Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Investigation of Structural Properties of CdS Thin Films by using a Transmission Electron Microscopy

Sung Ho Lee [a], Maeng Jun Kim [b], Sang Hyun Cho [c d], Sang Geul Lee [e c], Young June Hur [a] & Sang Ho Sohn [b]

[a] Department of Materials & Energy Engineering, Kyungwoon University, Gumi, Gyeongbuk, 730-739, Korea

[b] Department of Physics, KyungPook National University, Daegu, 702-701, Korea

[c] Department of Materials Science and Engineering, Pusan National University, Busan, 609-735, Korea

[d] Nano Convergence Research Team, Nano Convergence Practical Application Center, Daegu Technopark, Daegu, 704-801, Korea

[e] Korea Basic Science Institute Daegu center, Daegu, 702-701, Korea

Version of record first published: 20 Aug 2012.

To cite this article: Sung Ho Lee , Maeng Jun Kim , Sang Hyun Cho , Sang Geul Lee , Young June Hur & Sang Ho Sohn (2012): Investigation of Structural Properties of CdS Thin Films by using a Transmission Electron Microscopy, Molecular Crystals and Liquid Crystals, 564:1, 191-197

To link to this article: http://dx.doi.org/10.1080/15421406.2012.691776

Mol. Cryst. Liq. Cryst., Vol. 564: pp. 191–197, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.691776

Taylor & Francis
Taylor & Francis Group

Investigation of Structural Properties of CdS Thin Films by using a Transmission Electron Microscopy

SUNG HO LEE,[1,*] MAENG JUN KIM,[2] SANG HYUN CHO,[3,4]
SANG GEUL LEE,[5] YOUNG JUNE HUR,[1]
AND SANG HO SOHN[2]

[1]Department of Materials & Energy Engineering, Kyungwoon University, Gumi, Gyeongbuk 730-739, Korea
[2]Department of Physics, KyungPook National University, Daegu 702-701, Korea
[3]Department of Materials Science and Engineering, Pusan National University, Busan 609-735, Korea
[4]Nano Convergence Research Team, Nano Convergence Practical Application Center, Daegu Technopark, Daegu 704-801, Korea
[5]Korea Basic Science Institute Daegu center, Daegu 702-701, Korea Department of Materials Science and Engineering, Pusan National University, Busan 609-735, Korea

A transmission electron microscope and a scanning transmission electron microscope were used to investigate the structural properties of CdS thin films. The monograin of CdS thin film was looked at using TEM measurements. In the selected area, the diffraction pattern of the CdS films shows a pattern of circular dots. This implies that the CdS films have weakly preferred orientation properties, which is in good agreement with the data from the XRD measurements. In this study, various measurement techniques using TEM were utilized to study the structural properties of CdS thin films.

Keywords CdS thin film; XRD; ITO; TEM; STEM; structure property

Introduction

The importance of CdS thin films in the solar cells has been recognised for many years [1]. To-date, it they have been used in the role of an interface layer. The inclusion of this layer is essential for high efficiency solar cells, but its role has been the subject of much debate. The reported band gaps for CdS are 2.42 and 2.62 eV for cubic and hexagonal structures, respectively. Both cubic and hexagonal films can be deposited, but for solar cell applications, hexagonal structured films are preferable [2]. Despite hexagonal CdS showing a higher lattice mismatch with $CuInSe_2$(1.2%) compared to that of cubic CdS (0.7%), the hexagonal structure is more useful due to it's suitable band gap and stability [3]. In the CBD process, the influence of the deposition parameters on film formation, particularly the role of NH_3 on the film structure, are extremely critical.

*Address correspondence to Prof. Sung Ho Lee, Department of Materials & Energy Engineering, Kyungwoon University, Kangdongro, Sandong-myeon, Gumi, Gyeongbuk 704-801, Korea (ROK). (+82)54-479-1153; Fax: (+82)54-479-1029. E-mail: lpplsh@naver.com

Ortega and Lincot [4] and Dona Herrero [5] observed the CdS formation mechanism by studying the effect of various concentrations of $CdSO_4$ and thiourea at different bath temperatures on the growth rate of CdS films [6].

