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Comparative study of CdS films annealed in neutral, oxidizing and reducing atmospheres

Natalia Maticiuc*, Mart Kukka, Nicolae Spalatu, Tamara Potlog, Malle Krunks, Vello Valdna, Jaan Hiie

*Department of Materials Science, Tallinn University of Technology, 5 Ehitajate tee, 19086 Tallinn, Estonia

Faculty of Physics, Moldova State University, 60 A. Mateevici str., 2009 Chişinău, Moldova

Abstract

Chemical bath deposited CdS:Cl thin films on glass substrates were annealed in H2, N2 and air at 250 °C and 400 °C, and then characterized by XRD, Van der Paw, Raman, photoluminescence and transmittance - reflectance spectroscopy. Different properties of CdS film are found depending on the neutral, reducing or oxidizing annealing gas. Strong activity of chlorine as a flux and dopant agent is observed in the air- annealed CdS films. This is expressed by the strongest photoluminescence intensity of the 2.24 eV peak. Oxygen containing phases CdSO3 and CdO are shown by XRD patterns for air- and N2- annealed CdS films at 400 °C. Longest N2 annealing generated pure CdS layers, similarly with the H2- annealed ones. Also, the H2 annealing shows a shift of the main (111) CdS peak toward the pure cubic modification proportionally with the annealing time, while N2 and air annealing fixed the peak at intermediate cubic-hexagonal position. This could be explained by incorporation of oxygen in CdS lattice for N2 and air annealing, supported by the presence of oxide phases in CdS XRD patterns. H2 annealing removes the incorporated oxygen from the lattice and oxide phases from the grain boundaries, leaving pure CdS films. Behavior of CdS structural properties unambiguously demonstrates the incorporation of hydroxide group and oxygen into the CdS crystallite lattice and explains the changes of structural, optical and electrical properties of CdS films in the annealing process.

Keywords: CdS, H2 annealing; N2 annealing; air annealing; structural properties; optical properties; electrical properties.

* Corresponding author. Tel.: +372-620-3366; fax: +372-620-2020.
E-mail address: nataliamaticiuc@yahoo.com
1. Introduction

CdS thin film is widely used as n-type semiconductor partner and buffer layer in thin film chalcogenide solar cells [1]. Among possible deposition methods, chemical bath deposition (CBD) is one of the most suitable due to its low cost, low temperature processing and possibility to form large area films. As deposited CBD CdS layers have a high speed of recrystallization already at low temperatures with major changes in structural and optical properties [2,3]. A possible way to control these changes and reduce the extent of disorder in CdS films may be the thermal annealing in a defined atmosphere. The importance of CdS properties control is revealed by the application of CdS films in substrate configuration solar cells. For instance, in CIGS solar cell the i-ZnO and ZnO:Al layers are sputtered on CdS at 200 °C in O2+Ar or Ar ambient [4], influencing the properties of underlying CdS film and final parameters of the solar cell [5,6].

Generally, the influence of annealing ambient on CdS film properties was studied by many authors. The neutral (N2, Ar containing) annealing brings reorientation of as deposited CdS films with a significantly improved crystalline quality, diminishes their resistivity by increasing the grain size and decreasing the number of grain boundaries in CdS films [7]. Also, such an annealing leads to phase transition from the metastable cubic phase to a stable hexagonal phase of CdS [8], which is undesirable when stacking CdS film with a cubic CdTe absorber. Besides increased grain size and improved crystallinity of CdS films annealed in oxidizing (O2 containing) ambient, a substantial decrease in the band gap have been reported [9]. The thermal treatment in a reducing atmosphere of H2 has the advantage to eliminate the chemisorbed oxygen and oxides. Annealing in the presence of H2 preserves the same structural cubic phase during the complete thermal process [2] and decreases the resistivity by 4 orders of magnitude [10] compared to the neutral case [7].

However, a deep study of the mechanisms and understanding of annealing processes in CBD CdS films depending on reducing, oxidizing and neutral atmospheres is still missing. Here we present the analysis of structural, optical and electrical properties of CdS films and the mechanisms responsible for their changes when annealing in different ambient is applied.

