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CdS 박막제작 및 그 특성

(발광 및 수광 소자 응용을 위한에 II-VI족 화합물 반도체들의 접착에 관한 기초연구)

Growth and Properties of CdS Thin films

(A Study on the adhesion of II-VI compound semiconductor for applications in light emitting and absorbing devices)

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요 약

CdTe/CdS 태양전지 제작에 필요한 다결정 CdS 박막을 ITO 전도 유리기판위에 SSD법, SPD법 및 CBD법 으로 제작하고 열처리 한 후 그 결정구조와 광학적 특성을 조사하였다. 박막은 모두 Wurtzite 구조를 보였고 SSD법과 CBD법의 박막은 0.5μm 크기의 CdS 입자가 불규칙적으로 형성되어 증착되어 있음을 보였고, 400°C 로 진공중에서 열처리 할 때 입자의 크기가 약간 증가하였다. SPD법의 박막은 (002)방향으로 결정이 성장되고 입자의 크기가 0.1 - 0.3μm 이었다. 에너지 밴드갭 및 결함 상태를 광학적 흡수, 광 루미니센스, 라만 및 광·열 편기 스펙트럼(PDS) 측정을 통해 조사하였다.

ABSTACT

The structural and optoelectronic properties of polycrystalline CdS films up to several microns in thickness, fabricated by three different methods, are compared to one another for the purpose of preparing CdTe/CdS solar cells. All films were deposited on an indium tin oxide on glass substrate. The three methods are: 1) alternated spraying of cation and anion solution at room temperature; 2) spray pyrolysis with substrate temperature up to 500 °C; 3) chemical bath deposition (CBD). Deposited films were thermally treated in various ways. All films showed a well-developed wurtzite structure. Films grown by the alternated-spray method and the chemical bath method consist of randomly-oriented crystallites with dimensions <0.5 microns. Annealing at 400 °C increases the crystallite size slightly. Films which were grown by pyrolysis at substrate temperatures from 400°C to 500°C were oriented in the <002> direction. For growth by pyrolysis at 500°C, the surface is rough on a lateral scale of 0.1 to 0.3 microns. The optical band gap and defect states are investigated by optical absorption, photoluminescene, Raman, and photothermal deflection spectroscopies.

I. INTRODUCTION

Thin films of polycrystalline CdTe/CdS is promising material for high efficiency and low-cost solar cells[1]. CdTe has a direct gap of 1.5 eV, ideal for solar energy conversion; CdS acts as a wide band gap window or contact layer. For the fabrication CdTe/CdS devices, various deposition techniques, including vacuum evaporation, closed-spaced vapor transport, spray pyrolysis, screen printing, electrodeposition have been used. However large area CdTe/CdS solar cells are difficult to make because the CdS film on conducting glass often have pinholes which cause electrical short. The surface morphology, as well as other characteristics of CdTe thin films and CdTe/CdS thin film devices depend on the CdS films. CdTe/CdS solar cell reaserch has focused on increasing efficiency and investigations of electrical properties but relatively little work has gone into the morphorlogy, density and other properties of the CdS film which must depend on the nature of nuclear and adhesion onto the conducting oxide substrate.

It is our purpose here to compare the structural, morphological and optoelectronic characteristics for CdS films prepared by: Chemical Bath (CBD), spray pyrolysis

(SPD) and separated spray (SSD) deposition method. We can then make a more informed decision on the most appropriate deposition technique for optoelectronic devices. All of these technics have the merits of low cost and the absence of need for high vacuum. CBD and SPD techniques are well-known. The separate spray method(SSD) was introduced and developed by us[2,3]. Specifically, the CdS films were grown by the three methods above, and the surface morphology, the crystal orientation and quality, optical absorption coefficient, and defect states were studied by electro microscopy, X-ray diffraction, optical transmission, photoluminescence, Raman spectroscopy and Photothermal Deflection Spectroscopy(PDS)measurement.

II. FABRICATION AND PROCESSING OF THE CdS FILMS

a) Chemical Bath Deposition

CdS films were deposited on conducting glass (ITO:Vacuum Co., Japan. ρ=10 ohm/cm^2) through the method of H. Uda et al.[4]. For the growth of CdS films, we prepared the $CdCl_2$ (0.2 molar), NH_4Cl, (2.5 molar) and thiourea (1 molar) and mixed them in a Pyrex glass chamber container (Φ=15cm, L=15cm), stirring well.

Two sheet of ITO glass are placed back to back and are used to stir the solution while the bath is heated to and then held at 96°C. The substrate holder was rotated, at 100 rpm. This process continued for about 2 hours, after that, the films ceased to grow and CdS precipitated to the bottom of the chamber. The thickness of the film was about 0.85μm. For thicker films, deposition was carried out more times. Some of the films were annealed in vacuum at 400°C for 25 min. to reduce the resistivity of the film.