In this study we focus on investigating the structural properties of CdS thin films using various TEM equipment and analysis techniques.

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine in fine detail objects as small as a single column of atoms, which is tens of thousands times smaller than the smallest object resolvable by a light microscope. TEM forms a major analysis method in a range of scientific fields.

The STEM operates in a very similar way to a scanning electron microscope (SEM). A fine, highly focused beam of electrons scans over a thin specimen. Electrons which pass through the sample can be collected to produce a variety of transmission images, but, as with the TEM, backscattered electrons and X-rays are also produced. Secondary electrons (SE) are produced too, giving yet another imaging mode. Such dedicated STEM instruments are much more efficient than TEMs operating in STEM mode, they permit much higher resolution microanalysis than was previously attainable in TEM and are also easier to use. Thus under TEM conditions, similar images are obtained from the two instruments but the images from the STEM are rather noisier. There is clearly little benefit in operating the STEM in this non-optimum way. However, by using a much larger detector, the STEM becomes much more efficient.

In this study it is investigated the CdS thin films structural properties by utilizing these characteristic of various TEM measurement techniques.

Experimental

The CdS films were prepared using aqueous solutions of cadmium sulfate (3 mM), ammonia water (1.5 M) and thiourea (0.15 M). Films were deposited on commercially available indium tin oxide glass using an optimized solution temperature of 60, a pH of 11.5 and a deposition time of 20 min. The complete deposition process and the mechanism of film growth are described elsewhere [7,8].

The structural properties of the CdS thin films were investigated by using XRD (Philips X pert pro X-ray diffractometer) with a primary wavelength of Cu-Kα1 1.5406 Å.

A transmission electron microscope (TEM) and a scanning transmission electron microscope (STEM) were also used to study the physical properties of the CdS thin films.

Specimens for study by TEM and STEM were prepared by Ion milling (FB2200 Hitachi), this was performed using single beam 40 kV Ar+ ions. Tungsten was deposited on the CdS films to preserve the sample before measurements were carried out. Compatible specimen holders for the FB2200 and STEM (Hitachi HD-2300) are provided for specimen preparation with high precision and reliability. This arrangement allows milling and microscopy without specimen repositioning when transferring the sample minimizing specimen damage during repeated preparations and measurements.

For the TEM a FEI Tecnai G2 F20 microscope with a field-emission gun operating at 200 kV was used to acquire the HR-TEM images.

Results and Discussion

In order to study the structural properties of the CdS thin films, XRD measurements were carried out on the CdS thin films grown by the method described above. There are two

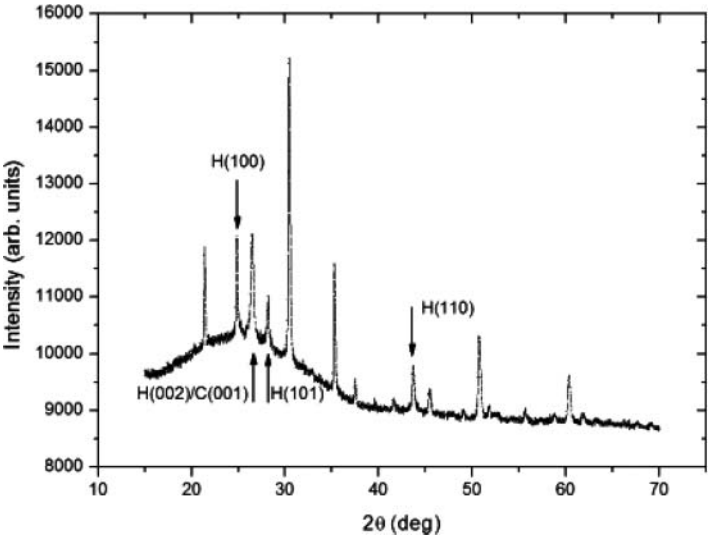

Figure 1. The X-ray diffraction (XRD) patterns of the CdS films grown at various temperatures.

