CRYSTAL SHAPE DETERMINATION IN THIN FILMS AND STUDIES ON THE SUBSTRATE INFLUENCE ON THE CRYSTAL SHAPE IN CBD-CDS THIN FILMS

T. PREM KUMAR[a], DANIEL SHERWOOD[b], BOSCO EMMANUEL[b]
K. SANKARANARAYANAN[a*]
[a]*Department of Physics, Alagappa University, Karaikudi – 630003, Tamilnadu, India*
[b]*Modeling and simulation groups, Central Electrochemical Research Institute, Karaikudi – 630003, Tamilnadu, India*

In the present work, the substrate-polishing effect on the structural characteristics, crystal shape, surface morphology, S:Cd ratio, room temperature photoluminescence emission and photoelectrical properties of chemical bath (CBD) deposited nano crystalline cadmium sulfide (CdS) thin films have been demonstrated. The 3D crystal shape of the deposited film was constructed based on the algorithm published elsewhere. The CdS on in-house, chemically polished p-Si (100) substrate shows a near hexagonal crystal shape when compared with the film on sonicated-unpolished p-Si (100) substrate. Also, it illustrates better crystallinity, closely packed surface morphology, S:Cd ratio of 52:48 and intense PL emission at room temperature. This indicates the feasibility of tailoring the habit of CdS nanocrystals by the selection of suitable chemical polishing of the substrate.

(Received November 5, 2009; accepted November 18, 2009)

Keywords: Crystal structure, Luminescence, Microstructure, Nanomaterials, Electrical properties, Solar energy materials.

1. Introduction

Extensive research have been reported on the deposition and characterization of semiconducting cadmium sulfide thin films (CdS) owing to their potential applications in the area of optoelectronic device fabrication [1-2]. Among several n-type materials, CdS is an excellent window layer for CdTe or $CuInSe_2$ thin film based hetero junction solar cells [3-5]. Recently, Daniel Sherwood and Bosco Emmanuel have developed an elegant mathematical technique to construct the 3-D nano crystal shape of CeO_2, Ge, ZnO, $Zr_{56}C_{44}$, In_2O_3, $MnFe_2O_4$ and iron (ii- iii) hydroxyl sulfate, etc, even in the presence of agglomeration [6]. Here, we have demonstrated the polishing effect of p-Si (100) substrate on the habit of the CBD deposited CdS nanocrystal, its surface morphology and their photoluminescence properties. The construction of crystal shape, SEM analysis and room temperature photoluminescence emission properties are presented and discussed.

2. Experimental

The deposition of CdS thin films were carried out on sonicated-unpolished and chemically polished p-Si (100) substrate. The chemical polishing was done with HF: HNO_3: H_2O reagents taken in the volume ratio of 1:6:10. For CBD, the composition of the bath was maintained with 5ml of 0.12M-$CdCl_2$, 10ml of 0.3M-NH_4Cl, 5ml of 0.7M-$CS(NH_2)_2$, 30ml of 2M-NH_4OH and 50ml of de-mineralized H_2O. Deposition was carried out at the constant bath temperature of 80°C.

* Corresponding author: hhrsankar@yahoo.com

The substrates were suspended vertically inside the chemical bath using Teflon disc and rotated at a rate of 20 rpm. The CdS growth occurred by the formation of CdS colloids and their subsequent adsorption on substrate. The proposed overall mechanism for the deposition of CdS is

$$CdCl_2 + (NH_2)_2CS + 2OH^- \text{--->} CdS + H_2CN_2 + 2Cl^- + 2H_2O$$

All the experiments were conducted over a period of 60 minutes by keeping the chemical bath stationary. The deposited films on the both Si substrates were cleaned under the flow of deionized H_2O to remove the loosely adhered particles.

3. Results and discussion

3.1 Structural analysis

The diffractogram of an as-deposited nano crystalline CBD-CdS thin film on unpolished and chemically polished p-Si (100) substrates are shown in Fig. 1 (a, b). The XRD pattern exposed the better crystalline quality of the film on chemically polished p-Si (100) substrate than the film on unpolished substrate.

