Degenerate Cadmium Oxide Films For Electronic Devices

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Highly conducting and transparent cadmium oxide films have been deposited on Corning 7059 glass substrates by ion-beam sputtering and by spray pyrolysis. The electrical and optical properties of CdO films prepared by the two techniques are similar. Typical films of 0.5 μm thickness have electrical resistivities of (2–5) $\times 10^{-3}$ ohm-cm, carrier concentrations of approximately 10^{20} cm^{-3}, and an optical transmission of higher than 70% in the wavelength range of 600–900 nm. An optical bandgap of 2.4–2.42 eV was deduced from the optical transmission data.

Key words: Cadmium oxide, semiconductor films, optical transmission, electrical resistivity, ion-beam sputtering, spray pyrolysis

INTRODUCTION

High electrical conductivity films of large bandgap semiconductors, such as tin oxide, zinc oxide, and cadmium sulfide, have major applications in electronic devices. They are all *n*-type, and the high conductivity results from the presence of anion vacancies or through doping. While cadmium sulfide is widely used in various devices, very little is known about cadmium oxide. Cadmium oxide crystallizes in the sodium chloride structure. Its room temperature bandgap energy has been reported to be 2.4 eV.[1] The reactive sputtering of Cd in an Ar-O_2 mixture has produced CdO films with electrical resistivity of 0.1 to 0.01 ohm-cm.[2] The sputtered CdO films have been used for the fabrication of CdO-Se and CdO-Si heterojunction solar cells.[3,4]

In this work, CdO films have been deposited on Corning 7059 glass substrates by ion-beam sputtering and by spray pyrolysis. The properties of these films were characterized by x-ray, electrical resistivity, Hall, and optical transmission measurements. The room temperature bandgap energy of CdO films was deduced from the transmission data. The experimental procedures and results are summarized in this paper.

CdO FILMS BY ION-BEAM SPUTTERING

The ion-beam sputtering technique has been used extensively for the deposition of refractory films. It is a slow process, 1 μm/min or less; however, good quality films can be deposited at relatively low temperatures, usually less than 100° C.

Commonwealth Scientific Model Millatron IV was used for the deposition of CdO films on Corning 7059 glass substrates by argon ion-beam sputtering. In this process, an argon ion-beam produced from the Kaufmann source is accelerated to about 1 kV at a current density of about 5 mA cm^{-2} and impinges on the water cooled CdO target. The emitted target material is deposited on the substrates, usually four $3 \times 3 \times 0.05$ cm Corning 7059 glass plates mounted on a holder. (To minimize the accumulation of positive charges, a source of electrons supplied by a hot filament is used in the ion stream external to the plasma enclosure.) The CdO target, prepared by the hot-press technique, was 12.5 cm in diameter and was of better than 99.9% purity. The impurities detected by emission spectroscopy included less than 50 ppm each of Ag, Al, Au, Bi, Cu, Fe, Ni, Pb, Sn and Zn.

To carry out the deposition process, the target and the substrate were placed about 10 cm apart in the deposition chamber. The chamber was first evacuated with a cryopump to a pressure of 10^{-6} Torr or less, an oxygen flow was introduced to maintain an oxygen partial pressure of (2–8) $\times 10^{-6}$ Torr, followed by the introduction of argon to maintain a total pressure of 2×10^{-4} Torr. The use of oxygen was essential to avoid the formation of free Cd in the deposited films. The target was presputtered onto a shutter for 10 min followed by deposition onto the substrate for a predetermined duration. During the deposition of CdO films, the substrate holder was rotated to maintain thickness uniformity. While the substrates were not intentionally heated, the surface temperature was measured to be 50–70° C.

