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Structural and optical properties of cadmium sulfide thin films modified by hydrogen annealing

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ABSTRACT

This paper provides a systematic study of structural and optical properties of cadmium sulfide (CdS) films annealed under hydrogen (H_2) in a wide range of temperatures (200–450 °C) and times (3–120 min). The aim is to present the properties of the CdS film as a function of hydrogen annealing conditions and to discuss the mechanism behind these changes. The stressed cubic lattice of as-deposited CdS film was relaxed by increasing the temperature and the time of H_2 annealing. The surface porosity of CdS films revealed the highest temperature and duration applicable to H_2 annealing. The dependence of the band gap as a function of annealing conditions is discussed. The origin of changed optical properties accompanying the shrinkage of the lattice is explained by the incorporation of the hydroxide group on the sulfur site in the CdS lattice during the deposition process and its decomposition after 300 °C. A relationship between CdS properties and the decomposition process of $Cd(OH)_2$ to water and CdO during annealing in H_2 was established at different low, moderate and high temperatures of annealing.

1. Introduction

Cadmium sulfide (CdS) is an important n-type semiconductor material which plays a key role in the fabrication of thin film solar cells. It has been successfully used as a window/buffer layer in the production of both CdTe and CIGS solar cells with record efficiencies [1].

Among various processes, chemical bath deposition (CBD) is one of the most advantageous due to low cost, low temperature processing and its suitability for forming large area thin films. However, a major problem is that the CBD film contains numerous adherent particulates of homogeneously nucleated CdS and other bath reaction products [2–4]. The presence of these impurities entails the layers with a high speed of recrystallization already at low temperatures with major changes in the structural and optical properties [5,6]. A possible method to control these changes and reduce the extent of disorder is the thermal annealing in a defined atmosphere. CdS layers have been annealed in oxidizing [7,8], reducing [5,8,9] and neutral [8,10] atmospheres. Several studies have covered the influence of each type of annealing on the properties of CdS.

Generally, the neutral annealing brings reorientation of an as-deposited CdS film with a significantly improved crystalline quality. Tomas et al. [8] have shown that the $Ar+S_2$ annealing diminishes the resistivity by increasing the grain size, therefore the number of grain boundaries decreases in the films. Also, the Ar annealing increases the grain size and produces a large amount of sulfur vacancies as a consequence of the non-equilibrium conditions. On the other hand, annealing in a neutral atmosphere leads to phase transition from the metastable cubic phase of CdS to the stable hexagonal phase [10]. Besides increased grain size and improved crystallinity of CdS annealed in an

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oxidizing ambient, Haider et al. [7] have reported a substantial decrease in the band gap. Moreover, the presence of oxygen creates both CdO and $CdSO_4$ layers on the surface, slightly increasing the resistivity of the films as compared to the neutral atmosphere [8]. The thermal treatments in a reducing atmosphere have the advantage of containing H_2, which is a strong agent for grain boundary passivation by oxygen removal. The presence of H_2 causes the resistivity to decrease by 4 orders of magnitude [11] compared to the neutral case [8]. Only CdS samples exposed to H_2 and air atmosphere preserve the same structural cubic phase during the complete thermal process [5]. The cubic structure increases the potential applicability of CdS for optoelectronic devices, because many semiconductors such as InP [12] also have a cubic structure. Annealing in H_2 is important as it requires lower exposure times and was shown by several authors [9,13,14] to have visible consequences for technological applications in solar cells.

Still, the pin-holes and irreproducibility are a concern for reliable CdS films [15]. To find the thermal process that produces CBD CdS films with the best combination of high band gap and low resistivity is the main task regarding to this semiconductor material. In addition, the mechanism that explains the microstructure and optical behavior as a function of annealing conditions is not completely understood.

