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Effects of $CdCl_2$ treatment on the properties of CdS films prepared by r.f. magnetron sputtering

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Abstract

Effects of the thickness of $CdCl_2$ layer and the annealing on structural and optical properties of sputter-deposited CdS films were investigated. The annealing process of evaporated $CdCl_2$ was carried out by heating the sample in air at 350–500 °C for 20 min. As the thickness of the $CdCl_2$ increases, the (002) peak of CdS becomes weak and the other peaks of CdS increases. Especially, for 200 nm $CdCl_2$, the preferential orientation of the (002) plane disappears and the *c*-axis of the CdS film tends to orient parallel to the substrate. As the $CdCl_2$ layer is thicker, the grains are enlarged significantly. The improvement of optical properties of CdS films with thicker $CdCl_2$ layer might be successfully employed in achieving better conversion efficiencies in solar cells.

Keywords: Cadmium sulfide (CdS); Heat treatment; Cadmium chloride ($CdCl_2$); Solar cell

1. Introduction

CdS thin films are the most commonly used window material for high-efficiency CdTe and $CuInSe_2$ polycrystalline thin film photovoltaic devices [1]. For example, efficiencies close to 16% have already been reported for CdTe/CdS thin film solar cells [2,3]. There are, however, many issues that still need to be understood for successful commercialization of CdTe/CdS solar cells. Especially, CdS films prepared through sputtering technique have disadvantages of small grain size and rough surface, and so on. In addition, these disadvantages badly affect the properties of the CdTe film deposited on the CdS film and the CdS/CdTe solar cell. Therefore, it is necessary to improve the disadvantages through various heat treatments. Among heat treatments, the one using $CdCl_2$ has been known to increase the grain size of CdS and to decrease the interdiffusion between CdS and CdTe [4]. Normally, $CdCl_2$ treatment is an additional process step for most of the device fabrication techniques and involves wet treatment followed by annealing at 500 °C. The wet $CdCl_2$ surface treatment is effective for small-cell fabrication but has several disadvantages for large area manufacture, such as uniform delivery of the $CdCl_2$ and handling and safe disposal. To overcome these problems, in present work, the vapor technique was developed which can uniformly deliver the chloride species to the CdS surface.

In this paper, CdS films were deposited by r.f. magnetron sputter method and annealed with $CdCl_2$. The effects of annealing and $CdCl_2$ thickness on structural and optical properties of CdS films were investigated.

2. Experimental

The CdS films were prepared onto Corning 7059 glass by r.f. magnetron sputtering system. A sintered ceramic CdS target with 99.999% purity of 3 in. in diameter was employed as source material. The separation between target and substrate was about 5 cm. The sputtering gas Ar of 20 sccm was controlled by a mass flow controller. The sputter power and pressure were fixed to 125 W and 2.7 Pa, respectively. After the chamber was evacuated to a base pressure below 6.6×10^{-4} Pa, pre-sputtering for 10 min was carried out at an argon gas pressure of 1.0 Pa in order to clean the target surface. During CdS film deposition, the sputter power and substrate temperature were maintained at 125 W and 200 °C, respectively. The thickness of the CdS film measured by surface profiler was

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about 600 nm. The as-deposited CdS thin films were yellow orange in color, uniform, highly adherent and specularly reflective. A $CdCl_2$ layer was deposited on the CdS film by evaporation of $CdCl_2$ of 99.999% purity in a vacuum of 1.33×10^{-3} Pa Torr. The CdS films were not heated during $CdCl_2$ deposition. The $CdCl_2$ thickness was varied from 70 to 200 nm. Annealing of the samples was done in air at the temperature range of 350–500 °C for 20 min.

X-ray diffraction (XRD) measurements were performed to study the preferential orientation and crystallinity of the film by using a Philips PW 1800 diffractometer with 1.5418 Å Cu-K_α radiation. The surface morphology and grain size of films were determined by field emission scanning electron microscopy (FE-SEM). The optical properties of the films were measured at normal incidence in the wavelength range from 300 to 900 nm with a double-beam spectrophotometer. Photoluminescence (PL) spectra were recorded with the excitation wavelength of 488 nm using Ar laser in the range of 350–900 nm at the temperature of 40 and 150 K.