crystalline phases, hexagonal and cubic in the cadmium sulfide fabricated by the CBD method 2. As shown in Fig. 1, the CdS films contain several diffraction peaks, indicating that the films are polycrystalline. The peak at $2\theta = 26.6^\circ$ is associated with a mixture of hexagonal (0 0 2) and cubic (1 1 1) planes. This primary peak appears in both specimens. The peaks at $2\theta = 24.84^\circ$, 28.18°, and 43.71° correspond to the hexagonal (1 0 0) plane, (1 0 1) plane, and (1 1 0) plane respectively. It is concluded that CdS thin films grown on ITO using the default method only contains hexagonal phase.

Sample preparation for TEM and STEM microscopy follows the method described above. After the FIB process, the compatible sample holder allowed STEM analysis to be performed without sample transfer or repositioning.

Figure 2 shows the dedicated STEM image and the image from a TEM operating in STEM mode (b) bright field images and dark field images taken by the dedicated STEM (c) of the CdS thin films grown on ITO with tungsten metal protection layer deposited. By comparing the bright field images of the dedicated STEM and the TEM operating in STEM mode, the dedicated STEM images clearly show individual grains of the thin films and also have no blurring. In addition to this crystal plane being arranged parallel to each other within grain can be detected. The dedicated STEM has a significant benefit that it can look at much thicker samples than is possible with the TEM. This is because as electrons travel through the sample, they lose energy depending on the thickness of the sample. In the TEM there is an objective lens below the sample and electrons of different energies are focused on different positions—this results in the well-known effect of chromatic aberration. This leads to a blurring of the image and a loss of resolution and contrast. In STEM, however, there is no lens below the sample so there is no defocusing effect. Bright field STEM can therefore satisfactorily image samples up to a few microns in thickness at 200 keV, compared to only about 0.5 micron for a TEM at the same energy. With this ability to image thicker samples, sample preparation is simplified and there is a better chance of finding the feature of interest in the viewable volume. For our specimens significant blurring occurred under condition,

