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Nanocolumnar CdS thin films grown by glancing angle deposition from a sublimate vapor effusion source

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Abstract: The glancing angle Deposition (GLAD) technique was used to grow cadmium sulfide (CdS) thin films on glass and indium tin oxide (ITO) coated glass substrates from a sublimate vapor effusion source. The samples were prepared under different incident deposition flux angles (α) of 0°, 20° and 80°, while both the substrate and the source were under rotation. The temperature of the source was 923.15 K. Scanning electron microscopy images showed that the GLAD method combined with the source produced dense nanocolumnar shaped structures with height and diameters of ~200 and ~30 nm respectively. The deposited films showed a hexagonal structure with preferential (002) plane orientation and crystallites sizes between ~25 nm and ~35 nm. A maximum solar weighted transmission of ~92% was obtained for the sample prepared at α =80°, with a substrate/source rotation velocity ratio of 55/20 in the wavelength region of 400-900 nm. The average band gap energy of the films was 2.42 eV. Refractive indexes between ~1.4 and ~2.4 at a 550 nm the wavelength were also obtained.

Keywords: Glancing angle deposition; Cadmium sulfide; Nanostructures; Thin film; Structural properties; Optical properties; Columnar structure

1. INTRODUCTION

Cadmium sulfide (CdS) is a II-VI semiconductor material with an optical band gap of 2.42 eV and a great diversity of applications, such as window layer for both CdTe and CuInGaSe₂ (CIGS) based solar cells devices (Elbar et al., 2015; Gerthoffer et al., 2015; Han et al., 2014; Mohamed, 2015; Lee et al., 2015; Li & Liu, 2015; Yun, Cha, Ahn, Kwon, & Al-Ammar 2014). The CdS/CdTe and CdS/CIGS heterojunction has been actively investigated as a photovoltaic junction, moreover, the CdS which acts as a window layer in aforementioned solar cells has been deposited by many techniques such as sputtering (Kim et al., 2015), close space sublimation (CSS) (Cruz et al., 2013), chemical bath deposition (Lisco et al., 2015; Yücel & Kahraman, 2015), spray pyrolysis (Yilmaz, 2015), sol–gel, spin coating (Zhang, H. Li, Li, & Yang, 2013), thermal evaporation (Baghchesara, Yousefi, Cheraghizade, Jamali-Sheini, & Saáedi, 2016), ion beam sputtering (Liang et al., 2013) and many others. The CSS technique
consists in a source of an evaporating material and a substrate which are separated by small distance in a controlled atmosphere. It has the advantage of being an inexpensive deposition method due to its simple configuration and cheap materials (Cruz-Campa & Zubia, 2009) and it also presents a high rate of deposition (Alami, 2003).

Glancing angle deposition is a novel and useful technique to grow nanostructured materials at low cost, which consists in tilting the substrate against the vapor flux. It is based in the oblique angle deposition (OAD) technique. In OAD the incident vapor flux arrives at non-normal angles (i.e. oblique angles) to a static substrate, therefore the vapor flux can be treated as a vector, which has two components, a vertical and lateral component with respect to the substrate, which produces a distinct and directional columnar growth, due to atomic shadowing mechanisms occurring at the substrate’s surface. At the initial stage of the deposition, adatoms condense onto the substrate creating individual separated islands of deposited material, or nuclei (Kaiser, 2002).

Tilting the substrate causes the incident vapor to arrive at oblique angles, which results in the appearing of shadowed regions; where the vapor flux cannot directly reach the substrate. The nuclei capture the vapor flux that would have landed in the aforementioned shadowed regions, leading to the formation of a columnar growth in the same direction as the vapor source, resulting in the creation of a nano-array pattern. The glad technique differs with respect from the OAD in that the substrate is no longer static; instead it is being azimuthally rotated by stepper motor. Controlling the substrate rotation and other deposition parameters, namely vapor flux incident angle, substrate temperature among others, it is possible to obtain three dimensional nanostructures such as nano columns, Zigzag, nanohelix, nanosprings and many others (Barranco, Borras, Gonzalez-Elipe, & Palmero, 2016; Jie, Yu, Qin & Zhengjun, 2008; Zhou, Li, Ni & Zhang, 2011).

