve를 보여주었고, spectra peak는 파장이 520 nm 근처에 위치하고 있으며, CdS : Ag 박막에서의 광전류(pc)와 암전류(dc)의 ratio(pc/dc)는 공기중에서 열처리한 시료의 값이 크다는 것을 알 수 있었다.

1. Introduction

The II-VI compound semiconductors are useful materials and in recent years there has been a growing interest in the use of thin films of them for opto-electronics because of their attractive proper-

ties in the visible region[1]. CdS is a semiconductor with a wide direct-transition energy gap of 2.4 eV at room temperature, and has potential applications as a "window" material for solar cells such as CdS/CdTe, CdS/InP, and also a photoconductor, and a visible-light deflector, etc.[2]

Evaporation in vacuum is a significant process for the production of thin films. The reason of the use of the electron beam for evaporation is the nature of the energy flow in evaporant heating. In all the other heating modes the energy flow goes through the crucible and the evaporant to the vapor-emitting surface. With electron beam evaporation, however, this surface is directly heated by impinging electrons, a kind of energy supply that, when compared to conventional heating modes, results in some significant advantages. In contrast to conventional heating modes, the evaporant is heated by a beam that impinges directly onto its surface; the greatest portion of the kinetic energy in the beam is converted into heat. Electron beam evaporation from water-cooled crucible allows the production of high-purity films because reactions with the crucible walls are avoided almost completely. Beam control with respect to time and location further enhances the energy flow to the evaporant, the evaporation rate and the vapor stream distribution[3].

Various deposition techniques such as vacuum evaporation technique[4], spray pyrolysis[5], metal-organic chemical vapor deposition (MOCVD)[6], and molecular beam epitaxy (MBE)[7], etc. have been tried by different groups for the deposition of CdS films.

CdS:Ag thin film of this work is deposited by using an electron beam evaporation technique, we are willing to develop into a photosensor of the photoconductive thin films. We here report detailed results obtained by X-ray diffraction patterns, morphology, Hall effect and photoluminescence(PL). The films must be a photoconductor with a intensive photocurrent and a broad spectrum in order to be a photosensor. For this purpose, the films are annealed at the proper temprature and for the proper time in the vacuum, the air, Cd and S vapor pressure. Subsequently, the photocurrent spectrum and

the ratio of the dark current(dc) and the photocurrent(pc) for these annealing films are measured. In the long run, we found that CdS:Ag thin film annealed in air atmosphere was the best one.

2. Experimental Procedure

CdS:Ag phosphor films were deposited by an electron beam evaporation technique using a model VI-5R vacuum coater system of ANELVA. The sample employed was CdS 6 N powder(ELECTRONIC SPACE PRODUCTS INC.) of the lectro-luminescent grade, 5 N Ag_2S and NH_4Cl of the special grade. CdS:Ag luminescent powder is produced when CdS powder containing activator of 10^{-4} mole% and flux of 10^{-2} mole% is fired. CdS:Ag luminescent powder was deposited by an electron beam evaporation onto thoroughly cleaned pyrex plates maintained at a temperature of 523 K. Prior to charging the water-cooled crucible with CdS:Ag luminescent powder, the powder was pressed together to make a compact pellet into a cylindrical block to prevent sputtering during the evaporation.