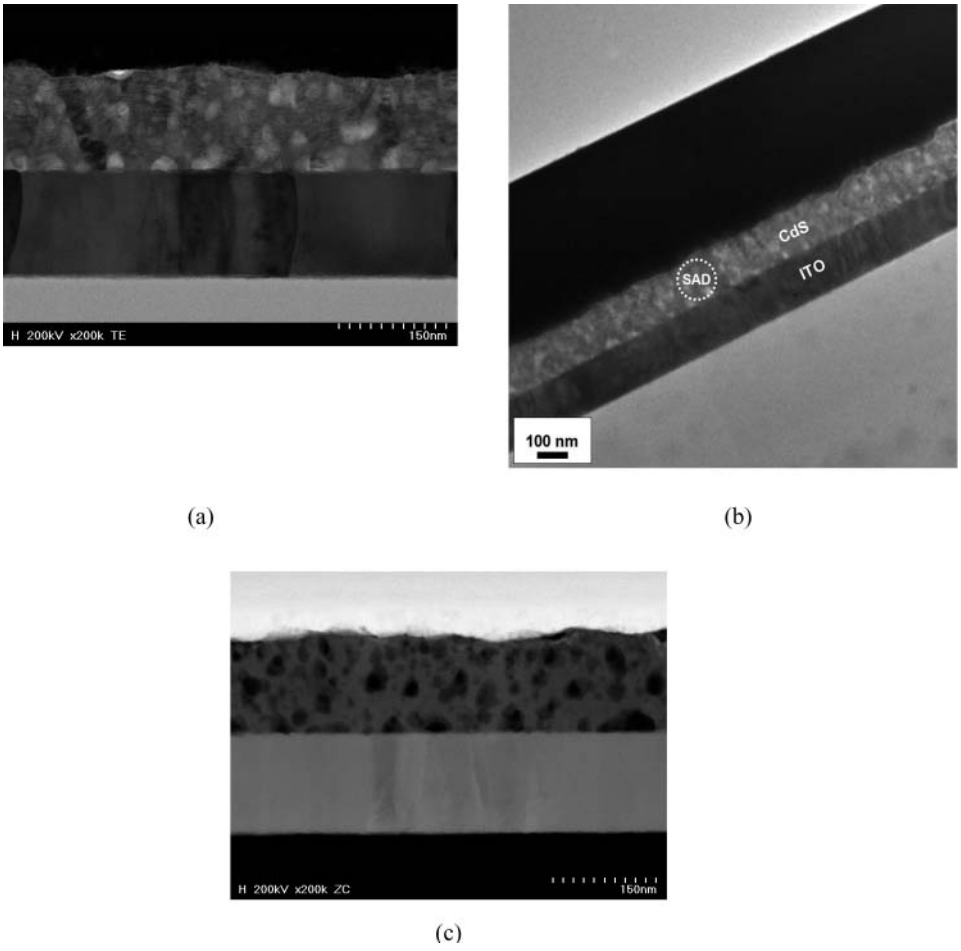

Figure 2. The dedicated STEM bright field image (a) and the image from a TEM operating in STEM mode (b) and the dedicated STEM dark field image (c) of the CdS thin films grown on ITO.

TEM operating in STEM mode. It implies that our specimen is not enough thin to be suitable for TEM measurement. In spite of this the dedicated STEM can supply an important information about the structural properties due to the fact described above. The STEM also offers significant benefits in dark field operation with a unique imaging mode, High Angle Annular Dark Field (HAADF) imaging (Fig. 2(c)). The inner angle of the annular darkfield detector is made so large (30 milliradians) that no Bragg diffracted electrons are collected. The images therefore come from elastically scattered electrons which have passed very close to the atomic nuclei in the sample. High (single atom column) resolution is possible with no unwanted diffraction contrast which can mask structural information. The HAADF signal is directly proportional to the density and thickness of the specimen and proportional to $Z^{3/2}$ where Z is the atomic number. Thus it is possible to produce images which show contrast due to variation of mass-thickness (i.e. the signal is proportional to the number of atoms) or Z contrast images (where the signal is proportional to the atomic