3. Results and discussion

Fig. 1 shows the XRD patterns of vacuum-deposited $CdCl_2$ films annealed at 350–500 °C in air for 20 min. The thickness of $CdCl_2$ films was 100 nm. No diffraction peak was observed in the as-deposited film, indicating the film had an amorphous structure. When the film is annealed at 350 °C, a diffraction peak at $2\theta=14.9°$, corresponding to the (003) reflection of rhombohedral phase or (020) orthorhombic reflection of the hydrate phase. As the annealing temperature increases, this peak is more intense and sharper. This means that the annealing gives rise to the improvement of the film crystallinity and the preferred orientation of the (003) plane. Meanwhile, the (003) diffraction peak of $CdCl_2$ decreases markedly after annealing at

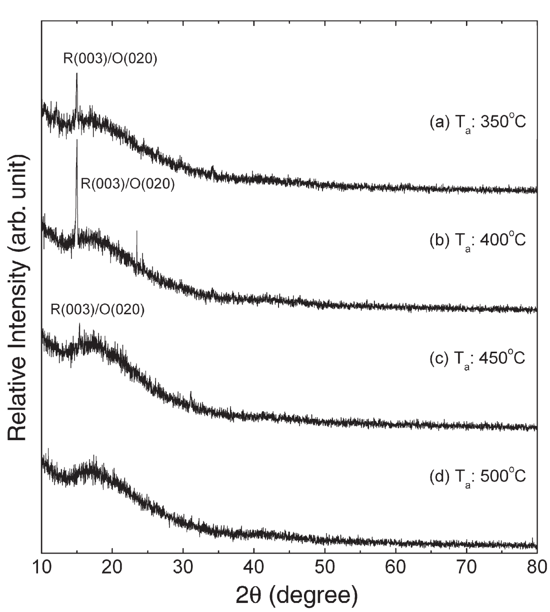

Fig. 1. XRD patterns of vacuum evaporated $CdCl_2$ films as function of annealing temperature.

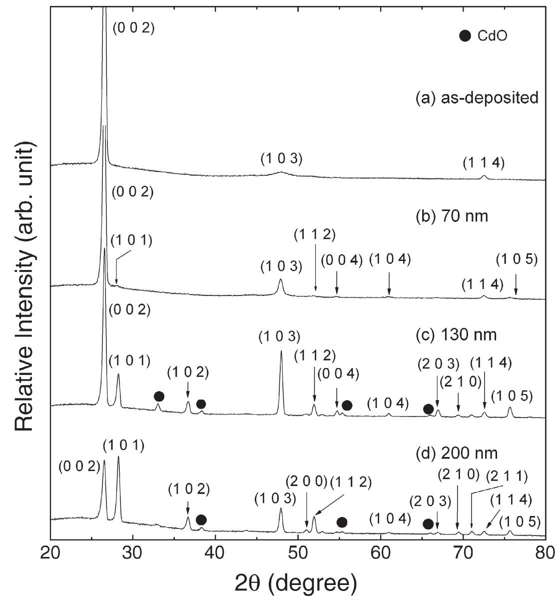

Fig. 2. XRD patterns of the CdS films annealed at 500 °C with different $CdCl_2$ thicknesses.

450 °C and almost disappears after annealing at 500 °C. These results can be explained by re-evaporation of the films.

Fig. 2 shows XRD patterns of CdS films annealed at 500 °C with different $CdCl_2$ thicknesses. The as-deposited CdS films without $CdCl_2$ layer exhibited a dominant XRD peak at $2\theta=26.56°$. Both the hexagonal (002) and cubic (111) reflections of CdS share a peak at this angle. However, no other peak corresponding to the cubic phase of CdS was observed while weak reflections at $2\theta=48.0°$ and 72.56° corresponding to the (103) and (114) reflections of the hexagonal phase were also observed. The relative absence of other reflections of the cubic phase indicates that the as-deposited CdS films posses a hexagonal (wurtzite) structure. A comparison of the observed peak intensities also implied preferred (002) orientation. Enhanced intensity of the (002) peak has been reported before in hexagonal phase CdS thin films obtained by chemical deposition [5], spray pyrolysis [6], and evaporation [7]. This is due to the preferred growth direction of the film along the *c*-axis perpendicular to the substrate, i.e. with (002) planes parallel to the surface. When the CdS film with $CdCl_2$ layer of 70 nm was annealed at 500 °C, the new peaks observed at $2\theta\sim28.0°$, 51.9°, 54.7°, 60.9°, 72.5°, and 75.6° corresponding to the (101), (112), (004), (104), (114), and (105) planes of hexagonal phase, respectively. At the same time, the intensity of the (002) peak decreased and the (103) peak increased. This indicates that the hexagonal structure content increases and the degree of the (002) preference orientation reduces. It should be noted that no peaks related to CdO phase were observed in XRD spectrum, despite annealed in air atmosphere. One of the effects of the thermal annealing is the oxidation of the films. This can be seen in the XRD patterns of the sample annealed at 500 °C with the $CdCl_2$ thickness of 130 nm. In these patterns, four diffraction peaks at approximately 33.1°, 38.3°, 55.4°, and 65.9° corresponding to the