We used pyrex plates. As substrates these were cut to the desired size of 20 mm×20 mm. The substrates were cleaned in isopropyl alcohol in an ultrasonic bath for 10 min. Then the cleaned substrates were fixed on the holder in the vacuum chamber and heated to 250℃ for 0.5 h to desorb surface impurities. Typical pressure of the chamber during heating was in the range 10^{-7} torr. The substrate temperature was measured using a chromel-alumel thermocouple. Under the depositions, the source-to-substrate distance was 10 cm. Our source materials, those were contained in the crucible, were irradiated by the low-density electron beams for 30 minutes to pre-heat the materals. During those procedures, the substrates was shadowed by using of movable shutter. The evaporation conditions were typically as follows: a vacuum of 5× 10^{-7}~1.5×10^{-6} Torr; acceleration voltage, 4 kV; electron beam current, 2.5 mA; deposition time, 1 hour. After deposition, the CdS:Ag films were subjected to annealing for 0.5 h at 550℃ under 1 atm pressure of the Ar gas ambience.
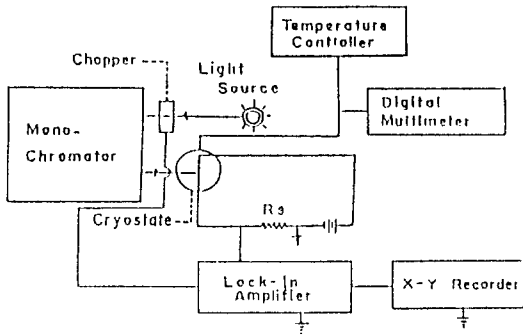
The crystal structure of CdS thin films of pre-

Fig 1. Block diagram of the arragements used in the photocurrent measurements.

and post-heat treatment was also investigated on the basis of X-ray diffraction(Cu Kα, λ=1.54Å) and the morphology of the films was observed by using scanning electron microscopy(SEM). Thickness measurements of the films were made by employing TAYLOR-HOPSON thicknessmeter. Optical measurements were carried out using a JARRELL-ASH monochromator(f=0.5 m). All the spectra were recorded for samples cooled down from 293 K to 33 K in a liquid-helium cryostat. All the curves were taken with excitation by 3650Å light produced by an Hg-lamp with an ultraviolet transmitting filter. The PL spectra were detected by a conventional lock-in system with a photomultiplier[8]. The samples of the photocurrent measurements were annealed at 550℃ for 0.5 h under the air and Ar ambience of 1 atm. The photocurrent was measured on the thin films apprpximately 8 mm×8 mm. The experimental arrangement used in the photocurrent measurements is like the block diagram shown in Fig. 1.

The electrodes of the photoconductive cells to be measured the ratio pc/dc were made by In metal around the center of the both sides. The experiment for measuring the ratio pc/dc consisted of applying a dc voltage and observing the dc current through the samples. For such purpose, we employed a dc power supply, a Keithley 610C electrometer and a power meter (ED model 250P). Then the power density of the light source was 10 mW/cm².
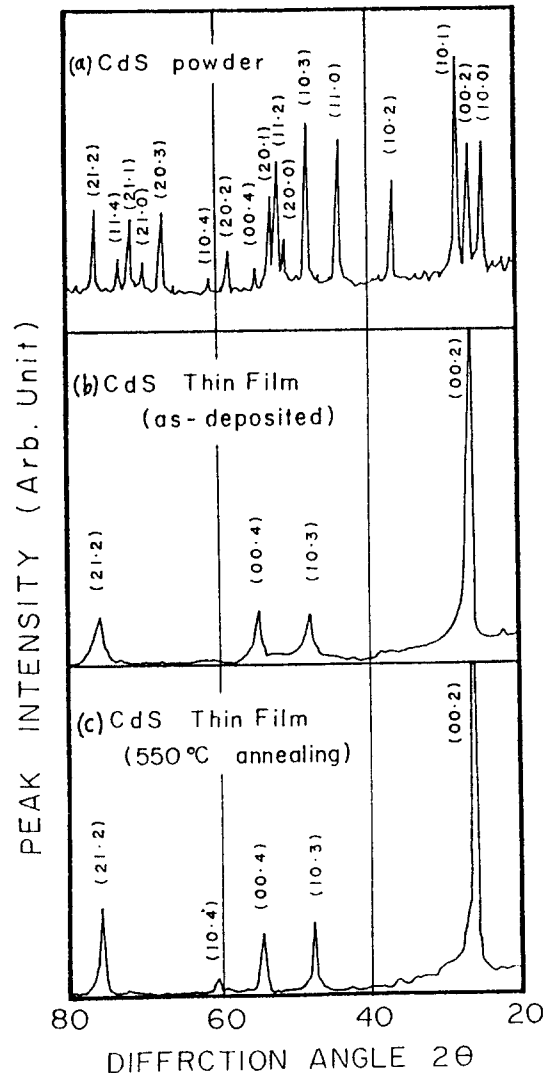
3. Results and Discussion

Fig 2. X-ray diffractograms of (a) pure CdS powder, (b) as-deposited film deposited by EBE, (c) CdS:Ag films annealed in Ar atmosphere at 550 ℃ for 0.5 h.