2. Experimental

CdS thin films were prepared by CBD, the experimental details being presented elsewhere [10]. After the deposition and vacuum drying CdS films were annealed in a closed process tube in three different atmospheres at normal pressure: hydrogen, nitrogen and air. Every annealing lasted 1h and the annealing temperatures were established at 250 °C and 400 °C.

CdS layers were characterized by X-ray diffraction (XRD), photoluminescence (PL), Raman, optical transmission - reflection spectra, Van der Pauw and Hall Effect techniques. XRD measurements were performed in the Bragg - Brentano (θ-2θ) geometry using a Rigaku Ultima IV diffractometer with Cu Kα radiation. Crystallite size and lattice constants were calculated using the software PDXL Version 1.4.0.3 on the Rigaku system. The optical total transmittance and reflectance spectra of CdS films were obtained in the wavelength range of 200 – 2500 nm on a Jasco V-670 UV-VIS-NIR spectrophotometer equipped with an integrating sphere. The PL was measured at room temperature (RT) with a green laser (532 nm) and 10 mW density of excitation. Spectra were registered by a Renishaw - type device with a built-in measuring Raman installation. The RT Raman spectra were recorded in a 180° backscattering geometry by using the Horiba's LabRam HR high resolution spectrometer. The incident laser light with the wavelength of 532 nm was focused on the sample within a spot of 10 μm in diameter and the spectral resolution of the spectrometer was about 1.5 cm⁻¹. Each spectrum was smoothed with Lorentz fitting and peak position and Full Width at Half Maximum (FWHM) were obtained. The electrical properties of the CdS films (resistivity, charge carrier concentration and mobility) were measured in the temperature range of -100 °C to +100 °C, using MMR's Variable Temperature Hall System and a Hall, Van der Pauw Controller H-50. The contact material used for electrical measurements was evaporated indium.
3. Results and discussions

CdS films grown on glass substrates and annealed in air, N₂ or H₂ were adherent, yellowish and reflecting. Independently of the annealing ambient, all the films annealed at 400 °C were more dark-yellowish compared to those annealed at 250 °C.

3.1. Structural properties

Structural properties of CdS thin films were analyzed on the basis of XRD and Raman measurements. At low annealing temperature (250 °C) the XRD patterns do not reveal any additional phases except CdS. At higher annealing temperature (400 °C) in air and nitrogen CdSO₃ and CdO phases were found (Fig. 1a). CdSO₃ which appeared during nitrogen annealing for 60 minutes has disappeared at longer annealing for 120 minutes, while in air CdSO₃ was transformed to CdO. Only annealing in hydrogen resulted in pure CdS (Fig. 1a).

![Fig. 1. (a) XRD pattern of CdS films annealed at 400 °C in H₂, N₂ and air for 1h (solid line) and 2h (dash line); (b) Shift oh the main 111 peak in dependence of annealing ambient, temperature and duration](image)

By high resolution analysis was shown the shift of the main (111) peak toward the cubic modification of CdS (Fig. 1b). In H₂ annealing process we explain this shift by the decomposition of incorporated OH group, creation of oxygen on sulfur site and by removal of oxygen from the crystalline lattice [10]. While atomic size of sulfur and OH group are similar, the atomic size of oxygen is smaller (compare the densities of cubic CdS 4.8 g/cm³ and CdO 8.1 g/cm³ [11]) and causes contraction of CdS lattice [12], like sulfur in CdTe [13] and boron in silicon [14]. In air
and N₂ the shift of the (111) peak is stabilized for 60 minutes annealing (Fig. 1b), which corresponds to the remained traces of oxygen in the CdS lattice and supported by the presence of oxide phases (Fig. 1a).

The traces of oxygen are present even in H₂-annealed CdS and only at 450 °C annealing the main peak reaches the position of pure cubic modification (26.46°) for CdS [10]. However, as the ambient is more active it showed a deeper removal of oxygen compared to H₂; this could be attributed to CdCl₂ dopant added in the deposition process of CdS. Due to the presence of CdCl₂ flux and high solubility of both cadmium oxides and CdS in CdCl₂ flux [15], the oxygen diffuses into the melted phase and at high temperature CdSO₃ and CdO are extracted.