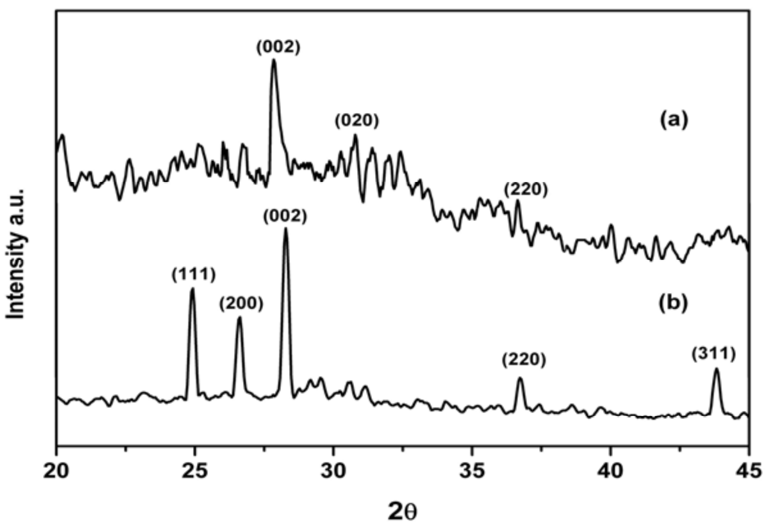

Fig.1 (a, b). The XRD pattern of CdS nano crystals on (a) unpolished and (b) chemically polished p-Si(100) substrates.

3.2 Crystal shape/habit of CBD-CdS nanocrystals

The shape control of nano and micro crystals is an important goal of modern materials chemistry as different shapes of the particles can introduce different electronic, optical, chemical, and biological processes, phenomena, and applications. The shape of the grown CdS nano crystals have been estimated by the present crystal shape algorithm using extracted XRD data as a source and are presented in the Fig. 2 (a, b). In the present work, we have investigated the influence of choice of substrate over the shape of the crystallites in the thin film by keeping the other experimental conditions as constant. The film on unpolished p-Si (100) substrate exhibits the disordered hexagonal crystal shape and the CdS nano crystal on chemically polished p-Si (100) substrate acquired the near hexagonal shape. Table 1 provides the details regarding the crystallite size, miller indices and exposed area of each set of planes. This led to the feasibility of tailoring the shape of the deposited CdS nano crystals with the aid of specific substrate polishing scheme.

These tailor made shape controlled growth of semiconducting nano crystals having desired properties will find many interesting applications.

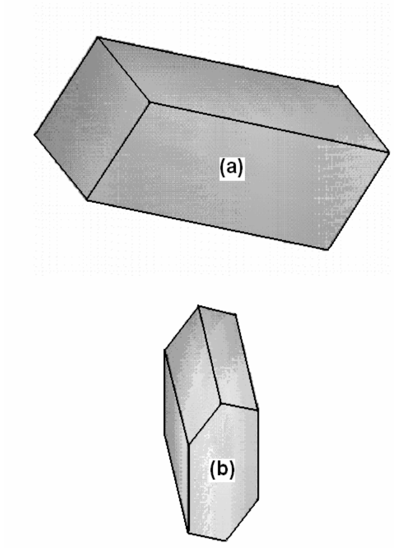

Fig. 2. (a, b). Calculated shape of the CdS nano crystals on (a) un polished and (b) chemically polished p-Si(100) substrate.

Table.1. represents the exposed Miller index derived from the XRD data and their corresponding exposed area calculated using the crystal shape algorithm.

Nanocrystalline CdS on	Miller index	Exposed area of crystal faces ($Å^2$)
Unpolished p-Si (100) substrate	(002) (020) (220)	16353 19729 13526
Polished p-Si (100) substrate	(111) (002) (200) (220) (311)	4695 19838 8308 7850 7850

3.3 Surface morphological analysis

The observed SEM images are presented in the Fig. 3 (a, b), and can be understood that the film on chemically polished p-Si (100) substrate shows a densely packed spherical granules with less pin holes than the film on un-polished substrate. The elemental composition (EDX) analysis of the nano crystalline CdS film on both polished and unpolished substrates exhibits a S:Cd ratio of 52:48 and 53:47 respectively.

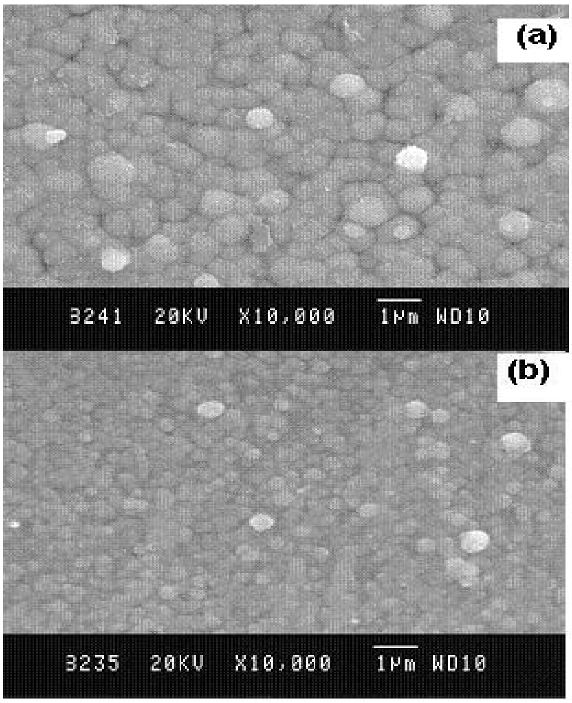

Fig.3 (a, b). The SEM images of CdS nano crystals on (a) unpolished and (b) chemically polished p-Si (100) substrates.