The expected chemical reaction is as follows:

1. $CdCl_2 + 4(NH_3) \text{ ---> } Cd(NH_3)_4Cl_2$
2. Diffusion of OH^- and thiourea for preparing the catalysis surface of CdS
3. $(NH_2)_2CS + OH^- \text{ ---> } CH_2N_2 + H_2O + HS^-$
4. $HS^- + OH^- \text{ « } S^{--} + H_2O$
5. $Cd(NH3)4^{++} + S^{--} \text{ « } CdS + 4NH_3$

For films deposited repeatedly, for one time, two times and four times, the thickness of films were nearly proportional to the number of deposition.

b) Spray pyrolysis method

The CdS films were made on ITO glass using the method introduced by R. H. Bube et.al .[5] For CdS film growth, the solutions, $CdCl_2$(0.1 molar) and thiourea (0.1 molar) were prepared and mixed. This solution is sprayed through a fine nozzle with 5.6 l/min spray speed onto a heated ITO substrate placed on a heated plate.

The chemical reaction is as follows.

$CdCl_2 + (NH_2)_2CS + 2H_2O$ ---> $CdS + 2NH_4Cl + CO_2$

To search for good adhesion conditions for CdS films on ITO, we grew films at substrate temperatures of 410°C, 450°C, 470°C and 500°C . Below 410°C, the CdS did not adhere well and above 500°C, the ITO substrate began to deform. Films were annealed at 300°C for 10 min in hydrogen atmosphere to improve the quality and lower the resistivity

c) Separate Spray method.

In order to achieve the efffect that the atomic layer of Cd and S deposit on the ITO glass alternately and repeatedly at room temperature, cation solution and anion solution were sprayed separately onto the substrate[2]. The cation solution($CdCl_2$: 0.05 mol,) was sprayed to form the Cd^{++} ions on the ITO surface which is attached to a rotating plate with 600rpm angular velocity. Distilled water was then sprayed to remove the remaining $2Cl^-$ ions. which is following, An anion solution (Na_2S : 0.05mol) is then sprayed to form S^{--} ions on the Cd layer, and again distilled water to remove the remaining $2Na^+$ ions. The whole process were repeated.

The chemical reaction is as follows:

1. $CdCl_2$ ---> $Cd^{++} + 2Cl^-$
2. Sweep out Cl^- ions by spraying with distilled water.
3. Na_2S ---> $2Na^+ + S^{--}$
4. $Cd^{++} + 2Na^+ + S^{--}$ ---> $CdS + 2Na^+$
5. Sweep out Na^+ ions by spraying distilled water.

III. RESULT AND DISCUSSION

a) Surface Morphology

The surfaces of CdS films prepared by these three method were observed by scanning electron microscope. The results are shown in Fig. 1, Fig. 2, and Fig.3.

Fig. 1. shows the surface of CdS films grown by CBD method. In the figure the films are composed of particles of CdS a few microns across and are made up grains with small dimensions of about 0.2 microns. The structures are not compact, and shows a great deal of open voids. This non-compact structure is undesirable for CdTe/CdS solar cells because it could create many pinholes and shorts between the electrode.

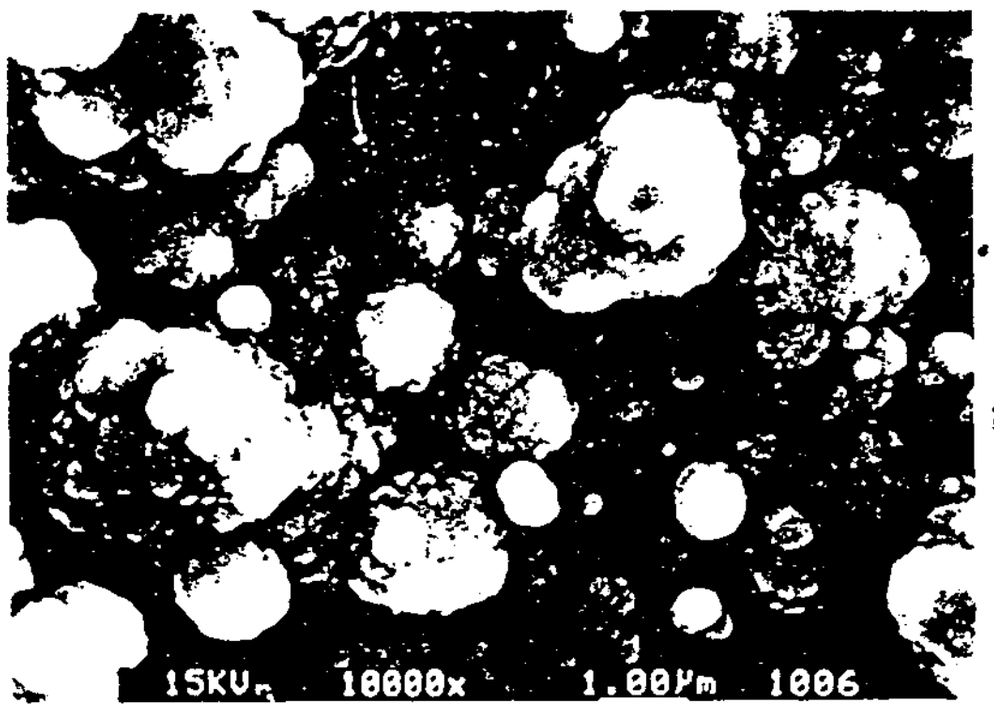

Fig. 1. Scanning electron micrographs of surface morphology of a CdS/ITO film grown by chemical bath deposition(CBD) method.

