Annealing effect on CdS films: transition from glass to ITO

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Abstract. Structural and optical properties of CdS films deposited on glass and ITO substrates and annealed in H_2, N_2 or H_2+N_2 atmospheres at 250 ^oC and 400 ^oC were compared. The optical thickness 405±10 nm of the CdS films was found not to be influenced by any annealing conditions or substrate. The as deposited films on both substrates had similar diffraction patterns with one narrow peak corresponding to the (111) cubic plane at 2θ 26.70° and 26.75°, respectively. Higher density of nucleation centres on the ITO surface generated denser CdS films. In the annealing process of CdS/ITO a slower shift of both (111) peak and lattice constant was observed in the direction of pure zinc blende modification. Similar values of band gap and transmittance were determined for as-deposited CdS while annealing at 400 ^oC decreased transmittance by 5% and 16% for CdS on glass and ITO, respectively. Transmittance dropped because of the destruction of hydroxide group in the CdS lattice, the formation of cadmium excess and the reduction of SnO_2 to black SnO in the ITO structure.

1. Introduction

CdTe- and CIGS- based photovoltaic solar cells in a superstrate configuration are made on glass substrates coated by transparent conductive oxide (TCO) like tin oxide (SnO_2) or indium tin oxide (ITO) over which CdS layer is deposited. Combined TCO–CdS window layers [1-4] and the effect of these bilayers on the final photovoltaic response [5] had been studied by many authors. Usually TCO-coated glass substrates with suitable photovoltaic quality are commercially available, while the optimization of CdS thin films remains in progress at laboratory scale.

As an optimization route for CdS thin film, annealing in different atmospheres at certain time-pressure-temperature conditions may be used. In [6] we studied the properties of CdS/glass thin films after H_2 annealing. A relationship between annealing conditions and desirable properties of CdS on glass was obtained: temperatures up to 400 ^oC had a weak influence on the morphological and optical properties; 1h annealing was enough to reach stable electrical properties; CdS films annealed at 250 - 400 ^oC had resistivity in the region of $2.3 \cdot 10^{-2}$ – 6.1 Ω·cm, respectively. It is interesting to verify if the knowledge gained about the properties of annealed CdS/glass may be applied for the annealed CdS/ITO/glass structures. Similar studies have shown the influence of annealing in air [7] or nitrogen [8] on CdS properties when deposited on different substrates such as glass, ITO, SnO_2 or other materials. However, information about CdS/ITO/glass bilayers annealed in H_2 atmosphere is scarce. This paper compares the optical, structural and electrical properties of CdS layers deposited on glass and ITO substrates and annealed in H_2, N_2 and H_2+N_2 gases.

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2. Experiment

Polycrystalline CdS films were deposited by chemical bath deposition (CBD) on both uncoated soda-lime glass and commercial ITO coated glass substrates. The plates were accurately cleaned and immersed in the deposition solution. The temperature and agitation speed of the solution were 85 ^{o}C and 500 rpm, respectively. One deposition lasted for 30 minutes, but for thicker CdS films the process was repeated three times. After deposition the films were vacuum dried at 120 ^{o}C to remove most of the secondary phases of water, hydroxides and organic impurities. This drying was the last stage of preparation for the so-called as-deposited CdS layers. We choose the thermal treatment conditions based on our investigation on H_2 annealing of CdS/glass: normal pressure, 1 h duration at 250 ^{o}C and 400 ^{o}C. For comparison, annealing in N_2 and H_2+N_2 (H_2 concentration of was 5%) was also applied.

Crystallographic investigations were performed using the X-ray diffraction (XRD) technique in the Bragg-Brentano (θ-2θ) geometry by a Rigaku Ultima IV diffractometer with Cu-Kα radiation. Crystallite size, lattice constant and interplanar distance were computed by the PDXL software (Version 1.4.0.3) on the Rigaku system. The optical characteristics were evaluated at room temperature in the range of 200–2500 nm on the Jasco V-670 UV-VIS spectrophotometer equipped with an integrating sphere. Total optical transmission and reflection spectra were used to determine the band gap and optical thickness of CdS.

3. Results and discussions

Optical properties were analyzed on the basis of transmittance spectra and E_g values shown in figure 1a and table 1, respectively.