3.4 Fluorescence spectra analysis

The existence of PL signal on CdS films at 10 K and nonexistence of photoluminescence signal at room temperature was demonstrated by J. Aguilar-Hernandez et al [7]. But, we have observed an intense PL signal at room temperature. Fig.4 (a, b) shows the room temperature photoluminescence spectra and it also exhibits the defect structure characteristics of the films. Films on unpolished and chemically polished p-Si (100) substrates revealed a broad blue emission which centered at 486 nm and a tolerant green emission, occurred at 529 nm for the excitation wavelength of 330 nm. The PL intensity was higher for the film on polished substrate than the film on unpolished substrate.

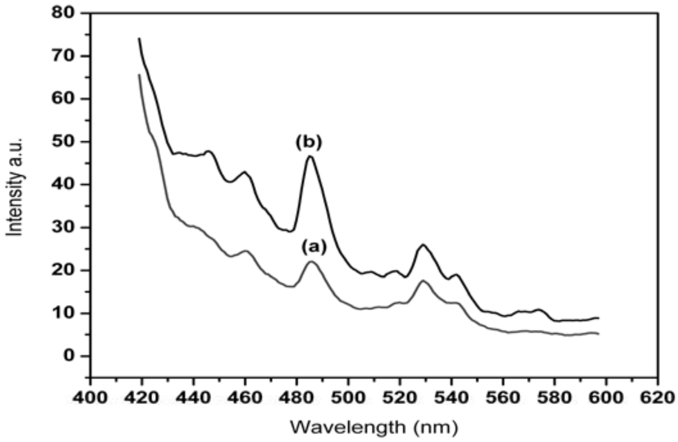

Fig.4 (a, b). The room temperature PL emission of CdS nano crystals on (a) unpolished and (b) chemically polished p-Si(100) substrates.

3.5 Photoelectrical measurements

Photoelectrical measurements such as the dark resistivity and illuminated V-I characteristics under white light condition were carried out on CdS nano crystals deposited on unpolished p-Si(100) and chemically polished p-Si(100) substrates. Photocurrent in the order of 0.12 mA/cm2 was observed in the CdS nano crystals on unpolished substrate whereas a maximum-photo current of 0.16 mA/cm2 was observed for the CdS film on chemically polished p-Si(100) substrate.

4. Conclusions

The substrate polishing effect on the shape of the CBD deposited CdS film was demonstrated using crystal shape algorithm developed earlier. The deposition of CdS nano crystals on polished p-Si (100) substrate achieved better structural characteristics, nano-crystallites having near hexagonal shaped crystals, closely packed micro-morphological surface and near stoichiometric S:Cd ratio when compared to the film on unpolished p-Si (100) substrate. The intense room temperature PL emission of the film on chemically polished substrate exhibits the optical quality of the crystalline material with low grow-in defects than the film on unpolished substrate. The observed high photo current in the CdS film on chemically polished p-Si (100) substrate illustrates an enhancement in the electronic property than the film on unpolished substrate. Hence it is suggested that a suitable polishing procedure may helpful to tailor the shape of the deposited nano crystal thereby required physical, electronic, and optical properties of the film.

References

[1] T.L. Chu, S.S. Chu, Solid State Electron, **38,** 533 (1995).
[2] J. Britt, C. Ferekides, Appl. Phys. Lett, **62**, 2851 (1993).
[3] H.R. Moutinho, D. Albin, Y. Yan, R.G. Dhere, X. Li, C. Perkins, C.S. Jiang, B. To, M.M. Al-Jassim, Thin Solid Films, **436**, 175 (2003).
[4] H. Metin, R. Esen, Semiconductor Science and Technology, **18**(7), 647 (2003).
[5] O.V. Galan, J.V. Larramendi, I. Riech, G. Pena Rodriguez, A. Iribarren, J. Aguilar-Hernandez, G. Contreras-Puente, Semiconductor Science and Technology, **17**, 1193 (2002).
[6] Sherwood Daniel and Emmanuel Bosco, Cryst. Growth Des, **6**(6); 1415 (2006).
[7] J. Aguilar-Hernandez, J. Sastre- Hernandez, N. Ximello- Quiebras, R. Mendoza- Perez, O. Vigil-Galan, G. Contrears-Punente, et al., Thin Solid Films, **511-512**,143 (2006).