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The transformation to cadmium oxide through annealing of cadmium oxide hydroxide deposited by ammonia-free SILAR method and the photocatalytic properties

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ABSTRACT

Cadmium oxide-hydroxide films were prepared on glass substrates from aqueous alkaline solution at room temperature which was prepared by a more simple and economic version of chemical bath deposition — SILAR (successive ionic layer adsorption and reaction) method. The films obtained were converted to polycrystalline cadmium oxide by annealing treatment at different temperatures. It was found that the annealing temperature affects the grain size and films' density. The morphology, crystallinity, optical and electrical properties of the material obtained confirms its high quality. Finally its photocatalytical effect on methylene blue colorant was observed and analyzed. We expect that this method of CdO films preparation might be of interest for applications in solar energy converter and photocatalytical reactors.

1. Introduction

CdO is a direct band gap semiconductor with rock-salt crystal structure having as a rule non-stoichiometric composition due to the presence of either interstitial cadmium or oxygen vacancies. Thus CdO is n-type semiconductor with high electrical conductivity, band gap of 2.5 eV and density of 8.15 g/cm^3 which makes it useful for various applications; sensor for liquefied petroleum gas [1] and ethanol gas [2,3], a component of solar cells [4,5,6,7], as antibacterial agent (ZnO–CdO [8], Ag doped CdO [9]), biosensor [10], photocatalyst in a mixture with another semiconductor (ZnO–CdO [11], TiO_2/CdO–ZnO [12], CdO–$CdTiO_3$ [13], CdO–CdS [14]), photoelectrochemical solar cells [15], or a diode [16,17] just to mention a few. In photocatalytic applications, pure CdO has been rarely studied; there are just a few reports about photocatalytic activity of cadmium oxide nanoparticles [11]. This opens the way for future research on cadmium oxide as photocatalyst.

Different physical and chemical deposition techniques such as chemical bath deposition (CBD) [2,4,18,19], sol–gel [20], spray pyrolysis [21,22,25], magnetron sputtering [26,27], thermal evaporation [26], vacuum evaporation [27], and electrodeposition [28] have been used to prepare CdO films. Among deposition methods, successive ionic layer adsorption and reaction (SILAR) at room temperature deserves special attention because it works without special equipment, which makes this technique an attractive process for large areas of deposition. In recent years several works reported the production of CdO films [29–33] and films doped with Sn [34], Ba [35] by the SILAR method. Those investigations coincide in using ammonia as complexing agent; nonetheless ammonia is considered a non-environmental friendly chemical so the method here described offers a greener alternative.

The CdO can be produced by a very well-established method, which involves annealing of $Cd(OH)_2$ [15,18,20,30,31,36]. Obtaining cadmium chalcogenide (CdSe and CdTe) films from a $Cd(O_2)_{0.88}(OH)_{0.24}$ or similar precursor employing a post-treatment is also possible [32,33,37]. Thus, we expected that CdO can be prepared by annealing of $Cd(O_2)_{0.88}(OH)_{0.24}$ as precursor. An important issue for the development of semiconductor films is the thickness control. In this regard, SILAR-CBD is a technique that offers an effective and easy way to control the film thickness.

In this work, $Cd(O_2)_{0.88}(OH)_{0.24}$ films have been obtained by SILAR technique. The properties of the films produced by this technique are strongly dependent on the deposition times and conditions. Therefore we optimized the experimental conditions that resulted in the best cadmium oxide-hydroxide properties. In order to produce cadmium oxide films, the cadmium oxide-hydroxide films obtained were submitted to thermal treatment at different temperatures (200, 300, 400 and 500 °C) and the thermal effect on the films was studied. The structural, optical and electrical properties of the films were studied after and before of thermal treatment. Also we studied the photocatalytic effect of both CdO and $Cd(O_2)_{0.88}(OH)_{0.24}$ on the degradation of methylene blue colorant.

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2. Experimental procedure

Cadmium oxide hydroxide was grown on glass substrate by successive ionic layer adsorption and reaction (SILAR) method at room temperature. The glass substrate was previously cleaned with detergent and distilled water, immersed in chromic acid (0.5 M) for 24 hours followed by rinsing with deionized water. Then the slides were immersed in nitric acid at 60 °C for 2 hours and finally washed with ethanol, dried with nitrogen gas and used for deposition. The SILAR method involves the immersion of the substrate separately into solutions, alternating cationic solutions and anionic solutions. The first one is a solution containing cadmium ions Cd^{+2} (cadmium acetate ($C_4H_6CdO_4$,0.1 M, 50 ml) and triethanolamine ($C_6H_{15}NO_3$, 0.4 M, 50 ml at pH = 9), followed by the second — hydrogen peroxide solution (28–30%) which provides the OH^- ions and oxygen.

Our modified-SILAR growth cycle involves the four following steps: (1) immersing the substrate in the cadmium-rich solution for 20 seconds to create a thin liquid film containing a complex that includes cadmium ions onto the substrate; (2) immediately immersing the withdrawn substrates in hydrogen peroxide solution for 20 seconds to form a $Cd(O_2)_{0.88}(OH)_{0.24}$ layer; (3) drying the substrate in air for 60 seconds; and (4) rinsing the substrate in a separate beaker for 20 seconds to remove loosely bonded particles. Only three cycles are necessary to form a white transparent layer over the substrate. The thickness of the film is controlled by the number of cycles, thus for a thicker layer, several cycles are needed. Up to 50 cycles were done in order to study the kinetics of growth.

The as-deposited films were annealed at 200, 300, 400 and 500 °C for 2 hours in an oven under ambient atmosphere in order to convert $Cd(O_2)_{0.88}(OH)_{0.24}$ to CdO. Annealing was set at two hours according with [23], where it is suggested that the electrical-resistivity does not vary after 30 minutes of thermal treatment. We did not use temperatures above of 500 °C because at higher temperatures the glass substrate begins to deform and melt. The effect of annealing on the structural, optical and electrical properties of the films was investigated.