3.1. X-ray diffraction pattern

X-ray diffraction measurements were carried out to determine the structure of the CdS powder as well as that of its thin films. Fig. 2(a) shows X-ray diffraction patterns of pure CdS powder. The appearance of X-ray diffraction peaks point out the hexagonal structure of the powder. Fig. 2(b) shows the X-ray diffraction pattern of the films deposited on the 523 K pyrex plates. As can be seen in Fig. 2(b), as-deposited films display the specific surface of
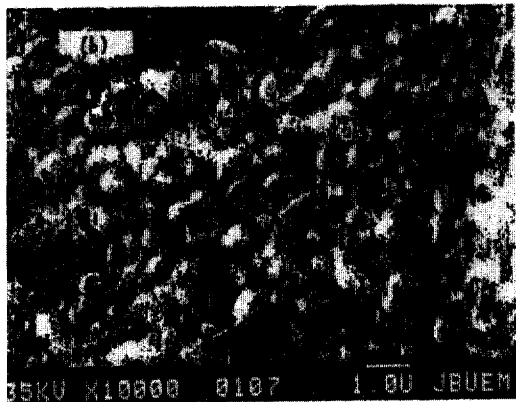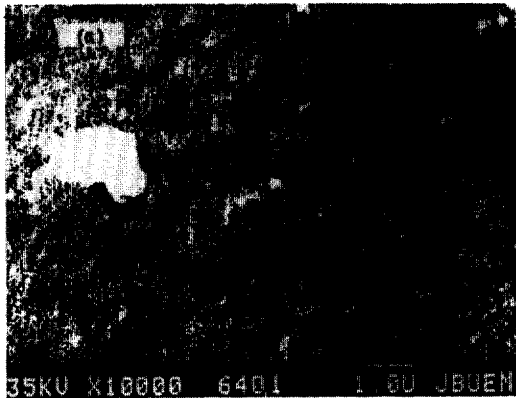
Fig 3. SEM micrographs; (a) as-deposited films, (b) CdS Films annealed in Ar at 550℃ for 0.5 h.

Table 1. Electrical properties of CdS:Ag films.

Sample	Annealing atmosphere (1 atm)	Carrier concentration (cm^{-3})	Mobility $(cm^2V^{-1}sec^{-1})$
CdS:Ag	as-deposited	8.99×10^{10}	1.27×10^2
CdS:Ag	air	2.70×10^{11}	5.82×10^2
CdS:Ag	Ar	2.70×10^{11}	4.36×10^2

ter and grains were grown to polycrystal state. Thickness of the films were almost 4~5 μm.

3.3. Hall data

The electrical characterization of the films was measured using the standard Van der Pauw method [9] at room temperature and their values are given in Table 1. Annealing of the films in the atmospheric pressure was carried out at 550℃ for 0.5 h.

3.4. Photoluminescence(PL)

Typical emission spectra from CdS:Ag films deposited on the pyrex plates by electron beam evaporation technique are shown in Fig. 4. In the following we summarize the current understanding of these luminescent spectra[10]. The luminescence light was detected in the range between 490 nm and 650 nm. The profiles of PL of CdS:Ag phosphor films show Gaussian type curves at room temperature. Fig. 4(a) shows PL spectra of as-deposited CdS:Ag films. Fig. 4(b) and (c) show PL spectra of the films annealed at 550℃ for 0.5 h under 1 atm pressure of the air and Cd atmosphere respectively. As the temperature is reduced from 293 K to 33 K, the position of the peaks shifts to shorter wavelengths by about 30 nm. The maximum peak of spectral sensitivity of CdS:Ag films annealed in Cd and air at 293 K is located at the wavelength of 520 nm.