The complex composition of as deposited CdS films [16] involves the formation of oxides like CdO and CdSO₃ in neutral and oxidizing atmospheres of annealing (1, 2).

\[
CdS + 1.5O₂ \rightarrow CdO + SO₂ \uparrow \quad (1)
\]

\[
CdS + 1.5O₂ \rightarrow CdSO₃ \quad (2)
\]

In N₂ annealing process, depending on the temperature and time, the oxides are expelled as metallic Cd and SO₂ (3, 4), while in H₂ ambient Cd and water are expelled (5, 6). The metallic Cd was confirmed by the black deposit on cold walls of the process tube. In air Cd forms on CdS surface CdO (7) as the most stable phase (Fig. 1a).

\[
CdS + 2CdSO₃ \overset{N₂}{\rightarrow} 3Cd \uparrow + 3SO₂ \uparrow \quad (3)
\]

\[
CdS + 2CdO \overset{N₂}{\rightarrow} 3Cd \uparrow + SO₂ \uparrow \quad (4)
\]

\[
CdSO₃ + 3H₂ \overset{H}{\rightarrow} CdS + 3H₂O \quad (5)
\]

\[
CdO + H₂ \overset{H}{\rightarrow} Cd + H₂O \quad (6)
\]

\[
CdSO₃ \overset{air}{\rightarrow} CdO + SO₂ \uparrow \quad (7)
\]

Raman spectra of CdS films annealed in different atmospheres (Fig. 2) present a well-resolved line at approximately 300 cm⁻¹, corresponding to the first order scattering of the longitudinal optical (LO) phonon mode.

Fig. 2. Raman spectra of CdS films annealed for 1h in different ambients at 400 °C.
The position of this peak is slightly shifted to lower wave numbers (Table 1) with respect to bulk CdS peak (305 cm\(^{-1}\)). Several authors explained this shift by the changes of grain size [17,18,19]. The narrowing of the 1LO peak of annealed CdS films (Table 1) is connected to the lattice stress shown by XRD data [12]. The decreased peak intensity with annealing is attributed to the shift of the crystalline structure of CdS films to a more cubic phase [20]. The second-order scattering of LO phonon is also visible at approximately 600 cm\(^{-1}\).

Both Raman and XRD measurements indicate that CdS films annealed in any atmosphere have a better crystallinity [17] than the as deposited ones. However, we observed at \(\approx 700\) cm\(^{-1}\) an additional Raman peak that for air- annealed CdS film has higher intensity compared to 2LO peak. This peak may correspond to CdSO\(_3\) and CdO [21,22], both phases representing the oxidation products of annealing at 400 \(^\circ\)C (Fig. 1a).

### Table 1.
Position of 1LO peak and its FWHM value in dependence of annealing ambient for CdS films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Main peak (cm(^{-1}))</th>
<th>FWHM (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited CdS</td>
<td>300.0</td>
<td>19.56</td>
</tr>
<tr>
<td>H(_2)-annealed CdS</td>
<td>302.4</td>
<td>14.36</td>
</tr>
<tr>
<td>N(_2)-annealed CdS</td>
<td>302.7</td>
<td>13.39</td>
</tr>
<tr>
<td>Air- annealed CdS</td>
<td>302.7</td>
<td>10.15</td>
</tr>
</tbody>
</table>

#### 3.2. Optical properties

Transmittance spectra of CdS films (Fig. 3a) show that annealing at low temperature (250 \(^\circ\)C) weakly influenced the optical properties of CdS films. However, air- annealed CdS has lower transmittance in the 500-700 nm region compared to N\(_2\) and H\(_2\) ambients. At high temperature (400 \(^\circ\)C) all the atmospheres substantially decrease the CdS transmittance due to the presence of metallic Cd precipitate in the CdS grains. Still, transmittance of the air- annealed CdS remained unchanged due to transformation of metallic Cd to transparent CdO (Fig. 1a). Absorption of light in the longer wavelength region is usually caused by crystalline defects such as grain boundaries and dislocations [23].