The aforementioned nanostructures enhance the contact area for certain materials, which in turn changes their optical and structural properties; this could be beneficial for certain applications such as: optoelectronic and photocatalytic devices (Jie et al., 2008; Zhou et al., 2012). Furthermore, these structures could be integrated into a solar cell, which makes them very attractive for a wide variety of applications (Leem & Yu, 2011; Zhou et al., 2012).

In this paper Cds thin films were prepared using the GLAD technique along with a sublimate vapor effusion source, which was under an azimuthal counter-rotation with respect to the substrate rotation direction, the effects of this deposition method on the morphological, structural and optical properties of the films is reported.

2. EXPERIMENTAL DETAILS

Fig. 1 shows the schematic representation of the evaporation source and the glass substrate in GLAD technique. $\omega$ and $\alpha$ are used to name the rotation velocity of the source and the substrate respectively. The evaporation source consists of graphite container axially rotated at $\omega = 20$ rpm and heated between two halogen lamps at 923 K. 2 g of a Cds powder (99.99% pure) were placed in the container. The pressure within the cavity was close to $7 \times 10^{-2}$ Pa, this was calculated assuming and ideal gas behavior ($PV = nkBT$), where $V = 14.73$ cm$^3$ is the volume of the container, $T$ (923 K) the evaporation temperature of the source, $k_B$ is the Boltzmann's constant and $n$ the numbers of moles, it must be clarified that although the ideal gas model might not be totally accurate to model the pressure of the container, it was made as a first approximation for the sake of simplicity, and for the immediate intents and purposes of this work it is considered sufficiently correct. The container has a top cover with 20 holes of ~1.5 mm diameter symmetrically distributed as is shown in Fig. 1(b); these holes have a vapor effusion function. The vapor flux density ($\phi$) for each hole was estimated using the cosine of Knudsen law (Herman & Sitter, 2012):

$$\phi = 3.153 \cdot 10^{22} \cdot \frac{a^2}{n_L} \left(\frac{P_G}{\sqrt{TM}}\right) \cos \alpha$$

where $a = 1.77 \times 10^{2}$ cm$^2$ is the area of a single hole, $L = 6.0$ cm is the distance between the substrate and the evaporation source, $P_G$ is the Cds vapor partial pressure within the container, $T$ (923 K) is the evaporation temperature of the source, $M$ is the Cds molecular weight and $\alpha$ is the incident deposition flux angle. The flux density has an angular distribution in each hole; this produces a confined region of Cds vapor distributed between the substrate and the evaporation source.

To grow vertical nanocolumnar structures of Cds thin films, the substrate was put in GLAD mode as shown in Fig. 1(b), and heated by radiation using two halogen
lamps as in shown in Fig. 1(a). The substrate was azimuthally rotated using angular velocities with values $\omega = 20, 30, 40, 55, 150, 350, 700$ and $1020$ rpm, and tilted using $\alpha = 0^\circ, 20^\circ$ and $80^\circ$ as shown Fig. 1(b). The experimental set-up procedure was as follows: Corning 2947 glasses and commercial ITO/Glass (Delta Technologies CB-40IN-0107) with dimensions of $25 \times 25 \times 0.7$ mm were used as substrates, which were sequentially cleaned prior to the deposition by an ultrasonic agitation bath in distilled water, acetone and isopropyl alcohol during 5.0 min each. Subsequently they were dried with $\text{N}_2$ and heated at a substrate temperature ($T_s$) of $623$ K. After reaching $T_s$, a shutter placed above the evaporation source was removed, the substrate was put in front of it and adjusted in GLAD mode with a separation distance of $L = 6.0$ cm. The source and the substrate were put in counter-rotation; this means that the source rotated in a direction opposite to that of the substrate. The background pressure in the vacuum chamber was $\sim 4$ Pa and the deposition time was 1.0 min. to 3.0 min for different types of samples.