The photocatalytic reaction was carried out in two 20 ml beakers containing the dye methylene blue (MB) 0.03 M, where the films of CdO and of $Cd(O_2)_{0.88}(OH)_{0.24}$) were placed separately. Another one (without any film) was used as a reference because the MB can be degraded by light, e.g. without catalyst. Before starting the experiment, we placed the film into the beaker with the solution and waited for 1 hour to reach the equilibrium between the film and methylene blue. Irradiation was carried out with xenon DC arc lamp of 130 watts, which produce a total irradiation of 600–700 W/m^2 over the film. This provides light with wavelength range between 365 nm to 900 nm that contains UV light and visible light (see spectrum below). The excitation wavelength of the materials is 501 nm for CdO and 370 nm for $Cd(O_2)_{0.88}(OH)_{0.24}$ (see optical properties). At specific time intervals small aliquots were collected and analyzed by measuring their absorbance using UV–visible spectrophotometer. We did not add bubbling or peroxide to the reaction, and it was carried out at ambient temperature (25 °C, in air flow).

2.1. Materials characterization

The deposited $Cd(O_2)_{0.88}(OH)_{0.24}$ and CdO films were characterized by X-ray diffraction (XRD) using a Rigaku diffratometer, Dmax2100, Cu-Kα radiation, 30 kV and 20 mA, λ = 1.54056 Å Kα1, and software WinJade by MDI. Optical reflection spectra and absorption spectra were recorded in the wavelength range of 300–800 nm using the equipment Ocean Optics model QE65000 with the light source DT-mini-2. Films morphology and samples thickness were verified by scanning electron microscope (SEM) (JSM-5800LV JOEL). An acceleration voltage was fixed at 25 kV. The chemical composition was measured by energy dispersive X-ray spectroscopy (EDAX) with an operating voltage of 20 kV. The resistivity, mobility and carrier concentration were obtained from Hall measurements, which were performed at room temperature under 0.5 Tesla magnetic fields, in accordance with the standard Van der Pauw configuration.

3. Results and discussion

3.1. Mechanism of film deposition

The mechanism of $Cd(O_2)_{0.88}(OH)_{0.24}$ film formation by SILAR method can be illustrated as follows. We used two main solutions; the first one with cadmium ions is composed of cadmium acetate $Cd(CH_3CO_2)_2$ (0.1 M) as a source of Cd^{2+} ions. In order to produce a complexed Cd^{2+} ion we add triethanolamine $C_6H_{15}NO_3$ (0.5 M) as complexing agent (Ph = 9 of solution). Eq. (1) below describes the chemical reactions.

$$Cd(CH_3CO_2)_2 + C_6H_{15}NO_3 \rightarrow 2CH_3COOH + C_6H_{13}CdNO_3 \quad (1)$$

When the substrate is immersed in the above solution, these complexed cadmium ions are adsorbed onto the substrate due to attractive force between ions in the solution and surface of the substrate. These forces can be Van der Waals forces, cohesive forces or chemical attractive forces [30]. The substrate is then immersed in dilute H_2O_2 solution to convert the cadmium complex into $Cd(O_2)_{0.88}(OH)_{0.24}$ by the following reactions (for evidence of the obtained material see structural part):

$$2H_2O_2 + H_2O \rightarrow 2H_2O + O_2 + (OH)^- + H^+ \quad (2)$$

$$Cd^{+2} + 0.88\ O^{+2} + 0.24OH^- \rightarrow Cd(O_2)_{0.88}(OH)_{0.24} \quad (3)$$

3.2. Morphological analysis and composition

The micrographs in Fig. 1 (a) show the view of $Cd(O_2)_{0.88}(OH)_{0.24}$ film surface after 40 cycles, where it is observed a dense film composed of small spherical grains with approximate size of 340 nm. Also we study the kinetic of growth using lateral views of the film at different cycles were we found a linear behavior of growth (Fig. 2 (a)), with a growth rate of 21.4 nm/cycle. Fig. 1 shows the cross section after 40 and 20 cycles in b) and c), respectively. Small deviations from the linear behavior are seen in the Fig. 2a (at 20 and 40 cycles), which are most probably due to the manual control of our experimental procedure. We expect that automatic control system that is ongoing in our laboratory will eliminate these deviations.

The films of $Cd(O_2)_{0.88}(OH)_{0.24}$ after 50 cycles (2 μm thickness) were annealed at different temperatures (200, 300, 400 and 500 °C) in order to obtain a CdO films by thermal reduction reaction. After the annealing process we observe a decreasing of the film thickness (Fig. 2b) together with a reduction of superficial roughness with increasing of annealing temperature (Fig. 3).

The reduction of film thickness due to annealing was also observed in Ref. [29] using a similar precursor $Cd(OH)_2$. Fig. 3d) shows the film annealed at 500 °C where a superficial cracking over the film. Similar effect was also observed in Ref. [29] where the conductance of the film remained regardless that to cracking occurred. In our case, after analysis of the cross section images on Fig. 3h), and the film's conductance (see electrical properties) we concluded that cracking has no noticeably effect.

The composition (EDAX) data are shown in Fig. 4. The material precursor $Cd(O_2)_{0.88}(OH)_{0.24}$ is composed of 25.22% of cadmium, 62.29% of oxygen, and 12.6% of silicon, all in atomic percentage. The composition changed to 34.94%, O in 49.48% and Si in 15.60% as a result of formation of CdO film by annealing at 500 °C. Similar results were obtained for the other annealing temperatures without significant variation. It is important to note that in this technique