The aim of this paper is to present the structural and optical properties of a CBD CdS film as a function of hydrogen annealing in a large range of temperature and time. Conditions of H_2 annealing for high transparency, band gap and porosity free CdS thin films will be analyzed. In comparison with previous works [2–8] on CdS films, the mechanism of changes in CdS properties on the basis of Cd $(OH)_2$ presence is discussed here.

2. Material and methods

Polycrystalline CdS films were deposited on 25 mm × 25 mm soda-lime glass substrates. The plates were properly cleaned and immersed in the chemical bath which consisted in a water solution of 1 mM $CdSO_4$, 10 mM thiourea, 0.2 M NH_4OH and 30 mM $(NH_4)_2SO_4$. For CdS doping [16], a low concentration of NH_4Cl solution (0.1 μM) was added in the deposition bath. The temperature and agitation speed of the solution were 85 °C and 500 rpm, respectively. One deposition lasted for 30 min, but for thicker CdS films the process was repeated thrice. After deposition vacuum drying at 120 °C was applied 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. Each layer was annealed then in hydrogen ambient under different conditions. The vacuumed process tube with samples was filled with 1 atm hydrogen gas at room temperature then closed and introduced into a cylindrical furnace where the constant temperature and time were set. Annealing temperature varied in the range of 200 °C to 450 °C while annealing lasted from 3 up to 120 min. The hydrogen pressure in the process tube was maintained by a standard gas reduction system and was not influenced by expansion of gas at high temperatures of annealing. Large diameter (55 mm) and volume (1500 ml) of the process tube ensured an excess of H_2 and the gas convection flow so that the reaction products were transported to the colder part of the tube.

Crystallographic investigations were performed using the X-ray diffraction (XRD) technique. The measurements were made in the Bragg–Brentano (θ–2θ) geometry by the 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 measured in the wavelength range of 200–2500 nm on the Jasco V-670 UV–vis–NIR spectrophotometer equipped with an integrating sphere. Total optical transmission and reflection spectra were used to determine the transmittance of CdS and the optical thickness; by calculation of the absorption coefficient, the band gap was obtained. Surface morphology of CdS films was examined by scanning electron microscopy (SEM). High-resolution SEM apparatus (Zeiss EVO-MA15) was used at an operating voltage of 10 kV. Surface topographies of the layers were studied by AFM using the NT-MDT Solver 47 Pro system operated in a “semi-contact” (tapping) mode. The image analysis of AFM 2D images was performed using the Media Cybernetics ImagePro-3.0 program. The elemental composition of films was determined by means of energy dispersive spectroscopy (EDX) analysis, using the Rontec EDX XFlash 3001 detector and the Oxford Instruments INCA Energy system. The quantitative results were obtained by the help of factory defined standard using the PAP correction – a method for light elements.

3. Results

CdS films grew in a columnar structure, perpendicular to the glass substrate (Fig. 1a). Independent of annealing conditions, up to 400 °C the surface view of the CdS layer remained unchanged (Fig. 1c and d). However, Fig. 1b shows that the H_2 annealing generated the recrystallization process which improved the contact between the vertical grains, smoothing the CdS film surface. Already after 10 min annealing at 450 °C pores appeared in the film surface; at longer annealing the CdS porosity clearly increased (Fig. 2). The CdS porosity might be caused by the contraction of the layer which in turn was triggered by the sintering process at high temperature annealing. The same processes were attributed to reduced thickness of CdS layers at high temperature of annealing (Table 1).

EDX analysis revealed a complex composition of CdS films which became stoichiometric when the annealing temperature increased (Table 1). The sulfur deficiency was found characteristic for all CdS films, the highest deficiency being detected at 300 °C annealing. The difference in Cd and S concentrations in the annealed layers could be assigned to the presence of residual oxygen and hydrogen impurities [3,17]. Data in Table 1 show that CdS thin films were transparent to the signals of Si, O and Na from the glass substrate, especially the layers annealed at 450 °C. By subtracting the concentration of SiO_2 from the total oxygen content, the concentration of oxygen in CdS films was