Oriented cadmium oxide thin solid films

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A chemical bath deposition technique has been developed for the preparation of $Cd(O_2)_{0.88}(OH)_{0.24}$ thin films on glass and quartz substrates from alkaline media at room temperature. These films were then annealed at 473 K in order to obtain cadmium oxide films. Two baths were used for film preparation. X-Ray diffraction analysis clearly showed that the CdO films obtained from a bath without KBr have a preferred crystalline orientation in the $\langle 200 \rangle$ direction while those obtained from a bath containing KBr had only slightly preferred crystalline orientation in the $\langle 111 \rangle$ direction. The optical bandgap, E_g, was evaluated from the VIS absorption spectra. It was found that E_g for the films oriented in the $\langle 200 \rangle$ direction is 2.63 eV, while it is 2.57 eV for those with the slight $\langle 111 \rangle$ orientation. The different values of the cross-over terminal points of absorption and transmittance spectra confirm the difference between the films with different crystalline orientation.

Thin solid films of cadmium oxide have been prepared by different methods, e.g. ion-beam sputtering,[1] pyrolysis,[1-4] reactive sputtering,[5] activated reactive evaporation[6] and chemical deposition.[7-9] Interest in the preparation of these films is due to their wide applications such as photovoltaic cells,[5,10] heat-reflecting coatings, large-area transparent conductors, displays, gas sensors for ambient air, C_2H_5OH, as well as gas sensors in conjunction with SnO_2 films for CO detection, and other electrical devices.

One of the most common and low-cost methods for the fabrication of CdO thin films from aqueous solutions is the electrodeless chemical deposition method. By this method, $Cd(OH)_2$ thin films are obtained initially, which after annealing are converted into CdO thin films.[7-9]

CdO crystallizes with the sodium chloride structure.[7] It is an n-type semiconductor with high conductivity which is due to either the presence of anion vacancies or doping effects. As expected, many of its physical properties were found to be dependent on the method and conditions of preparation.

In this paper, we present an electrodeless chemical bath deposition method for the fabrication of oriented cadmium oxide thin solid films, along with some basic properties of the as-deposited and annealed flms.

Experimental

$Cd(O_2)_{0.88}(OH)_{0.24}$ films were prepared from two baths, A and B, as described below. The overall chemical reaction can be written as shown in eqn. (1).

$$[Cd(NH_3)_4](OH)_2 + 0.88H_2O_2 \rightarrow \downarrow Cd(O_2)_{0.88}(OH)_{0.24}$$
$$+ 1.78H_2O + 4NH_3 \quad (1)$$
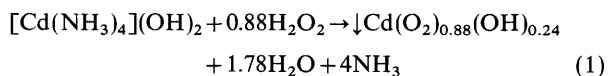
Besides the tetraamino complex of cadmium, bromine complexes of cadmium were also formed in the bath containing KBr (bath B; see below). The depositions were carried out in alkaline media (pH $\approx$ 10) at room temperature. Thin films were deposited on planar glass (75 mm × 25 mm × 1 mm) and quartz (40 mm × 10 mm × 1 mm) substrates. Since the temperature required does not exceed 298 K, a glass or plastic laboratory beaker can be used and stirring is necessary for good quality thin films.

Preparation of $Cd(O_2)_{0.88}(OH)_{0.24}$ thin films from bath A

Chemical deposition bath A contained a mixture of two solutions. Solution 1 consisted of $Cd(NO_3)_2$ (17 cm^3; $c = 1$ mol dm^{-3}), NH_3 (23 cm^3; 20%) and deionized water (52 cm^3); solution 2 contained H_2O_2 (2 cm^3; 25%), deionized water (2 cm^3) and NH_3 (1 cm^3; 20%).

The substrates (which had been cleaned previously in chromic acid) were inserted into the bath. Then, 3 cm^3 of deionized water were added in small portions. This volume corresponds to 293 K solution temperature; less water is added for higher temperatures (e.g. 1 cm^3 for 297 K). In ca. 3–10 min, a white precipitate of $Cd(O_2)_{0.88}(OH)_{0.24}$ began to fill the bath. The coated substrates were then taken out, rinsed with deionized water and dried in air before annealing.