The cross-sectional morphologies of Cds films were characterized using a field emission scanning electron microscope (FESEM) JEOL 7600F instrument. The X-ray diffraction (XRD) data was obtained by a D5000 Siemens X-ray Diffractometer with a beam under of CuK$\alpha$ filtered monochromatic radiation ($\lambda = 0.15418$ nm) by 40 kV with 35 mA and aperture diaphragm of 0.2 mm. The diffractograms were registered in the step scan mode with a beam incidence angle of $1^\circ$ and recorded in $\theta = 0.02^\circ$ steps with a step time of 10 s in a $2\theta$ range of 20–55°. The optical measurements were carried out using a UV-vis Agilent 8453 spectrophotometer with a 0.1 nm resolution, in the range of 400–900 nm. The optical band gaps were calculated with direct transitions only.

3. RESULTS AND DISCUSSIONS

The flux density value defined by equation 1 decreases as increases. Particularly, for $\alpha = 80^\circ$, $\phi$ was estimated to be $\sim 1 \times 10^{14}$ Cds-atoms/cm$^2$-sec. At first glance the films showed no evidence of pin-hole formation;

![Fig. 1. Experimental setup for GLAD method combined with sublimate vapor effusion source. Side left (a) show the GLAD apparatus as it is implemented in the effusion source. Substrate and source movements are accomplished by two independent motors. On the bottom right (b) the source container is shown.](image)
this could be explained by the counter-rotation between the substrate and the evaporation source, which in turn could favor a uniform angular distribution of the Cds vapor flux.

The optimal ratio of $\omega/\Omega$ was found to be 55/20, this value was selected from the optimization of the solar weighted transmission (SWT) calculation, while the other deposition parameters remained constant, this will be discussed in more detail later in the text.

After the growth of the Cds thin films, the transversal morphology was observed by FESEM with a magnification of 50000x and 100000x. In order to obtain a SEM image with good quality, that would allow the correct visualization of the nanocolumnar structures, it was necessary to employ a deposition time of 3 min and 2 minutes for the Glass and ITO/Glass substrate, respectively.

The cross-sectional image of the Cds arrays on glass substrates grown at $\alpha=80^\circ$ is shown in Fig. 2(a). Highly uniform and densely packed arrays of Cds nanocolumnar structures were successfully formed; they presented vertical alignments with great uniformity through all their thicknesses, which was of ~300 nm. The diameter of these structures was approximately 30 nm, and it was estimated from the zoom on the FESEM cross-section images. The presence of fissures with small gaps which divide some of these structures can also be observed.

Fig. 2 (b) shows a transversal structure for the sample grown glass/ITO substrate at $\alpha=80^\circ$. A uniform and dense columnar distribution was also observed and the thickness of the thin film was approximately of ~200 nm. However, the presence of fissures was less in comparison to the sample shown in Fig. 2(a), since they were not present through all the thickness of the film. This was evidence that the Cds deposition was more densely packed on the glass/ITO substrate.

Fig. 3 shows the XRD normalized pattern for the thin films grown at $\alpha=0^\circ$, 20$^\circ$ and 80$^\circ$ with 1.0 min of

Fig. 2. FESEM image of: vertical nano columnar Cds as nanostructure grown at $\alpha = 80^\circ$ on a glass substrate with a magnification of (a) 100000x and (b) 50000x. Vertical nano columnar Cds as nanostructure layer grown at $\alpha = 80^\circ$ on an indium tin oxide (ITO) coated glass substrate with (c) 100000x and (d) 50000x.
deposition time. The single-phase hexagonal CdS Wurtzite structure (Razik, 1987) is observed with a preferential orientation in the (002) plane. Low intensity peaks for the (100), (101), (110), (103) and (112) planes are also observed. The XRD data showed that all the peaks are shifted towards higher 2θ values in comparison to that of the standard pattern (2θ = 26.507°); this is evidence of compressive strain (Zak, Majid, Abrishami, & Yousefi, 2011). The crystallite size (D_XRD) was calculated from the plane (002) using the Scherrer’s equation (Bertaud, 1968):

\[
D_{XRD} = \frac{0.9λ}{β_{002}cosθ_{002}}
\]  