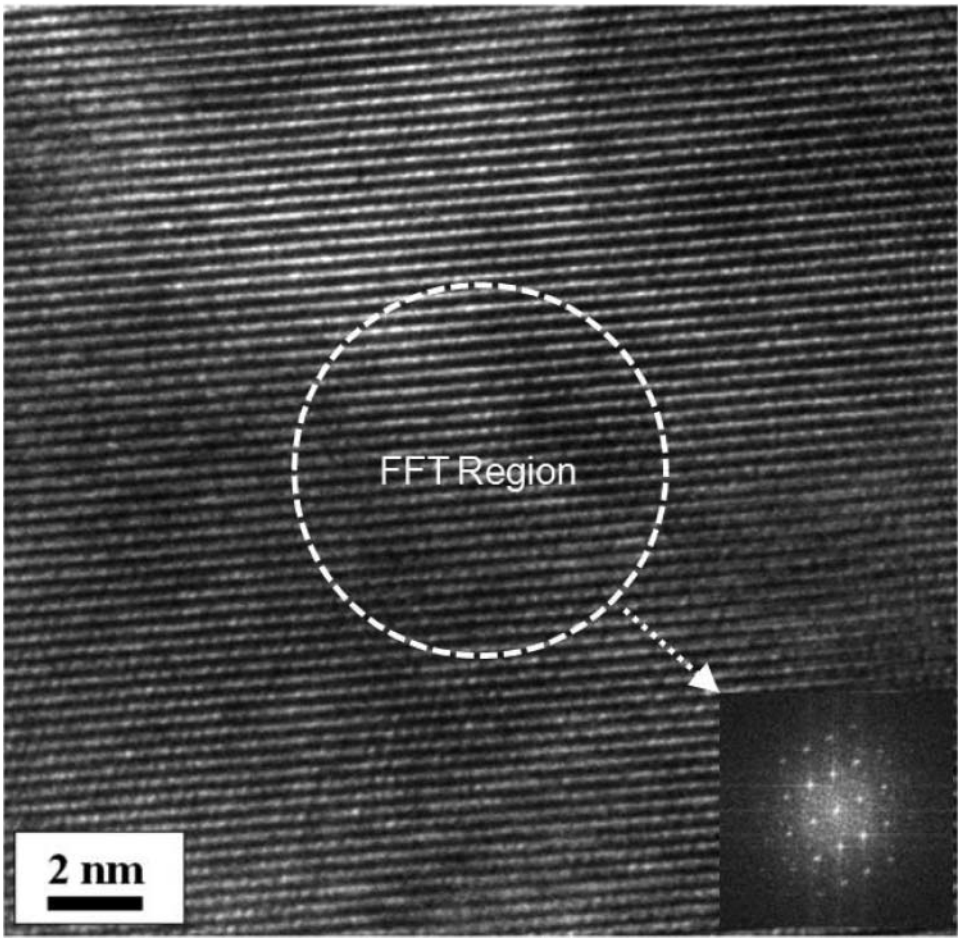

Figure 3. TEM Micrograph of the CdS thin film grown on ITO glass. Fast Fourier Transform (FFT) image (Fig. 3 inset).

number of the sample). From these optimized hardware of dedicated STEM, as shown in Fig. 2(c) within CdS thin films the darkest contrast portions reveal various grain size apparently. The grain size of the CdS thin films is widely distributed between 10 nm and 50 nm.

Figure 3 shows the TEM Micrograph of the CdS thin film grown on ITO glass. A Fast Fourier Transform (FFT) image (Fig. 3 inset) was also acquired in order to verify which kind of crystal structure is present in the CdS thin films. It shows that a hexagonal crystalline structure is the dominant crystal plane.

Figure 4 represents the selected area diffraction (SAD) pattern of the CdS thin film (area indicated in Fig. 2b) grown on ITO glass. A SAD pattern of the CdS thin film shows a semi-circular pattern. This implies that the CdS thin film has a small crystal size and weakly preferred orientation properties, these results are in good agreement with the TEM micrograph and XRD pattern data.