Preparation of $Cd(O_2)_{0.88}(OH)_{0.24}$ thin films from bath B

In order to fabricate very thin films (< 100 nm), we used bath B which was a mixture of the following two solutions. Solution 1 consisted of $Cd(NO_3)_2$ (6 cm^3; $c = 1$ mol dm^{-3}), NH_3 (8.5 cm^3; 20%), KBr (5 cm^3; $c = 1$ mol dm^{-3}) and deionized water (52 cm^3); Solution 2 contained H_2O_2 (2 cm^3; 25%), deionized water (6 cm^3) and NH_3 (1 cm^3; 20%).

Having combined the two solutions at 293 K, 1 cm^3 of deionized water was also added. For higher solution temperatures, there is no need to add water. The deposition procedure was the same as that described for bath A.

Preparation of CdO thin films

Cadmium oxide films were prepared by annealing the $Cd(O_2)_{0.88}(OH)_{0.24}$ thin films at 468 K for 30 min. $Cd(O_2)_{0.88}(OH)_{0.24}$ thin films were transformed into CdO according to the following pyrolytic reaction [eqn. (2)].

$$Cd(O_2)_{0.88}(OH)_{0.24} \rightarrow CdO + 0.44O_2 + 0.12H_2O \quad (2)$$
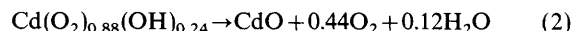
Films characterization

The thickness of the films was determined by the gravimetric method. The sheet resistance of the films was measured between two silver-pasted electrodes, 1 cm in length and 1 cm apart. The deposited films as well as the bulk precipitates were studied by X-ray diffraction, using a JEOL Model JDX diffractometer and nickel-filtered Cu-Kα radiation. Optical studies were carried out on a (Hewlett Packard) HP 8452 A UV–VIS spectrophotometer.
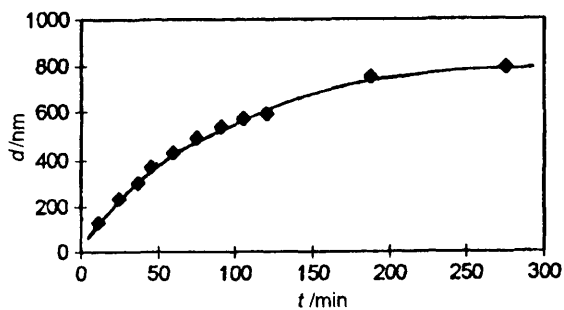
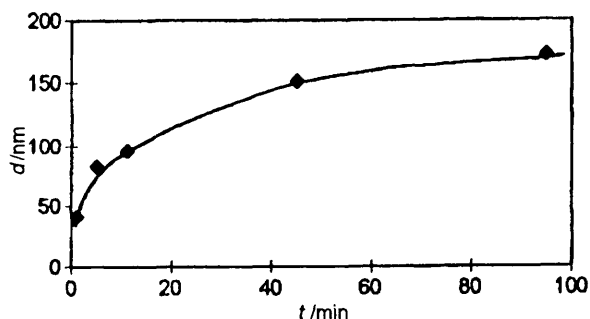**Fig. 1** Thickness of CdO films vs. deposition time for bath **A**

Fig. 2 Thickness of CdO films vs. deposition time for bath **B**
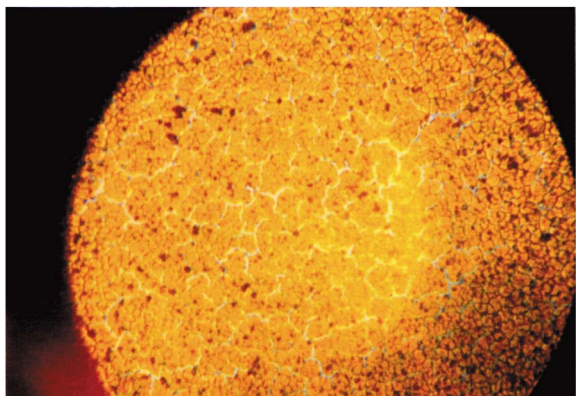

Plate 1 Micrograph of CdO film of about 700 nm thickness (magnification ca. 200)

Results and Discussion

The thickness of CdO films at 293 K as a function of the deposition time is shown in Fig. 1 for films obtained from bath **A** and in Fig. 2 for those from bath **B**. A terminal thickness of ca. 800 nm was achieved in ca. 275 min from bath **A** and 170 nm thickness for films prepared from bath **B**. Thicker films up to 500 nm were obtained by re-inserting the initially deposited $Cd(O_2)_{0.88}(OH)_{0.24}$ films; films thicker than 500 nm could not be obtained from bath **B**.