The thickness of CdO films, after removing a portion of the film with diluted HCl, was determined directly by using a Sloan Dektak profilometer. At an oxygen partial pressure of 2×10^{-6} Torr, the deposition rate was approximately 200Å/min. The deposited films were finely polycrystalline with a grain size of several hundred angstroms in films of 3000–6000Å thickness. The thickness uniformity was ±2% over the entire areas of the four substrates. The crystallographlic properties of CdO films were determined by x-ray diffraction using a GE Model XRD-6 diffractometer with CuKα radiation. Polycrystalline CdO powder of random orientation is known to show four strong diffraction peaks associated with {111} {200} {220}, and {331} reflections with d values of 2.712, 2.349, 1.661 and 1.416Å, and relative intensities of 100, 88, 43, and 28 respectively. The diffraction spectra of CdO films were obtained by scanning 2θ in the range of 30°–70°. A typical spectrum is shown in Fig. 1, where the observed diffraction peaks are at 33.2°, 38.6°, 55.6° and 66.2°, respec-

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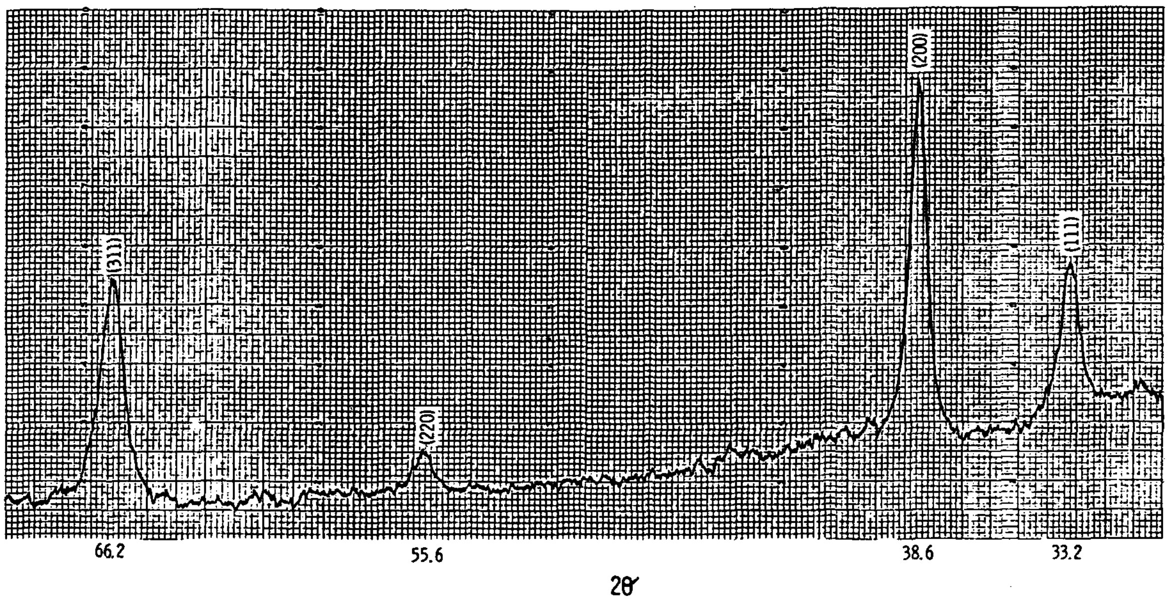

Fig. 1 — X-ray diffraction spectrum of a CdO film deposited on a glass substrate by ion-beam sputtering.

tively, as compared with 33.03°, 38.32°, 55.31° and 65.97°, respectively, for polycrystalline CdO. The shift of diffraction peaks in CdO films are due presumably to a slight change in lattice parameter associated with the high concentration of oxygen vacancies.

The room temperature resistivity of as-deposited CdO films on glass substrates was measured by four point probe technique. The resistivity was found to depend strongly on the partial pressure of oxygen as shown in Fig. 2; lower resistivities were obtained at lower oxygen partial pressures. For example, the resistivity of CdO films deposited at 4×10^{-5} Torr oxygen is about 5×10^{-3} ohm-cm, and the Hall mobility determined by the van der Pauw technique is 12–15 cm^2/V-s, corresponding to a carrier concentration of approximately 10^{20} cm^{-3}. The heat treatment of CdO films in a He atm at 400° C for 30 min has no effect on the resistivity, while heating in an oxygen atm increases the resistivity by about 30%.

