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Structural, optical and electrical properties of $CdO/Cd(OH)_2$ thin films grown by the SILAR method

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ABSTRACT

Successive Ionic Layer Adsorption and Reaction (SILAR) was used to form $Cd(OH)_2$ thin films from aqueous cadmium–ammonia complex on glass substrates at room temperature and the thermal annealing effect on thin films was studied. The as-deposited *films* were annealed at 200, 300 and 400 °C for 1 h in an oxygen atmosphere for conversion from $Cd(OH)_2$ to CdO and change in the structural, optical and electrical properties of the films and the effect of the light on the electrical properties of the films were investigated. The structural and surface morphological properties of the films were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that $Cd(OH)_2$ phase is converted into the cubic CdO films by annealing. The band gap energy values of films decreased from 3.59 to 2.13 eV through increasing annealing temperature. It was found that the current increased with increasing light intensity and CdO films were more conductive than the as-deposited films.

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1. Introduction

Transparent Conducting Oxides (TCOs), such as cadmium oxide, zinc oxide, indium oxide, tin oxide, etc. have been widely studied because of their use in optoelectronic devices. Due to their optical and electrical properties, TCOs are used for photovoltaic solar cells, phototransistors, liquid crystal displays, optical heaters, gas sensors, transparent electrodes and other optoelectronic devices [1]. Due to its low electrical resistivity, high carrier concentration and high optical transmittance in the visible region of the spectrum, cadmium oxide (CdO), which is one these TCOs, has attracted considerable attention to various applications, such as solar cells and photodiodes [2]. CdO films are transparent in visible and Near Infra Red (NIR) spectral regions and have n-type semiconductor properties with an electrical resistivity of 10^{-2} to 10^{-4} Ω-cm and a band gap between 2.2 and 2.7 eV [3].

CdO and doped CdO thin films have been prepared by various deposition methods, such as SILAR [4,5], spray pyrolysis [6], laser deposition [7], magnetic sputtering [2], etc. The SILAR method, introduced by Nicolau [8], is a unique method in which thin films of compound semiconductors can be deposited by alternately dipping the substrate into aqueous solutions of the ions for each component. Due to the intermediate rinsing step between the cation and anion immersions, the formation of the thin films in the SILAR method occurs only if it is heterogeneously on the solid–solution interface. Therefore, the thickness of the film can easily be controlled by the number of growth cycles used [9].

In this study, $CdO/Cd(OH)_2$ thin films were grown using the SILAR method. The influences of annealing temperatures on the structural, morphological, optical properties and the light effect on electrical properties of these films were studied. Characterization of the films was done using XRD, SEM, optical absorption measurements and the two-point-probe method.

2. Experimental procedure

In this study, CdO thin films were grown on glass substrates by Successive Ionic Layer Adsorption and Reaction (SILAR) at room temperature and ambient pressure. Aqueous cadmium–ammonia complex ions ($[Cd(NH_3)_4]^{2+}$) were chosen as the cation precursor (pH ∼ 12), using analytical reagents of $CdCl_2$ and concentrated ammonia (NH_3) (25–28%). The optimal concentration value defined for the cadmium solution was 0.1 M, and the molar ratio of Cd:NH_3 was 10:1, as a result of several experiments.

To deposit CdO, one SILAR growth cycle involves the four following steps: (1) immersing the substrate in the precursor solution for 20 s to create a thin liquid film containing $[Cd(NH_3)_4]^{2+}$ on the substrate; (2) immersing immediately the withdrawn substrates in hot water (90 °C) for 7 s to form a CdO layer; (3) drying the substrate in the air for 60 s; and (4) rinsing the substrate in a separate beaker for 30 s to remove large and loosely bonded CdO particles. After four or five deposition cycles, a dense and lustrous CdO layer becomes visible. In this experiment, we generated 100 nm as-deposited films by

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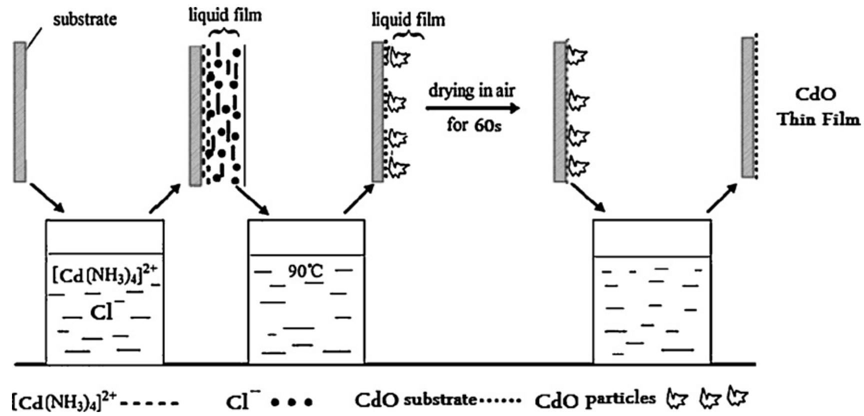

Fig. 1. Experimental scheme for the deposition of CdO thin films.

repeating 30 times the SILAR growth cycle. Fig. 1 shows the scheme for SILAR deposition of CdO films.