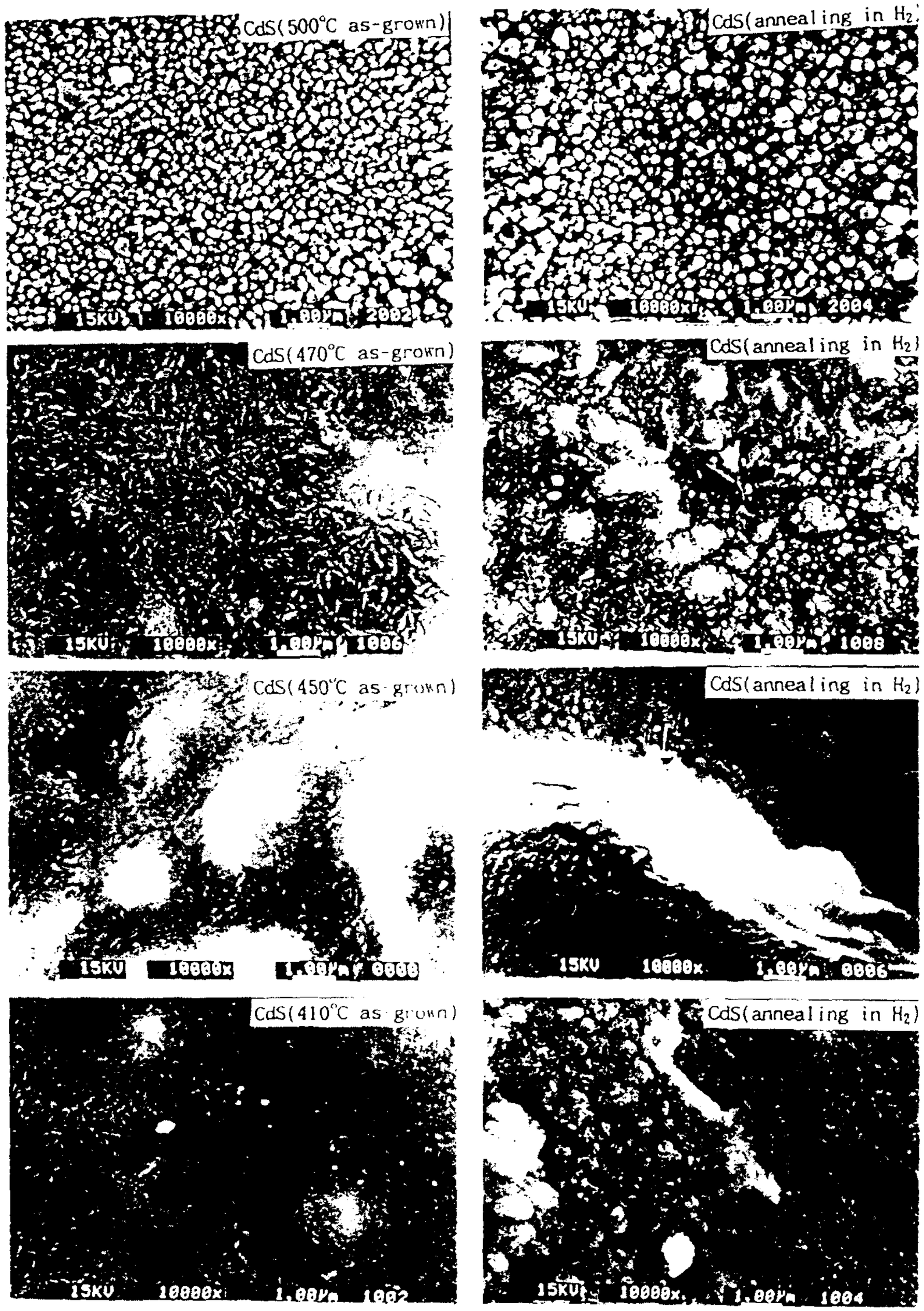

Fig. 2. Scanning electron micrographs of surface morphology of a CdS film prepared by the pyrolysis deposition(SPD)

Fig.2 shows the surface of CdS films grown by the spray pyrolysis. During the growth process, the substrate were kept at 410°C, 450°C, 470°C or 500°C, and then all films were post annealed at 300°C for 10 min. in hydrogen atomosphere. We could observe that the films grown at 500°C are uniform, compact and consisted of grain with dimesion 0.2 micron. However, at low temperature, the films show a herringborn pattern. After annealing the dimension of grains was found to increased at 500°C, but no change was observed for films produced at lower temperatures.