The sheet resistance varied between 20 and 2 kΩ□$^{-1}$ and were not reproducible. Thicker films had higher sheet resistances, a phenomenon reported previously.[7] We believe that the reason for this unusual behaviour is fracturing of the films, shown in Plate 1. Namely, $Cd(O_2)_{0.88}(OH)_{0.24}$ decomposes violently, according to reaction (2), therefore conversion to CdO is difficult to control. The fracturing is probably caused by the liberation of formed gases.

X-Ray investigations

X-Ray diffractograms of the bulk precipitate from the chemical deposition are shown in Fig. 3. During the preparation of the precipitate for X-ray analysis, CO_2 from the air was chemi-
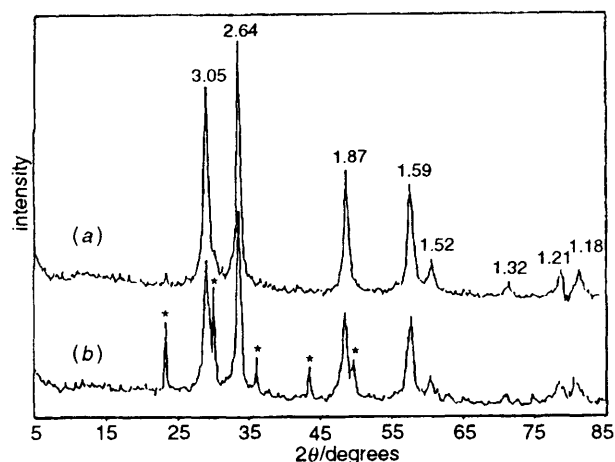

Fig. 3 XRD pattern of (a) carefully prepared (with minimal exposure to CO_2) precipitate; (b) ordinary prepared precipitate with $CdCO_3$ peaks present (indicated by *). d Values are shown above the peaks.

sorbed. As a result of this, $CdCO_3$ reflections were detected in the precipitate, as shown in Fig. 3(b). When precautions were taken (i.e. the precipitate was washed with ethanol, filtered, dried on filtered paper, and at 373 K for 15 min) hardly any $CdCO_3$ peaks were detected, as shown in Fig. 3(a). Comparison of these peaks with the standards[11] confirmed that the material is $Cd(O_2)_{0.88}(OH)_{0.24}$.

XRD patterns of $Cd(O_2)_{0.88}(OH)_{0.24}$ (bulk and films) are shown in Fig. 4., while the corresponding bulk and films XRD patterns of CdO are shown in Fig. 5. The hkl indices were identified according to available literature data.[8,12] XRD analysis clearly indicates a highly preferred crystalline orientation in the ⟨200⟩ direction for films prepared from bath **A** (without KBr), while a slightly preferred crystalline orientation in the ⟨111⟩ direction was noticed for films prepared from bath **B**. It has been reported[13] that the presence of H_2O_2 in the solution influences the crystalline orientation of PbS films in the ⟨200⟩ direction. At the moment, we have no appropriate explanation for the differently preferred orientation of our films obtained from the two baths (**A** and **B**).

In order to estimate the optimal annealing time, the phase transformation was studied by XRD analysis of a single film (from bath **A**; thickness ca. 500 nm). Fig. 6 shows the results,
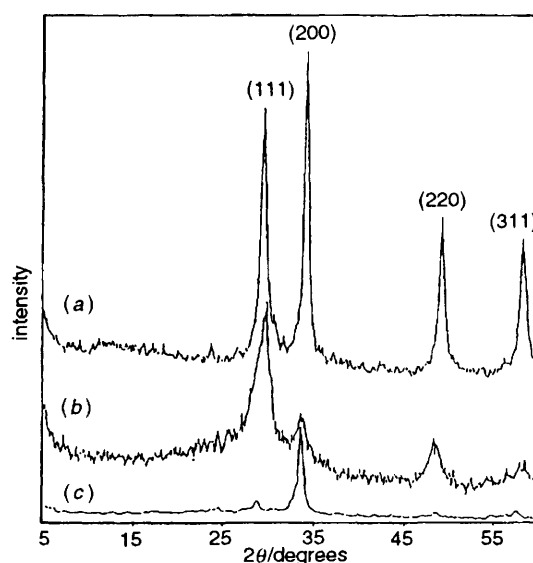