The PL spectra of annealed-phosphor films is shifted by approximately 60 nm towards shorter wavelengths of the absorption edge in comparision with as-deposited films. From these PL spectra, we found that the energy band gap of the films of the before and after annealing is increased by about 0.24 eV. The PL spectra in Fig. 4(b) and (c) is called green edge emission and has been studied intensi-

the hexagonal structure. Fig. 2(c) shows X-ray diffraction patterns of CdS phosphor film annealed at Ar gas ambinence. X-ray diffractograms, as that shown in Fig. 2(b) and (c), displayed strong (00.2) peak. From the above-mentioned facts, films generally show a strong preferential orientation with the c-axis perpendicular to the substrate.

3.2. SEM micrographs

Scanning electron microscopy was used to examine film morphology. The results are shown in Fig. 3; the as-evaporated CdS:Ag film is illustrated in Fig. 3(a). A clear distinction among the grain boundaries is not evident, and the grains appear small, as shown in Fig. 3(a). After heat treatment at 550℃ for 0.5 h in Ar atmosphere, Fig. 3(b) presents grain sizes were approximately 1 μm in diame-
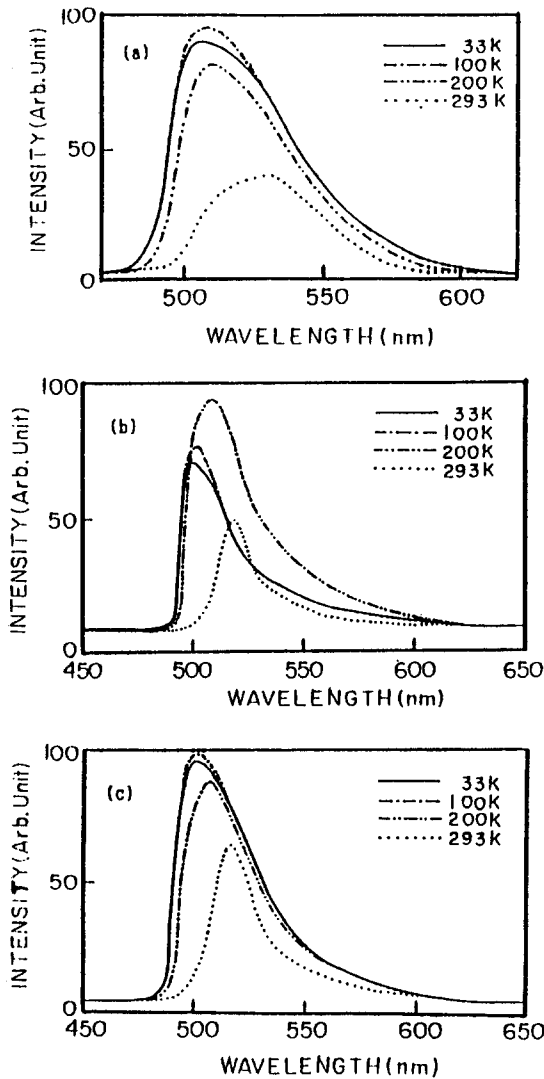
Fig 4. PL spectra of (a) as-deposited CdS:Ag film, (b) CdS:Ag film annealed in air at 550℃ for 0.5 h, (c) CdS:Ag film annealed in Cd vapor at 550 ℃ for 0.5 h.

Fig 5. Photocurrent spectra of CdS:Ag as-deposited thin film.

Table 2. The energy values of the double peaks of the as-deposited films and of the films annealed in the air and the Ar atmosphere.