Fig.3 shows the surface of CdS films grown by separate spray method. The

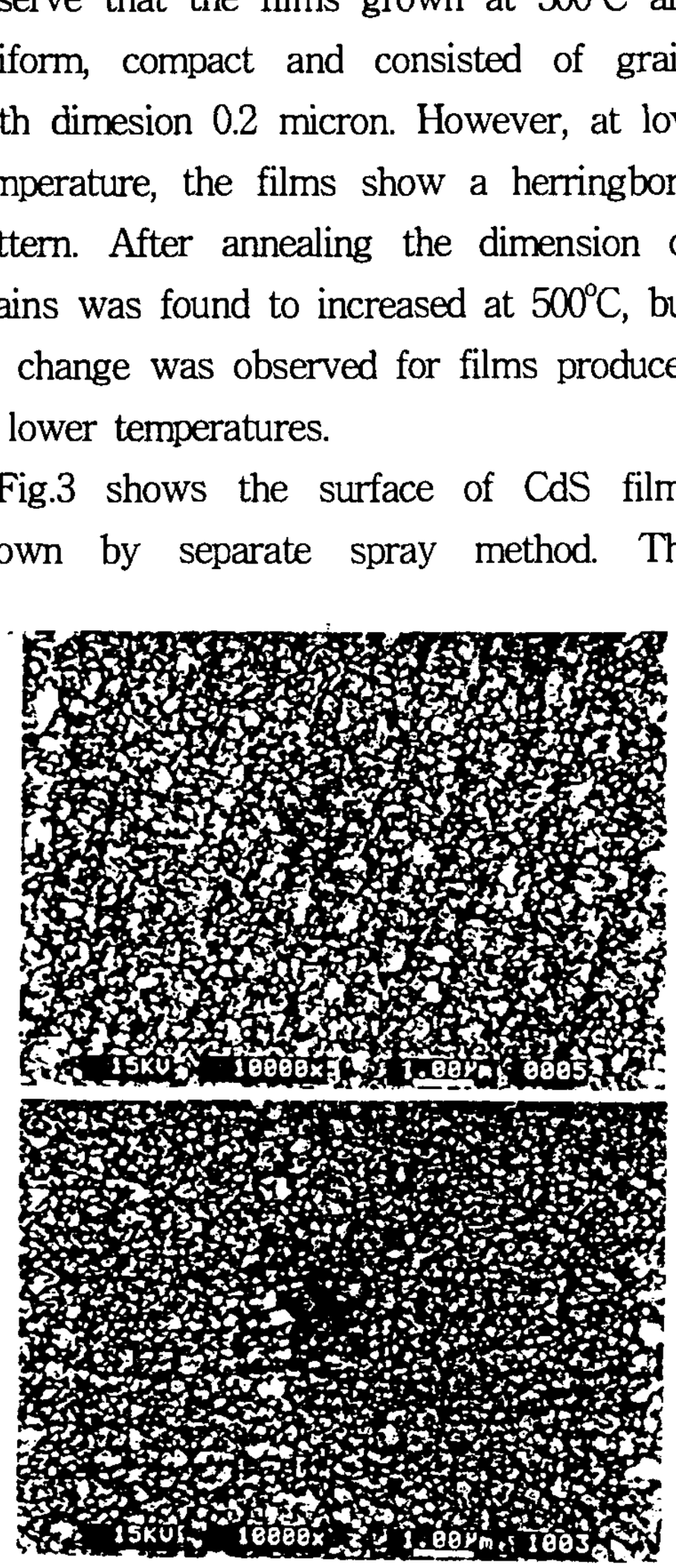

Fig. 3. Scanning electron micrographs of surface morphology of a CdS film prepared by separate spray deposition(SSD) method.