Fig. 4 XRD patterns of $Cd(O_2)_{0.88}(OH)_{0.24}$: (a) bulk precipitate; (b) films obtained from bath **A**; (c) films obtained from bath **B**
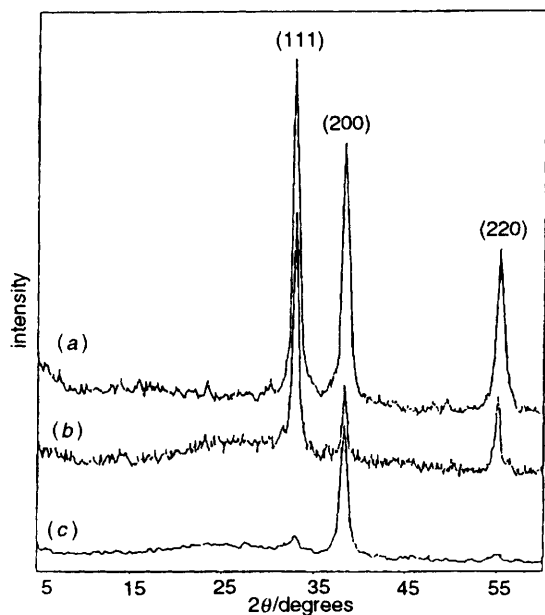
Fig. 5 XRD patterns of CdO: (a) bulk precipitate; (b) films obtained from bath A; (c) films obtained from bath B
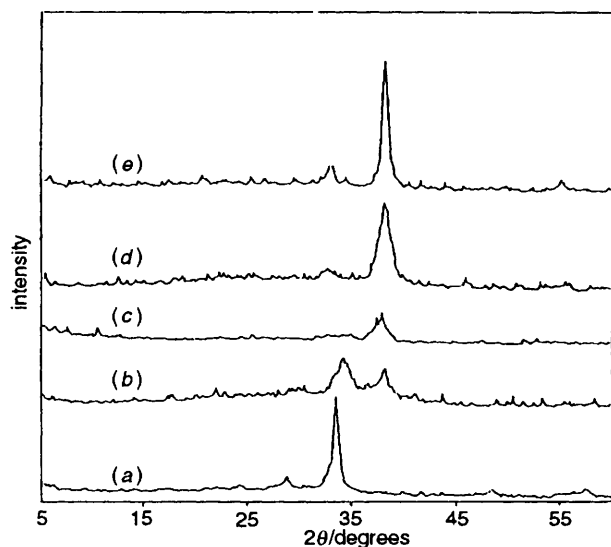

Fig. 6 Gradual chemical conversion detected with XRD: (a) film of $Cd(O_2)_{0\,88}(OH)_{0\,24}$; (b)–(d) intermediate phases; (e) film of CdO. As deposited (a); annealing times: 2–3 min (b); 4–6 min (c); 6–10 min (d); and 16–20 min (e).

which indicate that the chemical conversion was completed in less than 30 min.

Optical investigations

In order to study the optical changes during the chemical conversion, a very thin film (ca. 30 nm) of $Cd(O_2)_{0.88}(OH)_{0.24}$ on quartz was deposited from bath **B**. Successive annealing and spectra recording were performed on this single film. The results are shown in Fig. 7. The notable shifts in the absorption edges correspond to the observed changes from colourless for $Cd(O_2)_{0.88}(OH)_{0\,24}$ to bright yellow for the CdO films. Owing to the very low thickness of the film, the applied annealing time was shorter than 15 min. Using optical transmission data, in the region between 434 and 660 nm, the room-temperature optical bandgaps were determined from plots of $(\alpha h\nu)^2$ vs. E. Extrapolation of the linear plots gave bandgap energies of 2.63 eV for films obtained from bath **A** and 2.57 eV for those
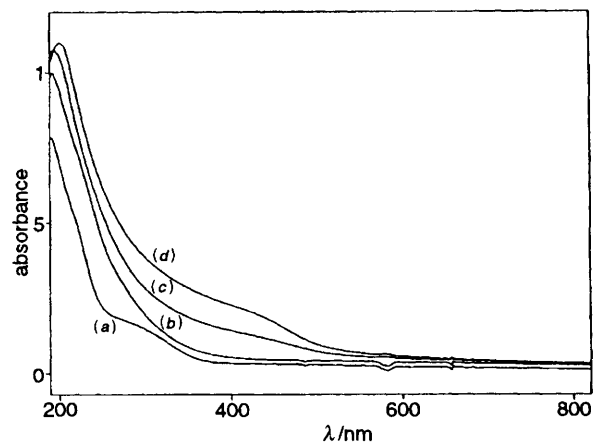