The glass substrates were cleaned ultrasonically for 10 min, first in acetone and then in a 1:1 ethanol:water solution. The substrates were dried and stored in desiccators.

The as-deposited films were annealed at 200, 300 and 400 °C for 1 h in an oxygen atmosphere to convert $Cd(OH)_2$ to CdO. Annealing effect on the structural, optical and electrical properties of the films was investigated. The film thickness was decreased with increased annealing temperature, and this change is shown in Table 1. For the effect of light on the films, *I–V* curves were measured in the dark and under 150, 300 and 500 W light intensity. For structural studies, a Rigaku 2200D/Max, X-ray diffractometer of Cu Kα (λ = 1.5405 Å) radiation with 2θ of 20–70° was used. Surface morphology was studied using the Zeiss Supra 50 VP model SEM. In order to study the optical properties of the generated films, the absorption measurements were carried out using a PerkinElmer UV/VS Lambda 2S Spectrometer with a wavelength resolution better than ±0.3 nm at room temperature. Electrical characterization of the films was performed using the two-point-probe method.

Table 1
The film thickness values of as-deposited and annealed films.

Sample	Film thickness (nm)
As-deposited	100
Annealed at 200 °C (CdO)	95
Annealed at 300 °C (CdO)	86
Annealed at 400 °C (CdO)	80

3. Result and discussion

3.1. Mechanism of film deposition

In this study, the mechanism of CdO film formation by the SILAR method can be explained as follows: we have made full use of the

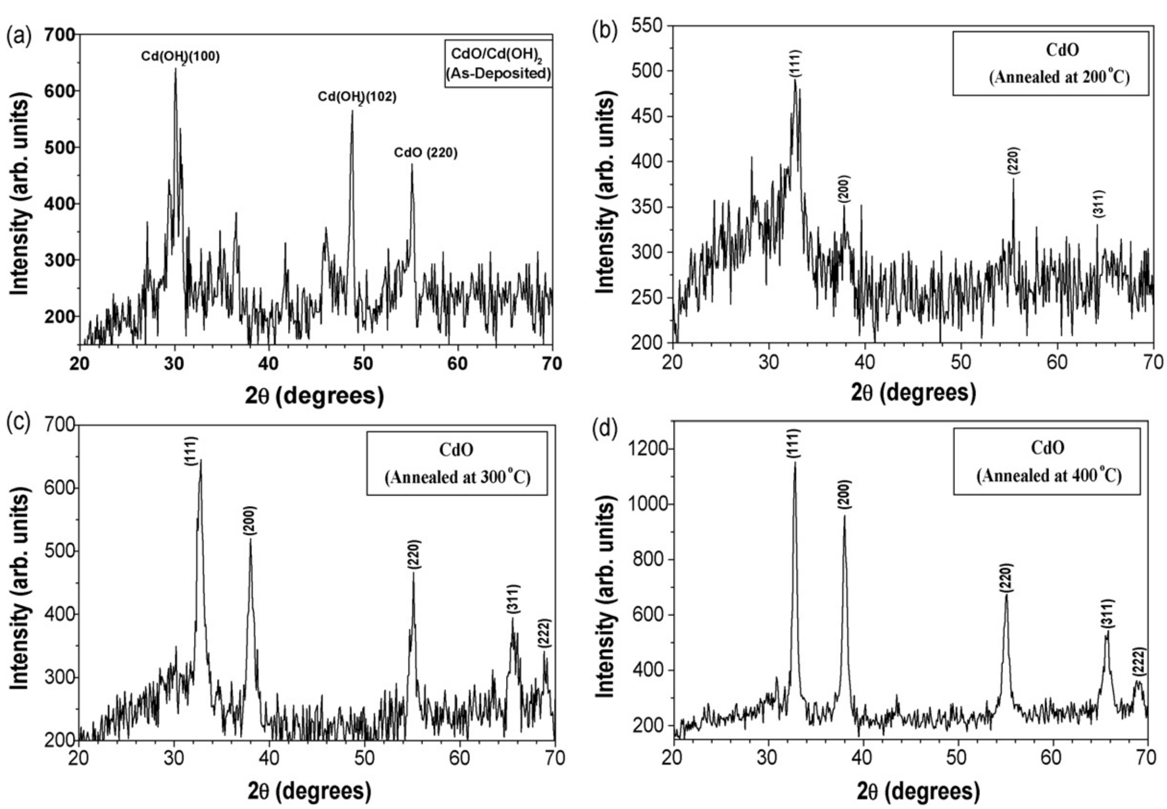

Fig. 2. The XRD patterns of as-deposited ($CdO/Cd(OH)_2$) and annealed at 200, 300 and 400 °C (CdO) thin films.

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