Where \( β_{002} \) is the full-width at half-maximum and \( λ \) is the wavelength of the X-ray radiation employed (\( λ = 0.15418 \) nm). The values of \( D_{XRD} \) are given in Table 1. The Crystallite sizes values were between ~25 nm and ~35 nm. The lattice parameter \( c_{002} \) was calculated employing the standard lattice geometry equations for the hexagonal structure (Iribarren, Hernández-Rodriguez, & Maqueira, 2014; Kaur, Kumar, Sathiaraj, & Thangaraj, 2013). As it was mentioned before, the shifting of the 2 positions to higher values with respect to the CdS standard pattern is evidence of a negative compressive strain, this suggests that the lattice parameters of the unit cell would show a decreasing, this agrees with the reported \( c_{002} \) lattice parameter values summarized in Table 1, which are in general smaller than those of the standard CdS (\( c_0 = 0.6719 \) nm).

The \( c_{002} \) parameter decreases for higher incident deposition flux angles, this correlation between the aforementioned parameters is illustrated in Fig. 4. The general reduction of the \( c_{002} \) values indicates that there is shrinkage on the c-axis for the CdS unit cell with respect to pattern value. Furthermore, the strain \( ε \) along the c-axis was calculated by using the expression \( ε = (c_{002} - c)/c_0 \times 100\% \) (Ghosh, Basak, & Fujihara 2004). The absolute values of the c-axis strain increase as \( α \) increases, this is also shown in Table 1. The negative values of \( ε \) confirm shrinkage in the c-axis. This suggests that a high incident deposition flux angle leads to a lattice compression effect along the c-axis direction, as it was also stated in the XRD analysis.

In order to find the optimal \( ω/Ω \) ratio the solar weighted transmission (SWT) was calculated for the thin films grown at different substrate rotation speeds (ω). Fig. 5 shows the SWT as a function , for different samples all grown at \( α=80° \) and with 1.0 min of deposition time. Based on the SEM images, this value of was selected since it allowed observing with more clarity the nanocolumnar deposition on the substrate. The SWT formula is given by (Mendez-Gamboa et al. 2016):

\[
SWT = \frac{\int_{λ_1}^{λ_2} T(λ)S(λ)dλ}{\int_{λ_1}^{λ_2} S(λ)dλ}
\]  

Where \( S(λ) \) is the AM 1.5 solar radiation spectrum, \( T(λ) \) is the optical transmittance, and the numerator of equation 3 represents the solar photon flux-weighted transmittance for the sample. The SWT is the ratio of the usable photons transmitted from the total available photons, it can be estimated through the normalization of the transmittance spectra, and this was done by integrating the solar spectral photon flux over the wavelength range of 400-900 nm. From Fig. 5 it’s seen that SWT reached a maximum of ~92% at \( ω = 55 \) rpm, and for greater \( ω \) it decreased to ~71%. In accordance with the calculations of SWT a ratio of \( ω/Ω = 55/20 \) was selected as the optimum value.

Fig. 6 shows the transmittance spectrum of samples grown at \( α = 0° \), 20° and 80° with 1.0 min deposition time. A transmittance value of ~95% was observed for the sample with \( α = 80° \). The increasing in the transmittance value is due to the change in the thickness, since a larger tilting angle leads to a smaller deposition rate (Nagiri et al., 2015), resulting in thinner samples, which in turn will produce higher transmittance values. As can be seen, the transmittance for the film grown at \( α = 80° \) at the 400 nm wavelength is less than 80%, while it is below 40% for the samples with \( α = 0° \) and 20°. The optical band-gap energy \( (E_g) \) was calculated using the Tauc formalism (Tauc, Grigorovici, & Vancu, 1966) as is shown in the Fig. 7, \( E_g \): values between ~ 2.43 eV and ~ 2.45 eV were obtained, which agrees very well with the previous reports of the band gap energy for the CdS (Mohamed, 2015). Additionally, the refractive index \( (n) \) was calculated from the equation (Kim, Yim, Son, & Leem, 2012):

\[
n = \frac{1 + R}{1 - R} + \frac{4R}{\sqrt{(1-R)^2 - k^2}}
\]  