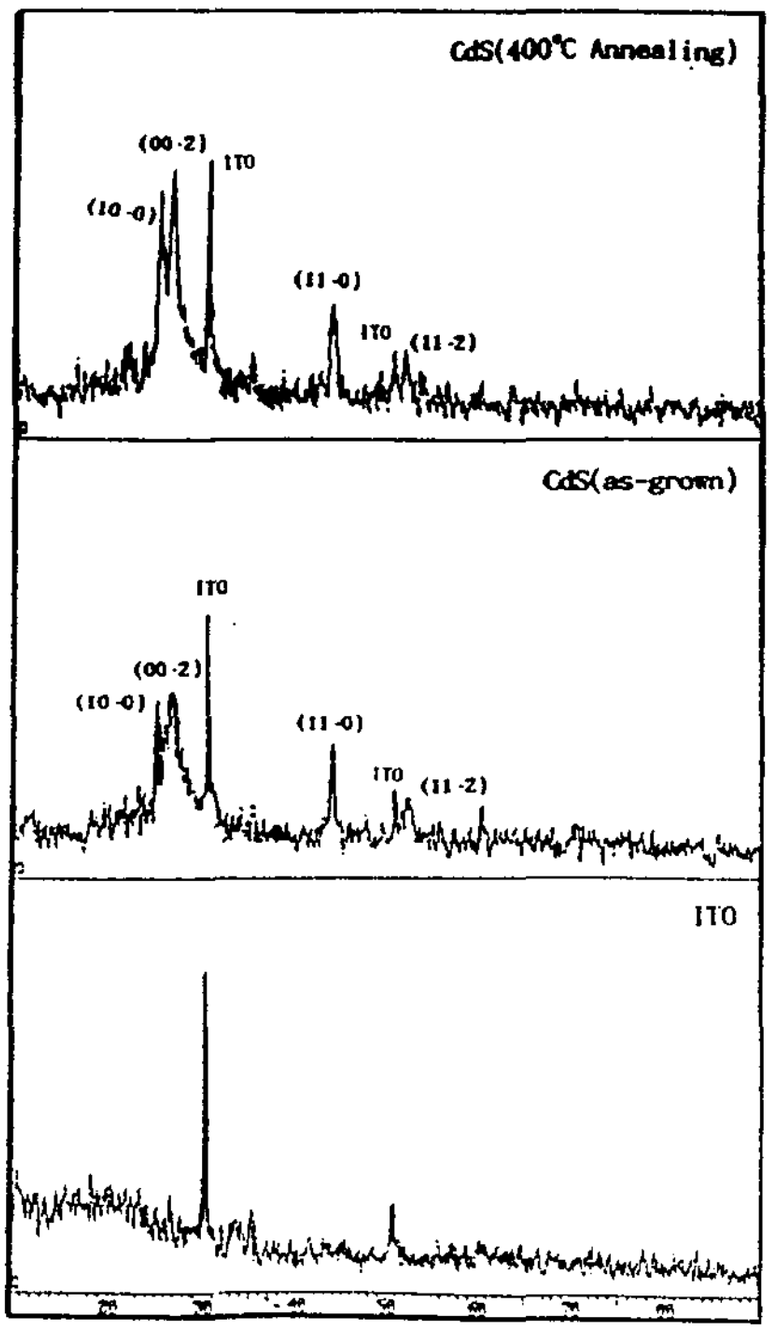

Fig. 4. X-ray diffraction scan of CdS films grown by CBD on ITO.

separate spray films exhibited a clustered-particle morphology which suggested that the growth is not layer-by-layer as we had hoped. In some cases we wiped off the large cluster with a soft sponge. The resulting films had a tree-back type of morphology which probably resulted from scratching with particles on the sponge.

b) X-ray diffraction Patterns

The X-ray diffraction patterns of three kinds of CdS films are shown in Figs.4, Fig. 5. and Fig.6. All of the patterns show the well developed Wurtzite crystal structure. In particular the films grown by spray pyrolysis show the pattern of a

preferred orientation in the <002> direction (Fig. 5). The remaining films show peaks from the (100), (002), (001), (110), (103) and (112) planes, indicating a randomly oriented polycrystalline state. The highest crystal quality, as determined by X-ray peak width and intensity and surface morphology was oriented in the SPD films. The crystal quality of the as-grown SSD method appeared to be better than that of the CBD films. After all of the CdS films were annealed, they had more intense X-ray diffraction peaks , so we believe that the film density had improved larger size grains.

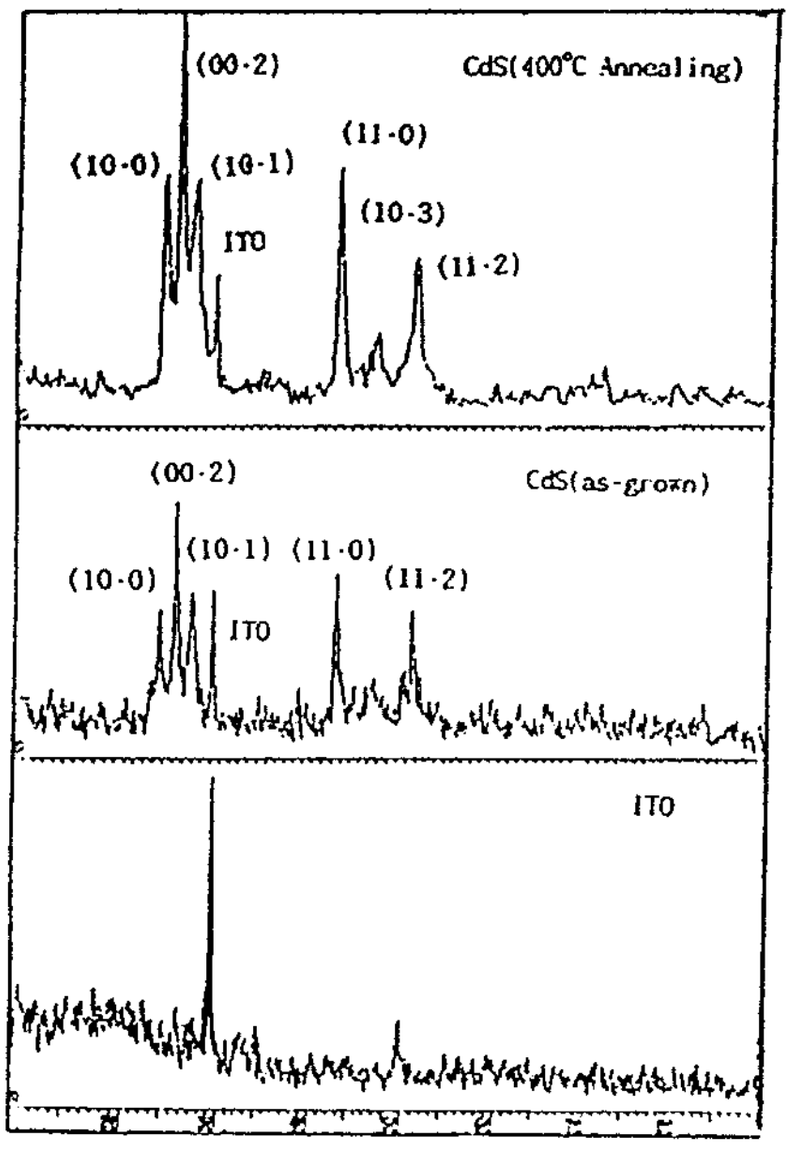

Fig. 6. X-ray diffraction scan of CdS films grown by SSD on ITO.