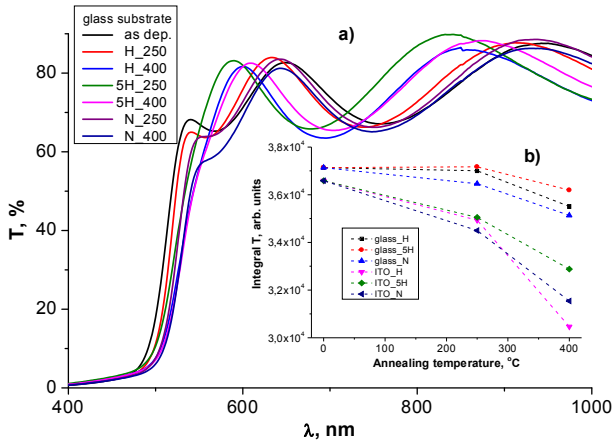

Figure 1. a) Optical transmittance spectra of the CdS films. b) Calculated integral transmittance of CdS/glass and CdS/ITO as a function of annealing temperature and ambient.

Table 1. Band gap (E_g), lattice constant (a), interplanar distance (d) and crystallite size (S) of the CdS films deposited on different substrates and annealed in H_2 (H), N_2 (N) and H_2+N_2 (5H) ambient.

	E_g, eV		**a, Å**		**d, Å**		**S, Å**	
Substrate →	*glass*	*ITO*	*glass*	*ITO*	*glass*	*ITO*	*glass*	*ITO*
as deposited	2.454	2.464	5.783	5.775	3.337	3.330	405.2	428.0
H-250 ^{o}C	2.412	2.373	5.803	5.793	3.346	3.341	428.3	457.0
H-400 ^{o}C	2.364	2.379	5.821	5.804	3.354	3.347	391.3	394.3
5H-250 ^{o}C	2.391	2.373	5.792	5.790	3.340	3.340	430.9	460.0
5H-400 ^{o}C	2.348	2.365	5.806	5.802	3.345	3.346	377.4	364.0
N-250 ^{o}C	2.377	2.376	5.797	5.787	3.344	3.338	420.0	472.0
N-400 ^{o}C	2.352	2.367	5.806	5.797	3.351	3.343	368.3	347.7

Almost similar changes of band gap were found for CdS on glass and ITO substrates, independent of the annealing atmosphere. When the annealing temperature increased, the band gap of CdS/glass gradually decreased for all three atmospheres from 2.45 eV (as-deposited CdS) to 2.35 eV (annealed at 400 ^{o}C). With ITO the E_g of CdS reached a constant value (2.375 eV) for N_2-containing ambients at both annealing temperatures (table 1).

We estimated the integral transmittance in the region of 500-1000 nm as the area under the T plot (figure 1b). With a glass substrate a similar trend of CdS transmittance was observed for all annealing gases - a slow decrease at 250 ^{o}C followed by an abrupt decrease at 400 ^{o}C (~5 %). However, the lowest transmittance was emphasized for a CdS sample annealed in N_2. The decreased transmitance of CdS could be explained by hydroxide group incorporated into the CdS lattice the destruction of which starts at 300 ^{o}C [6]. Independent of the annealing atmosphere, the hydroxide group incorporated into the CdS lattice leads to the formation of $CdS_{1-n}n(OH)_S$ solid alloy. When temperature is applied, H_2O evaporates and Cd precipitate [9] is formed (1, 2).

$$CdS_{1-n}n(OH)_S \xrightarrow{t} CdS_{1-2n}n(O_S)n(V_S) + nH_2O \uparrow \quad (1)$$

$$CdS_{1-2n}n(O_S)n(V_S) \xrightarrow{t} Cd_{1-m}S_{1-2n}n(O_S)n-m(V_S) + mCd \downarrow \quad (2)$$

When CdS/glass was annealed, the Cd precipitate (2) decreased the transmittance of CdS (figure 1b). However, in the presence of H_2 the CdO decomposes, as oxygen is eliminated by the release of H_2O, and CdS band gap increases [6]. Therefore, the CdS transmittance was higher after the H_2 annealing than that of N_2 one. This reveals an advantage of H_2 annealing for CdS films.