Fig. 7 UV–VIS spectra of the films: (a) film of $Cd(O_2)_{0\,88}(OH)_{0\,24}$; (b), (c) mixtures of $Cd(O_2)_{0\,88}(OH)_{0\,24}$ and CdO; (d) film of CdO

Table 1 A comparison of CdO films prepared using different deposition methods

deposition method	ref.	thickness/ nm	optical bandgap/eV
ion-beam sputtering	1	500	2.4–2.42
spray pyrolysis	1	500	2.36
chemical bath deposition	9	—	2.2
chemical deposition	7	320	2.6
chemical bath deposition	this work	78, 115	2.57, 2.63

from bath **B**. Table 1 gives a comparison of our results with those reported elsewhere.

Conclusion

Thin solid films of CdO were prepared by chemical bath deposition with thicknesses from ca. 100 to 800 nm (bath A) and from 40 to 170 nm (bath B). XRD analysis showed a highly preferred crystalline orientation in the $\langle 200 \rangle$ direction for films prepared from bath A (where no KBr was added), while a slightly preferred crystalline orientation in the $\langle 111 \rangle$ direction was found for films prepared from bath B. In both cases, the crystalline orientation of the CdO films was the same as the crystalline orientation of the previously deposited films of $Cd(O_2)_{0.88}(OH)_{0.24}$. During the annealing process, a chemical conversion took place and the liberation of formed gases caused fracturing of the films. As a result, most of the annealed films were not conductive. This is one of the disadvantages of our method at the moment. Further efforts will be aimed at finding ways to prevent film fracturing during annealing.

References

1   T. L. Chu and S. S. Chu, *J. Electron. Mater.*, 1990, **19**, 1003.
2   W. Shixing and C. Michael, *Chem. Mater.*, 1993, **5**, 577.
3   C. Saravani, R. P. Sredhara and R. P. Jayarama, *Mater. Lett.*, 1992, **12**, 406.
4   I. Moriguchi, I. Tanaka, Y. Teraoka and S. Kagawa, *Nippon Kagaku Kaishi*, 1991, **10**, 1392.
5   C. H. Champness, Y. F. Go and Z. A. Shukri, in *Proc. 4th Int. Symp. Uses Selenium and Tellurium*, ed. S. C. Carapella, Jr. Selenium–Tellurium Dev. Assoc., Darien, CT, 1989, p. 600.
6   C. Saravani, R. K. T. Ramakrishna and R. Jayarama, *Mater. Lett.*, 1993, **15**, 356.
7   M. Ristov, Gj. Sinadinovski, I. Grozdanov and M. Mitreski, *Ann. Phys.*, 1990, **40**, 53.
8   R. L. Call, N. K. Sesan and J. R. Whyte, *Sol. Energy Mater.*, 1980, **2**, 375.

9 M Ocampo, A M Fernandez and P J Sebastian, *Semicond Sci Technol*, 1993, **8**, 750

10 C H Champness and C H Chan, *Sol Energy Mater Sol Cell*, 1993, **30**, 65

11 *Inorganic Index to the Powder Diffraction File*, 1972, Joint Committee on Powder Diffraction Standards

12 C W Hoffman, R C Ropp and R W Mooney, *J Am Chem Soc*, 1959, **81**, 3830

13 I C Torriani, M Tomyiama, S Bilac, G B Rego, J I Cisneros and Z P Arguello *Thin Solid Films*, 1981, **77**, 347