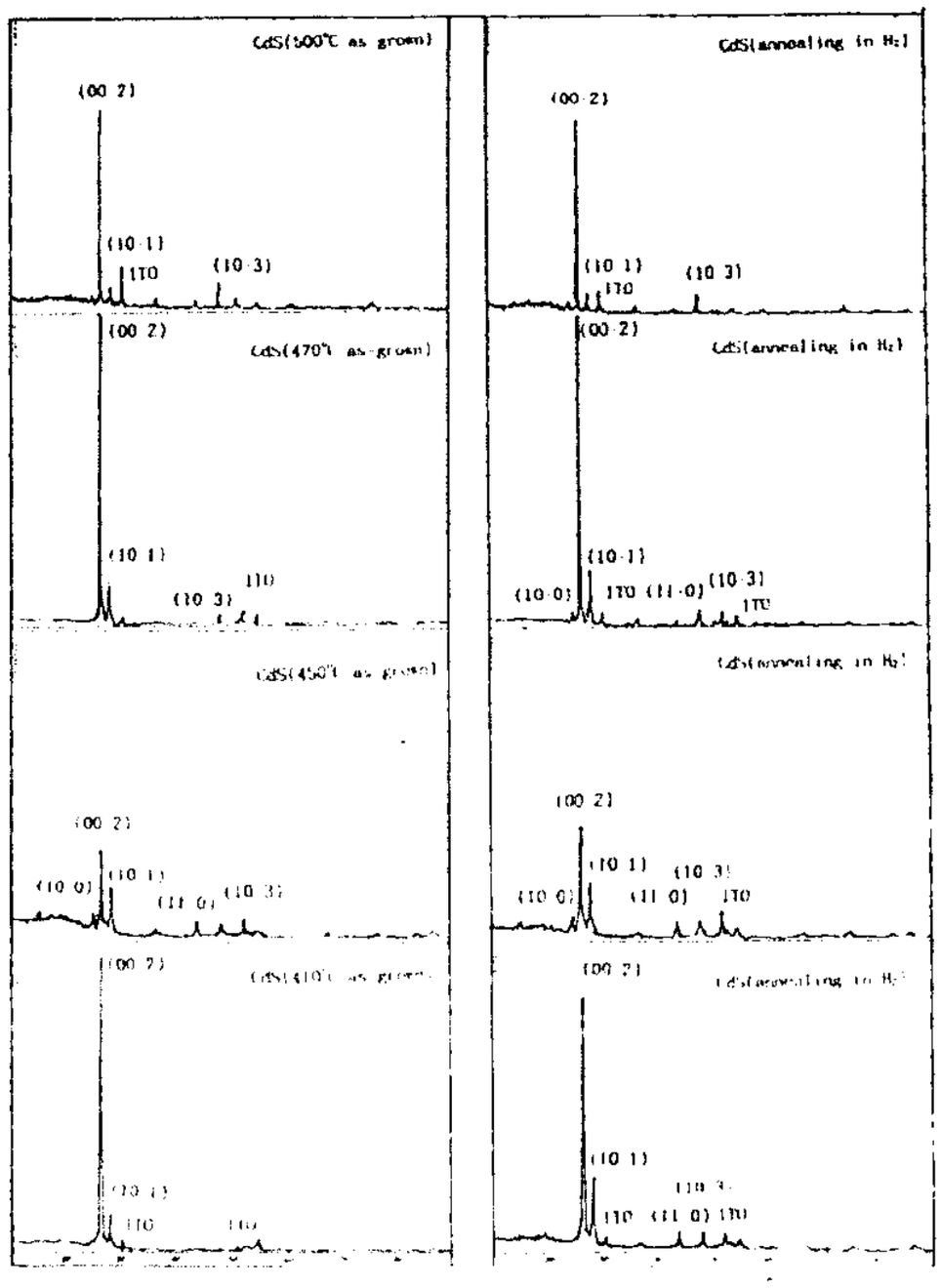

Fig. 5. X-ray diffraction scan of CdS films grown by SPD on ITO.

c) Photo-thermal Deflection Spectroscopy (PDS)

We measured the PDS of all 3 series of CdS films. In PDS the optical power absorbed in a thin films was detected by a heat - induced index gradient in a probe medium[6]. It was particularly useful for films which scatter light because it measured the absorptance rather than transmittance. The pumping light source was derived from the output of a 320W tungsten - halogen lamp which was passed through a 1/4 meter Jarell - Ash monochrometor and then focused at near normal incidence onto the sample. The probe light beam was a tightly focused

beam from a 1mW He-Ne laser which was passed nearly parallel to the sample surface in the probe medium(Fluorinert FC-70). The pump beam was chopped with 10Hz and the deflection in the probe beam was synchronously detected using a position sensitive detector(UDT), amplified by lock in amplifier (Stanford Research Inc.,SR530) and stored in the computer.

The PDS of all of the 3-series CdS films showed nearly the same shape with an absorption edge between 2.3eV and 2.4eV and a strong peak centered at about 1.55eV. An example of the spectrum for a film made by spray pyrolysis method at 550°C is shown in Fig. 7. We believe that the low energy absorption was due to a Cd vacancy - related deep defect [7,8,9]. We could also calculate the thickness of films through the interface from the plane between front and backside of the CdS films. In CBD films, the film thickness was about 0.85 micron for a single growth cycle. After the second and fourth cycles, the thickness increased proportionally. For CBD films the absorption edge curve were shifted slightly to lower energy side with respect to SPD films grown at 500°C. The absorption edge curves are slightly different with substrate heating temperature.