For a CdS film on ITO, the transmittance decreased faster up to 250 ^{o}C than with the glass case. Thus, the contribution of Cd precipitate (2) to the decomposition of SnO_2 should be taken into account (3, 4). Both products of reaction (3) resulted in the reduced transmittance of the CdS/ITO bilayer.

$$SnO_2 + Cd \rightarrow SnO + CdO \quad (3)$$

$$2SnO \rightarrow Sn + SnO_2 \quad (4)$$

Still, when CdS/ITO was annealed at 400 ^{o}C in H_2, the transmittance decreased by 16% compared to as-deposited CdS. A new reaction (5) may compete with (3) due to higher activity of the H_2 compared to the metallic Cd from CdS. These processes resulted in the blackening of the ITO substrate and an abrupt drop of CdS transmittance.

$$SnO_2 + H_2 \rightarrow SnO + H_2O \uparrow \quad (5)$$

The transmittance behavior of CdS on both glass and ITO substrates suggested that H_2+N_2 mixture instead of pure H_2 or N_2 gases is needed for annealing.

The structural properties of CdS were analyzed based on XRD measurement results. Similar XRD patterns with one narrow (111) diffraction peak of the cubic plane at 26.70° and 26.75° were found for CdS films on glass and ITO substrates, respectively. Figure 2 shows that both peaks are in the close proximity of the (002) hexagonal plane at 26.83°. Twice higher (111) peak of CdS/ITO than that of CdS/glass suggests a more oriented CdS film. This is attributed to the strong influence of the oriented crystalline surface of ITO. The high density of nucleation centers on ITO generates a denser CdS film, which might also explain the decreased transmittance of CdS on ITO (figure1b).

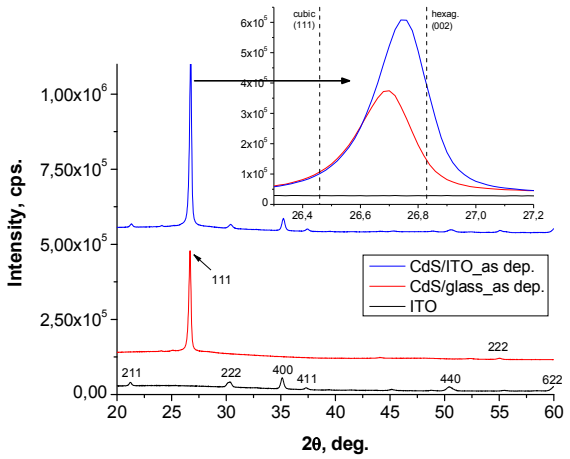

Figure 2. XRD pattern of as-deposited CdS on glass and ITO substrates.

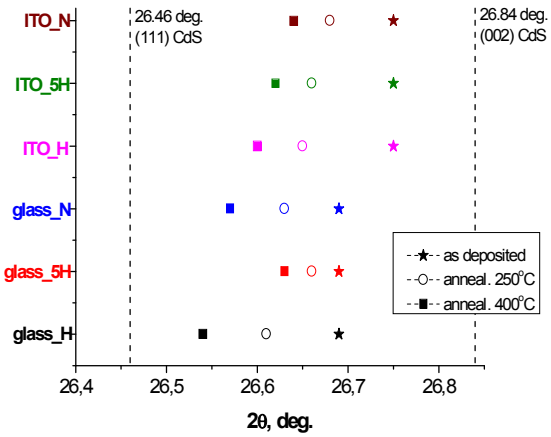

Figure 3. Influence of annealing conditions on the shift of the main (111) peak of CdS.

Interestingly for both substrates, the main (111) peak shifted in the direction of the zinc blende CdS plane at 26.46° in all three ambients when the annealing temperature increased (figure 3). However, a slower shift of the main cubic peak and lattice constant (table 1) in the direction of zinc blende modification of CdS was found in the case of the ITO substrate during annealing. The shift of this main peak infers that the stressed lattice of as-deposited CdS relaxed during annealing at 250 - 400 ^{o}C, after which a more pure cubic CdS phase was obtained. The comparison between the three annealing atmospheres in the case of glass substrate shows that the H_2 ambient contributed to a more cubic structure of CdS, while the H_2+N_2 ambient had a weak influence on the CdS lattice. In the case of the ITO substrate no significant differences were found when CdS was annealed at higher temperatures.

4. Conclusions

An abrupt reduction of transmittance was found for CdS/ITO annealed in H_2 at 400 ^{o}C. This might limit the applicability of CBD CdS for superstrate solar cells. We minimized the transmittance by annealing CdS/ITO in a mixture of H_2 + N_2. The oriented ITO contributes to denser CdS films. The typical shift of the main (111) peak is characteristic for CdS on both glass and ITO. Generally, the structural and optical properties of CdS films on glass and ITO are quite similar.

Acknowledgements

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