The optical transmission of an as-deposited CdO films was measured using a Cary 17D spectrophotometer. Part of the film was annealed in helium at 400° C for 30 min and the other part annealed in oxygen at 400° C for 30 min. The optical transmission of the annealed films was also measured, and the results are shown in Fig. 3. All films show very similar optical transmissions in the 600–800 nm range, and the difference becomes more pronounced at shorter wavelengths. The film annealed in helium shows higher transmission than the as-deposited film due presumably to the removal of defects, while the film annealed in oxygen shows slightly lower transmission and sharper bandedge due to the reduction in the concentration of oxygen vacancies. Using the optical transmission data of the oxygen annealed film, the plot of α^2 versus E yields a straight line, indicating that CdO is a direct gap material. The extrapolation of the linear plot yields a room temperature optical bandgap of 2.4–2.42 eV.

CdO FILMS BY SPRAY PYROLSIS

Spray pyrolysis has been used for the deposition of many conducting oxide films. Its simplicity and the use of low cost materials are attractive for many applications. However, the process parameters, such as the chemical composition of the starting material, the concentration of the solution, the substrate temperature, and the deposition rate, must be controlled in order to obtain device quality films with

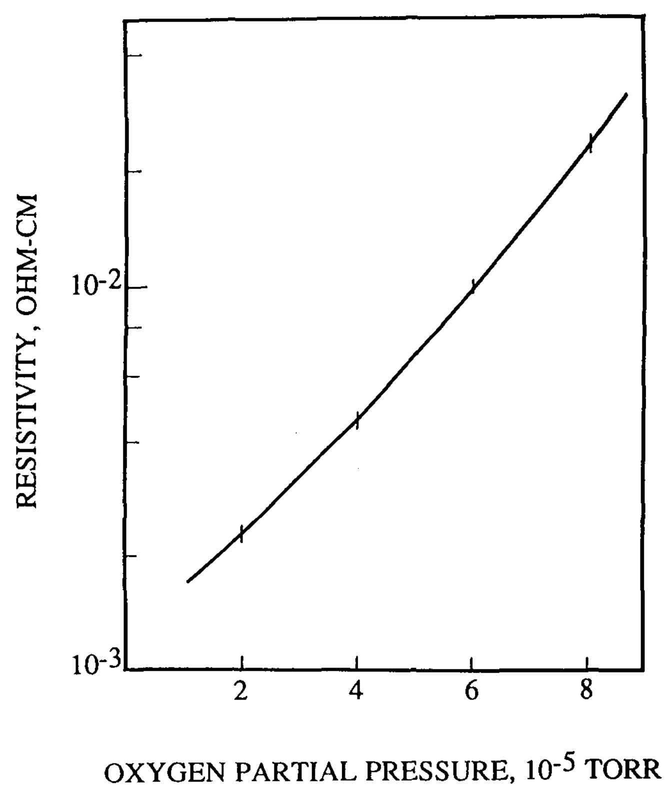

Fig. 2 — The electrical resistivity of CdO films as a function of the oxygen partial pressure during sputtering.

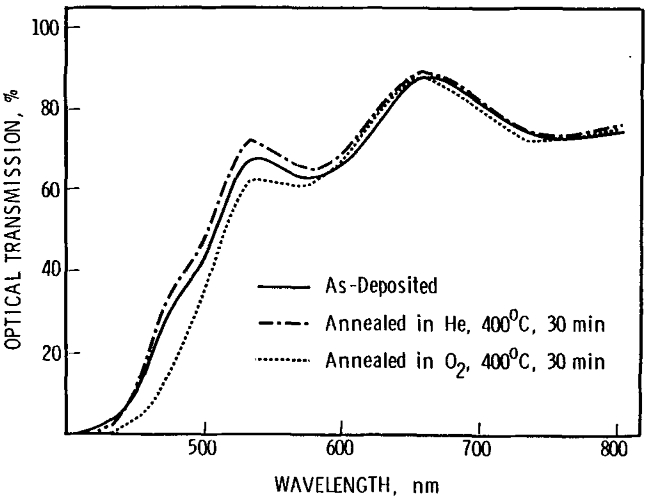

Fig. 3 — Optical transmission of as-deposited and annealed CdO films on Corning 7059 glass.