Fig. 3. (a) Transmittance spectra of CdS films annealed at different annealing time and ambient for 1h; (b) Band gap values of CdS films versus annealing time for different ambient and temperature.
Band gap ($E_g$) of CdS films annealed in H$_2$ and N$_2$ at low temperature (250 °C) show small decrease with increasing annealing time (Fig. 3b), while for air-annealed CdS $E_g$ decreased from 2.4 eV to 2.34 eV. Oxygen from the air ambient assured a higher presence of CdO [24] in CdS film, which decreased $E_g$ already at 250 °C. At 400 °C $E_g$ decreased faster, lowest value (2.32 eV) being reached for air-annealed CdS. This could be explained by the incorporation of oxygen on the vacant sulfur site appeared in the process of hydroxide group destruction in the CdS lattice. High concentration of oxygen in CdS lattice is also supported by the presence of CdSO$_3$ and CdO phases for annealing in N$_2$ and air (Fig. 1a).

### 3.3. Electrical properties

Time dependence of electrical resistivity measured at RT for CdS films shows stable electrical properties after 60 minutes annealing for each annealing temperature and ambient (Fig. 4a). At low annealing temperature the hydroxide group decomposes with formation of excess Cd and V$_S$.

![Fig. 4](image)

**Fig. 4.** (a) Electrical resistivity of CdS films at RT as a function of annealing time, temperature and atmosphere. (b) Time dependence of electrical conductivity and activation energy values for CdS films annealed for 1h in H$_2$, N$_2$ and air.

The high conductivity is controlled by the ClS$^+$ and (OH)$_3$S shallow donors [10] (considering annihilation of sulfur and cadmium vacancies) at ~9-30 meV under conduction band (Fig. 4b). At 250 °C the process stabilized in 30 minutes for N$_2$ and H$_2$ annealing. For air-annealed CdS resistance will be differently increased than for H$_2$ and N$_2$ due to incorporated oxygen on sulfur site and its reaction with Cd, forming CdO. Same processes with higher rate take place at annealing temperature 400 °C and significantly higher resistances are achieved in air and N$_2$ annealing due to the background oxides in CdS (Fig. 1a). At 400 °C annealing, due to full destruction of hydroxide groups and out diffusion of chlorine, the concentration of electrons decreased [10] and CdS conductivity is determined by the deep donor defects at ~120 meV in the region of measurement temperatures 20 - 100 °C (Fig. 7).

The PL spectra (Fig. 5) for all samples consist of two prominent bands at approximately 1.7 eV and 2.24 eV. The 1.7 eV PL band was interpreted [25] in terms of commonly accepted neutral complex $(\text{V}_{\text{Cd}}2\text{Cl}_S)^0$. The sharp peak (2.24 eV) corresponds to the emission of donor – acceptor pairs due to the thermal dissociation (8) of the neutral complex to ClS$^-$ donors and $(\text{V}_{\text{Cd}}\text{Cl}_S)^-$ acceptors [26].

$$
(V_{\text{Cd}}2\text{Cl}_S)^0 \leftrightarrow (V_{\text{Cd}}\text{Cl}_S)^- + \text{Cl}_S^-
$$

(8)
The unexpected high PL intensity of air-annealed CdS films is connected with the incorporation of oxygen on $V_S$ and the spatial compensation of contraction in Cd sub-lattice by $V_{Cd}$. The oxygen should enhance formation of $V_{Cd}$ and therefore to increase the intensity of both PL peaks. However, due to concentration quenching, lower intensity of the 1.7 eV peak (showing the neutral complex concentration) is observed. This explanation is confirmed by one order of magnitude increase of PL peak intensity for the air-annealed CdS film which was over-annealed in $H_2$ (Fig. 5).

4. Conclusions

Changes in structural, optical and electrical properties of CBD CdS layers in the annealing process are connected with decomposition of OH group incorporated in CdS lattice in the deposition process, with outdiffusion of $H_2O$ and destruction of crystallites, and with creation of Cd excess resulting in transition from $CdS_{1-x}(OH)_x$ to $CdS_{1-y}O_y$ solid solution. Annealing in air and $N_2$ creates stable $CdS_{1-y}O_y$ solid solution while $H_2$ annealing removes the oxides and chloride dopant resulting in pure CdS films. Excess of Cd as precipitate decreases the transmittance while incorporation of oxygen into CdS lattice decreases the band gap of the CdS film. The gained knowledge about influence of annealing conditions on the properties of CdS film will facilitate further investigations on CdS/absorber heterostructures for elaboration of high-quality solar cells.

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References