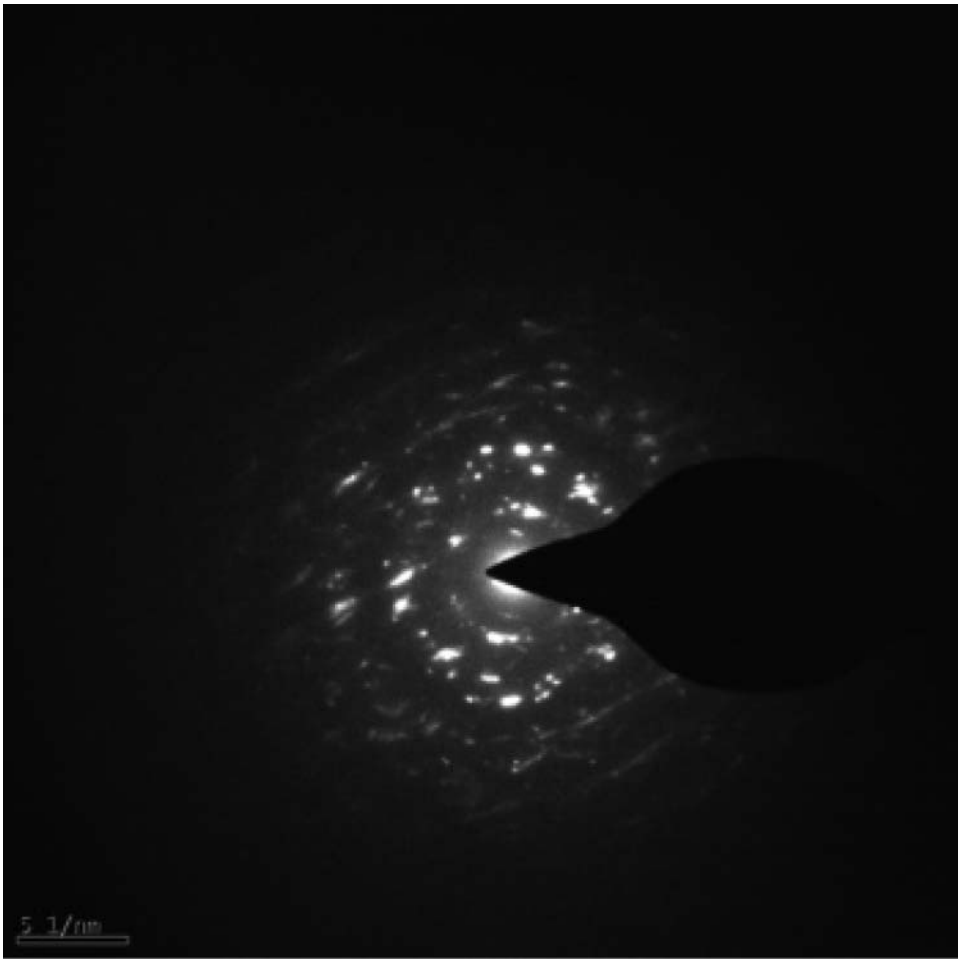

Figure 4. The SAD pattern of the CdS thin film (area indicated in Fig. 2 b) grown on ITO glass.

Conclusions

In summary, we fabricated CdS thin films on an ITO substrate by using the chemical bath deposition method. TEM and STEM were used to investigate the structural properties of the CdS thin films. HAADF signal reveals the darkest contrast portions exhibiting various grain size distributions between 10 nm and 50 nm. A SAD analysis exhibits that the CdS thin film has a small crystal size and weakly preferred orientation properties.

Acknowledgment

This work was supported by the Ministry of Knowledge Economy(MKE) grant funded by the Korea government. This work was partially supported by KBSI(Korea Basic Science Institute) grant K3108B.

References

[1] Fraas, L. M., & Ma, Y., *J. Cryst. Growth.*, *39*, 92, (1).
[2] Kaur, I., Pandya, D. K., & Chopra, K. L. (1980). *J. Electrochem. Soc.*, *127*, 943.
[3] Yeh, C. Y., Lu, Z. W., Froyen, S., & Zunger, A. (1992). *Phys. Rev. B*, *46*, 10086.
[4] Ortega, R., & Lincot, D. L. (1993). *J. Electrochem. Soc.*, *140*, 3464.
[5] Dona, J. M., & Herrero, J. (1992). *ibid*, *139*, 2810.
[6] Ramaiah, K. S., Pilkington, R. D., Hill, A. E., Tomlinson, R. D., & Bhatnagar, A. K. (2001). *Materials Chemistry and Physics*, *68*, 22.
[7] Kim, M. J., Lee, S. H., & Sohn, S. H. (2011). *Thin Solid Films*, *519*, 1787.
[8] Kim, M. J., Kim, H. T., Kang, J. K., Kim, D. H., Lee, D. H., Lee, S. H., & Sohn, S. H. (2010). *Mol. Cryst. Liq. Cryst. 532*, 21.