		Peak Wavelength(nm) ⟨Energy(eV)⟩		
T(K)	Eg(eV)	As-deposited films	annealed in the air	annealed in the Ar
293	2.4276	510(2.4310)	502(2.4698)	509(2.4360)
				501(2.4760)
250	2.4500	508(2.4406)	500(2.4797)	506(2.4500)
			508(2.4406)	498(2.4900)
200	2.4760	508(2.4406)	496(2.4997)	499(2.4850)
			490(2.5303)	496(2.5300)
150	2.5020	508(2.4406)	494(2.5098)	484(2.5100)
			488(2.5303)	486(2.5510)
100	2.5280	508(2.4406)	494(2.5098)	
			488(2.5303)	
50	2.5540		494(2.5098)	
			488(2.5303)	
33	2.5628		494(2.5098)	
			488(2.5303)	

vely in the past[10]. The green edge emission lines have been variously ascribed to free-to-bound recombination[11] and to bound-to-bound[12] and internal transitions within a complex centre consisting of nearest-neighbour donor-acceptor associates [13]. Most of these investigations were carried out with bulk crystals[14].
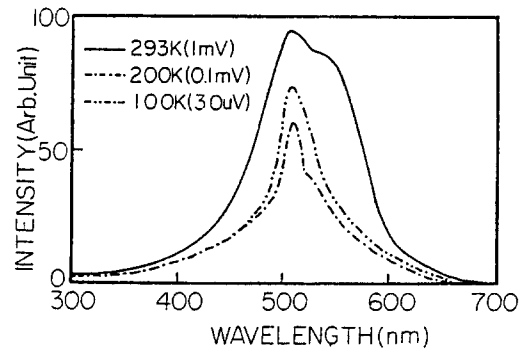
3.5. Photocurrent

Fig. 5 shows the photocurrent spectra of CdS:Ag as-deposited thin films. The values of the peak spectra of as-deposited films and of the annealed films varied with the temperature were shown in Table 2. in order to be compared with the energy band gap $E_g(T)$[15]. As shown in Table 2, the photocurrent peaks of the films annealed are shifted towards shorter wavelengths in comparision with as-deposited films. The films annealed almost have two photocurrent peaks. Most of the peak position of as-deposited films and of the films annealed is obser-
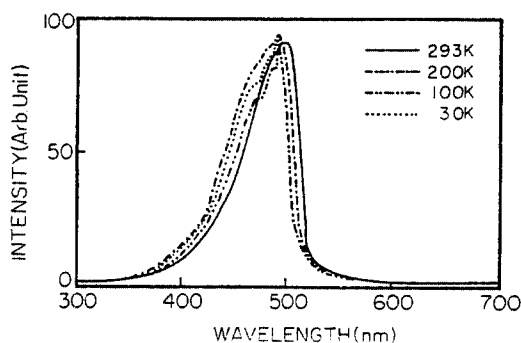
Fig 6. The photocurrent spectra of the films annealed in Air at 550℃ for 0.5 h.

Fig 7. The photocurrent spectra of the films annealed in Ar atmosphere at 550℃ for 0.5 h.

Table 3. The intensities of the peak of the photocurrent spectra of the films in air and Ar at 550℃ for 0.5 h.

Sample/Temp.	293K	250K	200K	150K	100K	50K	33K
CdS(as-depo.)	10	2.7	0.7	0.3	0.3		
CdS(air)	92	95	95	92	92	94	93
CdS(Ar)	28	26	27				

ved in the similar place.

The energy difference between the energy of the peak spectrum and the energy band gap $E_g(T)$ is due to the polarization effect of the light. The photocurrent peaks for the incident light perpendicular to or parallel to the c-axis of CdS are shifted to 509.5 nm(2.4334 eV) and 513.4 nm(2.414 eV) respectively. The energy difference between the two band gaps is 0.018 eV in CdS(only about 1% of the band gap)[16]. Judging from the peak wavelength of the photocurrent spectrum, the incident light is parallel to the c-axis. The energy band gap varies from 2.42 eV to 2.433 eV. The peak of the photocurrent spectrum means that the electron of the valence band $\Gamma_9(A)$ is excited to the conduction band Γ_7 by the absorption of the photon energy.

Fig. 6 and 7 show the photocurrent spectra of the films annealed at the air and Ar atmosphere. In Fig. 6 and 7, the photocurrent for the shorter wavelength is much smaller than the ones for absorption edge. The absorption of the photon energy extremely occurs in the surface. The photocurrent decreases because the life time of the conduction electron excited is much smaller than the life time of the conduction electron with increasing wavelength[17]. The peaks corresponding to the absorption edge are the ones generated by band-to-band transition called intrinsic transition[18-20].