Where \( R \) is the normal-incident light reflection, \( k \) is the extinction coefficient defined as \( k = a_{ab}/4π \), where \( a_{ab} \)
is the absorption coefficient and $\lambda$ the wavelength. In the
region below the band gap energy the absorption follows
$A \to 0$. Then the expression $T + R + A = 1$ can be reduced
to $R = 1 - T$ from where it is possible to estimate the
reflected light. The calculated refractive index at different
incident deposition flux angles are shown in Fig. 8, which
shows that it decreases as $\alpha$ increases. For $\alpha = 80^\circ$ the
refractive index was $\sim 1.6$ at wavelength near to 550 nm,
for $\alpha = 0^\circ$ and $20^\circ$ it was $\sim 2.4$, which is very close to the
refractive index value that is required for a thin film that
is desired to be used as an antireflection layer between
ITO and CdTe according to the law $(n_{ITO} n_{CdTe})^{1/2}$ (Prevo,
Hwang, & Velev, 2005) where $n_{ITO}$ and $n_{CdTe}$ are the
refractive index of ITO and CdTe layers respectively.

Table 1. Structural parameters for samples with different incident
deposition flux angle.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$2\theta_{002}$</th>
<th>$\beta_{002}$</th>
<th>C_{002}</th>
<th>$\varepsilon$</th>
<th>$D_{XRD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(degree)</td>
<td>(degree)</td>
<td>(radians)</td>
<td>(nm)</td>
<td>(%)</td>
<td>(nm)</td>
</tr>
<tr>
<td>0</td>
<td>26.54</td>
<td>4.6</td>
<td>0.6711</td>
<td>-0.119</td>
<td>~31</td>
</tr>
<tr>
<td>20</td>
<td>26.57</td>
<td>4.1</td>
<td>0.6705</td>
<td>-0.208</td>
<td>~35</td>
</tr>
<tr>
<td>80</td>
<td>26.63</td>
<td>5.7</td>
<td>0.6691</td>
<td>-1.61</td>
<td>~25</td>
</tr>
</tbody>
</table>

Fig. 3. XRD normalized pattern for CdS thin film grown
with different incident deposition flux angles.

Fig. 4. c=parameter versus the tilting angle of the substrate.

Fig. 5. Solar weighted transmission (SWT) measurements of
CdS thin films as a function of substrate rotation grown
with deposition flux angle of $\alpha = 80^\circ$.

Fig. 6. Transmittance spectra of CdS thin films grown with
incident deposition flux angles.
4. CONCLUSIONS

In this paper an innovative source for vapor effusion is reported, the aforementioned source was employed to provide a vapor flux in the GLAD deposition mode which led to the obtaining of CdS vertical nanostructured thin films. The source and the substrate were counter-rotated with respect to each other, at an optimal ratio \( \theta/\Omega \): 55/20. The effect caused on the morphological, structural and optical properties for the CdS thin films grown at different incident deposition flux angles was investigated. The principal characteristics of these CdS nanocolumnar thin films were a uniform distribution over the substrate with dimensions of height and diameters of \(~200 \text{ nm}\) and \(~30 \text{ nm}\) respectively. The films showed a single hexagonal wurtzite structure phase with a preferential \( \{002\} \) plane orientation, band gap energy of \(~2.42 \text{ eV} \) and a refractive index between \(~1.4\) to \(~2.4\) in wavelength of \(~550 \text{ nm}\).

ACKNOWLEDGMENTS

Authors thanks Oswaldo Gómez, Mario Herrera, Daniel Aguilar, Dora Huerta and Wilian Cauich for technical assistance and to Lourdes Pinelo for her secretary assistance. This work has been supported by the Project No. CB/2012/178748 CONACYT/México. One of the authors (A. Iribarren) also thank to CONACYT/México under the program No. 260967 for sabbatical stances for Mexican and foreign researchers living abroad.

CONFLICT OF INTEREST

The authors have no conflicts of interest to declare.

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