In the case of SSD films, the absorption edge curve are shifted to significantly lower energy relative to SPD films. In particular films which were annealed in hydrogen atmosphere had a large shift to lower energy. This is probably caused by sulfur vacancies or sulfur vacancy complexes[10,11]

d) Photoluminescence spectroscopy

Photoluminescence(PL) measurements were carried out using a 30mW He-Cd laser(2.81eV) as the excitating light source.

The emitting light analyzed with a 2m double monochromator(Jobin-Yvon Rama-nor) and detector with a GaAs photo-multiplier in photon counting mode. The measurement range is from 1.62eV to 2.48eV. All measurement were carrierd out at room temperature.

The PL spectra of the CBD films had generally low intensity with a peak centered at about 1.5eV. This coincided with observation from PDS. CBD films also had a broad peak centered about 1.6eV-1.7eV. We suggest that this could be due to Cd vacancy - S complex[7,8,9,10]. We observed peaks at 2.1 - 2.4 eV from ITO in the 0.84 micron thick (single layer) film. In double layer films the ITO PL is reduced and in quadruple growth thick films (3.4 micron) there only remained small trace of the ITO PL. We concluded that the films from this method had empty space or pinholes which permitted the excitation light to penetrate to the substrate and hence are not suitable for solar cell devices.

The films which were made by the spray pyrolysis method did not exhibit the ITO

PL peaks, indicating that the coverage is uniform and dense. Most of these films had very strong intensity PL. The peak centered at 1.5eV is very strong. In particular the films deposited at 500°C exhibit an edge emission peak centered around 2.4eV. Examples of the PL spectra are shown in Fig. 8. The films grown at the lower substrate temperature have shown another wide and intense peak centered at about 1.4eV with a slight signal from the ITO substrate.

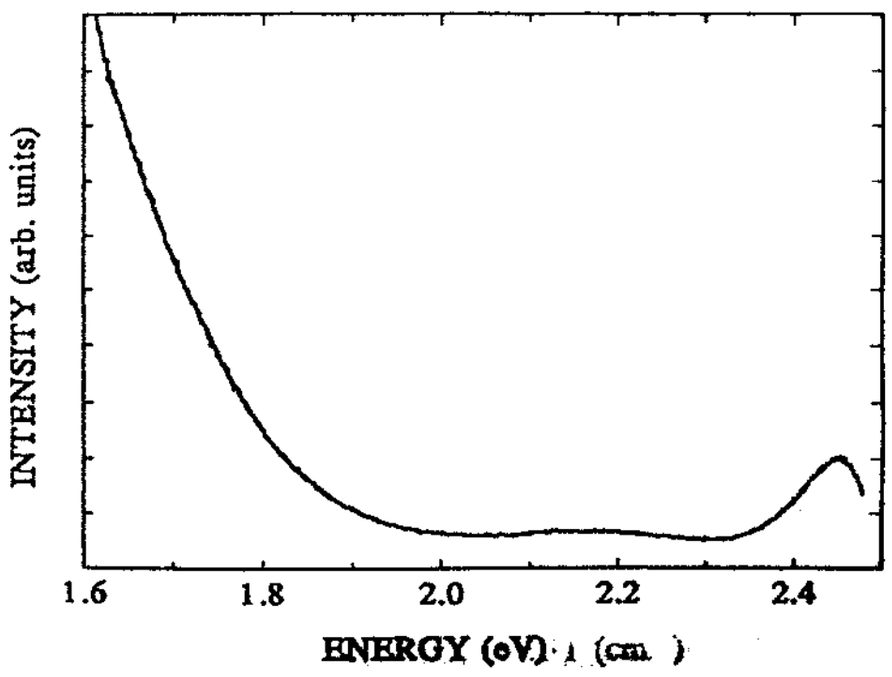

Fig. 8. Room temperature photoluminescence spectrum of CdS thin film grown by spray pyrolysis at 500°C.

The films from separate spray method have relatively low intensity PL spectrum. The PL from the ITO substrate are also observed. Furthermore, the films which are annealed in H_2 atmosphere show another broad peak centered at 1.9eV. We think this originated from sulfur or related vacancy[10,11]

From the PL analysis we also concluded that thin films which were made from spray pyrolysis with substrate temperature at 500°C are the most suitable for the thin film solar cell devices.

e) Raman spectroscopy

Raman scattering measurements were carried out on the same measurement system as the PL measurement, except that the excitation source was the 2.41eV line of an Ar ion laser which is closer to the band gap of CdS. We observed both the first order and second order LO phonon stockes Raman peaks in all films.

In the CBD films the peak shifts are 303-309 and 606-609 cm^{-1}. The Raman peaks of SPD films which are grown at 500°C substrate temperature are found at 300cm^{-1} (first phonon) and 604cm^{-1} (second phonon), and spectrum intensity is very strong as shown in Fig. 9. In the case of lower substrate temperature growth, the Raman shifts are 310cm^{-1} and 610 cm^{-1},and the back groud signal is increased, furthermore an ITO PL signal from the back-side also appeared.