When CdS is annealed in air or in vacuum, SO_2 is generated[21]. The ratio of the ionic bond to the covalent bond for II-VI compounds is 60%: 40% [22]. Two Cd vacancies V_{Cd} is created when CdS forms SO_2[23]. If V_{Cd} accepts the hole, p-type CdS
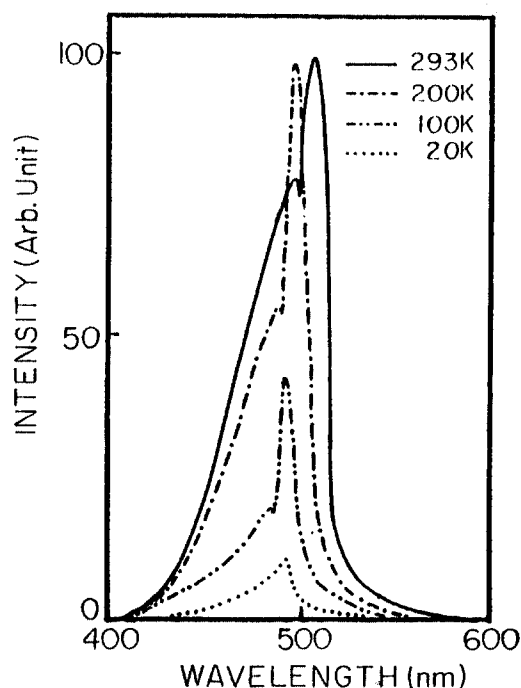
can be made[24]. But until now p-type CdS does not exist. Therefore it is discussed that V_{Cd} is compensated with the electrons from the donor and V_{Cd}^- is acted. The negative charges of the acceptor compensated interact Coulomb repulsive forces with the free electrons in the conduction band and interrupt the recombination. Then the life time of the free electrons in the conduction band is to be long and the photocurrent is increased[25].

The intensites of the peaks of the photocurrent spectra of the films annealed in air and Ar are shown in Table 3.

The highest peak of the photocurrent spectra is the one of the films annealed in air. The highest

Table 4. The photocurrent and dark current of CdS thin films annealed in vacuum, air, Cd, and Ar.

Samples	dc(A)	pc(A)	Ratio(pc/dc)
CdS(as-depo.)	3.1×10^{-6}	1.1×10^{-5}	3.55×10^{0}
CdS(Ar)	1.6×10^{-8}	1.5×10^{-5}	9.3×10^{2}
CdS(air)	1.2×10^{-8}	1.1×10^{-4}	9.2×10^{3}

peak of the films annealed in air is about 300 times as large as the one of as-deposited films. Therefore the best films as the photoconductor are the ones annealed in air.

3.6. Measurements of the photocurrent and the dark current

The photocurrent and dark current were measured to develope the films into the photosensor. The photocurrent and dark current were measured using the films annealed in vacuum, air, Cd and Ar and the applied voltage was 1.5 Volt. The dark current was measured in the dark and the photocurrent was measured from the films irradiated with the white light. The values measured are indicated in Table 4.

The current ratio was increased much extremely in the films annealed in air and compared with the data of the reference. We belive that the films annealed in air and Ar will be developed into the good photosensor.

4. Conclusions

CdS:Ag thin films were deposited on the pyrex plate by using an electron beam evaporation technique to develop into a photosensor and their electrical and optical characterization were investigated.

The results are as follows;

1. X-ray diffraction patterns of CdS films annealed at Ar displayed a (00.2) strong peak.

2. The size of grain boundary were about 1 μm and the thickness of the films were 4~5 μm.

3. The carrier concentration and the mobility of the films annealed in air were 2.70×10^{11} cm^{-3} and 5.82×10^{2} cm^{2} V^{-1}sec^{-1} respectively.

4. PL spectra of the films were green edge emission.

5. CdS:Ag thin films annealed in air atmosphere are the best ones as the photoconductors.

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