high optical transmission and low electrical resistivity. In some cases, post-deposition annealing is used to improve the optical and electrical properties of the films.

The spraying of a cadmium acetate, $CdAc_2$, solution on glass or other substrates at 180–250° C was used for the deposition of CdO films. 0.1–0.2M solutions of $CdAc_2$ in equi-volume methanol-water mixture were suitable for the spray pyrolysis process, and indium acetate, approximately 10^{-3} M in concentration, was used as a dopant. Nitrogen at a flow rate of 5–8 ℓ/min was used to carry the $CdAc_2$ solution, at a rate of about 1 cm^3/min, to the substrate surface. The substrates were placed about 30 cm below the spray source in order to obtain 5 × 5 cm films of uniform thickness, and the space in between was enclosed in a glass cylinder to minimize any deviations of the solution stream. To compensate for the rapid energy loss due to the vaporization of $CdAc_2$ solution and the high flow rates of N_2, the substrates were placed on a resistance-heated metal block and heated by a 650 W quartz-halogen lamp. The temperature of the substrate surface was monitored by a thermocouple. This arrangement can maintain the substrate temperature constant within ±5° C of the desired temperature.

CdO films deposited under the conditions described above are adherent to the substrates. The deposition rate, determined by direct measurements using a Dektak Profilometer, was 800–1500Å/min, depending on the substrate temperature, the concentration of $CdAc_2$ solution, and the nitrogen flow rate. The deposition rate increases with increasing substrate temperature; however, the deposit was no longer adherent at temperatures above about 300° C.

Adherent CdO films of 3000–6000Å thickness deposited on glass substrates were used for electrical and optical measurements. All films are of *n*-type conductivity with room temperature resistivity of (2–5) × 10^{-3} ohm-cm, independent of substrate temperature in the range of 180–250° C. The room temperature Hall mobility was determined by the van der Pauw technique to be 10–18 cm^2/V-s, also independent of substrate temperature. The carrier concentration in CdO films is thus (1–1.5) × 10^{20} cm^{-3}. The optical transmission of spray-deposited CdO films is very similar to that of ion-beam sputtered films. The room temperature optical bandgap deduced from the α^2 vs E plot is 2.36 eV.

PHOTOVOLATIC CHARACTERISTICS

In view of its relatively high bandgap energy and high conductivity, CdO appears to be suitable as a heterojunction partner in photovoltaic devices. Thin film CdO/CdTe heterojunction solar cells were made from p-CdTe films on Sb/graphite substrates[5] by depositing a CdO film of about 0.4 μm thickness, followed by the deposition of grid contacts. Under simulated AM1 conditions, a solar cell of 1 cm^2 area showed an open-circuit voltage of 0.73 V, short-circuit current density of 20.4 mA/cm^2, and fill factor of 0.61, corresponding to an AM1 efficiency of 9.1%. The electron affinity of CdO is not known. The solar cell characteristics indicate that there are no major discontinuities in the conduction band of the heterojunction.

SUMMARY

Adherent CdO films have been deposited on glass substrates by ion-beam sputtering and spray pyrolysis. Films obtained by the two methods are very similar in properties: optical bandgap ≃ 2.4 eV, carrier concentration ≃ 10^{20} cm^{-3}, and resistivity ≃ (2–5) × 10^3 ohm-cm. These films are suitable as a transparent conducting semiconductor in photonic devices.

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