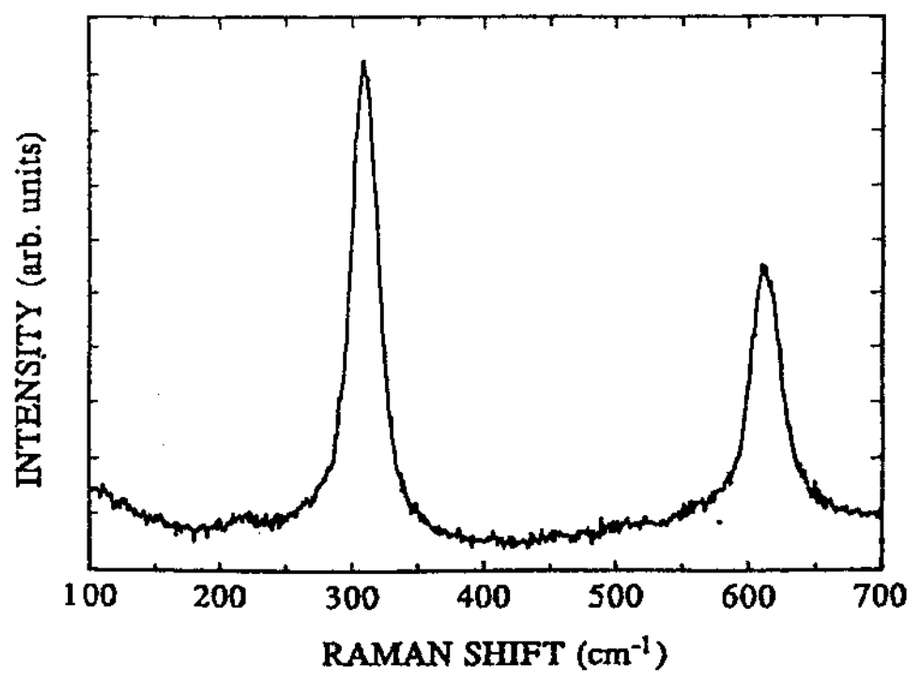

Fig. 9. Room temperature Raman spectrum of CdS thin film grown by spray pyrolysis.

In the films from separate spray deposition low spectrum intensity was exhibited, and first order Raman shift was 300 cm^{-1} but it moved to 315 cm^{-1} after heat treatment in hydrogen atmosphere. The second - order Raman shifts were 588 cm^{-1} and 616 cm^{-1} in the former and latter.

f) Optical Transmission

All films exhibit optical extinction due to scattering losses. chemical bath deposition and separate spray deposition films showed greater loss, implying larger scale microstructure.

Chemical bath deposition films exhibit lower absorption density than high temperature spray pyrolysis or separate spray films. Low temperature spray pyrolysis films also shown lower optical absorption density. We believe that this is due to the non-compact nature of the films.

In the CdS films from CBD, the absorption edge of thick films is shifted down in energy by 0.8eV with respect to the bulk. Annealing films in hydrogen atomosphere caused a larger shift of 1eV. These observations agree with the PDS spectra.

In the case of SPD films the absorption of the energy band gap is similar to bulk CdS crystals but the samples grown with lower temperatures substrate showed the lower absorption density. We think that is caused by non-compacting grain epitaxy. films grown at 500°C show relatively high optical density in the range below the energy band gap (transparent region of CdS). This is due to ITO absorption. Optical density curves of CdS films grown at 500°C substrate temperature(point and dashed line) and with 450°C substrate (points line) are shown in Fig.10.

In the films from separate spray deposition the optical density did not have a steep slope in the region of band to band transition region. and is probably due to the incomplete crystallinity and very high density of defects near the energy band gap edge. From these optical density measurements we also concluded that the film which is grown by spray pyrolysis deposition has best condition for the CdS /CdTe thin film solar cell among the threeseries of films.

IV. CONCLUSION

We have fabricated and studied polycrystalline CdS thin films prepared by three different methods: 1) chemical Bath Deposition(CBD);2)Spray Pyrolysis Deposition(SPD);and 3) Alternated spraying of cation and anion solution at room temperature(Seperate Spray Deposition (SSD)). The structure and surface morphology of three series of CdS films were compared and charactrized by observing X-ray diffraction pattern and scaning electron microscopy. The films from spray pyrolysis deposition grow with

a preferred orientation in the <00·2> direction of the Wurtzite structure and CBD and SSD films grow with randomly-oriented Wurtzite crystallites.

From the optical measurements; PDS and PL, we found that all of the films have a high density of defects which we believe are related to Cd vacancies. We also observe PL due to defects related to S vacancies. In case of the spray pyrolysis deposition with 500°C substrate temperature, the defect of S vacancy or S vacancy related complex are less commom.

PL and transmittance(absorption)measure-ments inform us on the compactness of the CdS films. In non-compact films the absorption edge is not sharp and PL from the substrate is observed, which suggests many pinholes. CBD and SSD techniques both gave rise to non-compact films. Films from spray pyrolysis deposition with 500°C substrate exhibit a sharp absorption edge, high absorption coefficient, and no substrate PL.

We conclude that the best films for the purpose of CdTe/CdS polycrystalline thin film solar cells are films from spray pyrolysis method with 500°C substrate temperature. Although these films are the best in the current experiments, it is clear that much development work remains to be done. Cd vacancy defects are evident in PL and PDS and pinholes remain a major problem, suggesting that nucleation and adhesion are still major problems. We propose that some of these problems can be addressed by ionizing the ITO surface to improve adhesion of CdS.

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ABSTACT

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