

Recent developments in RF sputtered cadmium stannate films

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Abstract

A method for producing single-phase cadmium stannate thin films is reported. Polycrystalline films were prepared by RF sputtering onto water-cooled Corning glass substrates, followed by a high temperature anneal. Resistivities as low as $1.28 \times 10^{-4} \text{ ohm} \cdot \text{cm}$ have been achieved, lower than any previously published results for this material. Even with sheet resistivities as low as 2.5 ohm sq^{-1} , exceptionally high film transparency ($\sim 85\%$) is maintained, with very low absorption in the visible spectrum.

Keywords: Cadmium stannate; RF sputtering; Single-phase

Transparent conductive oxides (TCOs) are used in architectural windows for energy savings, in flat panel displays, in photovoltaic devices, in photochromic windows and in de-icing heaters on vehicles. Tin oxide (SnO_2), zinc oxide (ZnO) and indium tin oxide (ITO) have been the most commonly used TCOs in these applications. Cadmium stannate (Cd_2SnO_4), or cadmium tin oxide (CTO), is a transparent conductor that has not yet been commercialized, but which has electrical and optical properties that are potentially superior to these conventional materials [1].

The properties of cadmium stannate films were first reported by Nozik [2], who prepared amorphous films by RF sputtering and reported mobilities as high as $100 \text{ cm}^2 (\text{Vs})^{-1}$ at a carrier concentration of $5 \times 10^{18} \text{ cm}^{-3}$. Nozik attributed this unusually high mobility to a low carrier effective mass ($m^* = 0.04 m_e$). Haacke [3,4] investigated the effects of deposition and annealing parameters on the properties of polycrystalline Cd_2SnO_4 films prepared by RF sputtering. Cd_2SnO_4 films with excellent transparency and resistivities as low as $1.49 \times 10^{-4} \text{ ohm} \cdot \text{cm}$ were reported. The electrical properties of sputtered Cd_2SnO_4 films were found to be negatively impacted by the presence of the secondary phases, namely CdO and CdSnO_3 , and these could be minimized by adjusting the sputtering parameters and by post-deposition annealing. Subsequently there have been numerous investigations of various deposition methods to prepare cadmium stannate thin films [4], including, but not limited to, dc reactive sputtering [5], ion beam sputtering [6], chemical vapor deposition [7], spray pyrolysis [8] and

electroless deposition [9]. None of these methods has surpassed the resistivity reported by Haacke [4]. We report here on recent results in our study of CTO films prepared by RF magnetron sputtering.

We have developed a novel procedure to prepare single-phase Cd_2SnO_4 films: sputter deposition in pure oxygen at room temperature, followed by an anneal in argon at elevated temperature. RF magnetron sputtering was carried out in a CVC SC-3000 system, evacuated to a background pressure of 2×10^{-7} torr and then back-filled with oxygen (99.993% purity). Corning 7059 glass and polished crystalline silicon (c-Si) wafer substrates were placed on a water-cooled sample holder parallel to the target surface. The distance between the substrate and the target was varied from 6–9 cm. A two-inch-diameter planar hot-pressed oxide target (99.5% purity) was prepared by Cerac Inc., who prereacted the component oxides (33 mol% SnO_2 and 67 mol% CdO), following the procedure outlined by Nozik [2]. X-ray diffraction (XRD) showed that the target was single-phase orthorhombic Cd_2SnO_4 . Deposition was performed at a pressure of $10\text{--}17.5 \times 10^{-3}$ torr (pure oxygen) with an RF power between 100 and 140 watts. The average deposition rate was about 10 nm min^{-1} . After deposition, all samples were annealed in a tube furnace containing an ambient of flowing (1500 sccm) argon (99.999% purity) at temperatures ranging from 580–700 °C, for 10–30 min. Some samples were also treated in CdS vapor in argon at the same temperatures, since Haacke [4] has shown that this can significantly increase carrier concentration.

XRD patterns were acquired using a Rigaku diffractometer, with Cu K_α radiation. Hall effect measurements were made using the Van der Pauw technique with indium dot

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Table 1
Electrical parameters of the best CTO film

Sample	Thickness (nm)	μ ($\text{cm}^2 (\text{Vs})^{-1}$)	n (cm^{-3})	ρ ($\text{ohm} \cdot \text{cm}$)	σ ($\text{ohm} \cdot \text{cm})^{-1}$	R_s (ohm/sq)
CTO63-CT	510	54.5	8.94×10^{20}	1.28×10^{-4}	7800	2.50

contacts. Sheet resistance was measured using a four-point probe. A Cary 2300 Spectrophotometer was used to acquire the UV/visible transmittance and reflectance spectra. Film thickness was determined from the position of neighboring interference maxima in optical transmittance curves, and checked using a Dektak 3 step height profilometer.

The electrical parameters of our best sample are listed in Table 1. This sample was annealed in a CdS atmosphere at 680 °C.

Because it has been suggested that the electrical parameters of CTO films are dependent on the presence of amorphous or secondary phases [4], XRD was critical to this study. Fig. 1 shows typical XRD patterns for as-deposited and annealed CTO films. The as-deposited films are amorphous, with a broad peak occurring around $2\theta = 32^\circ$ (the broad peak at $2\theta = 26^\circ$ is due to the Corning glass substrate). After annealing, the films crystallize with the cubic spinel crystal structure, as has been previously reported [10]. However, there is no evidence for secondary phases (CdO , SnO_2 or CdSnO_3) in polycrystalline films prepared by our method. Results are the same regardless of whether Corning glass or c-Si substrates are used.

Fig. 2 shows XRD patterns for samples from the same CTO deposition, annealed for 20 min at different temperatures. The films are all nominally 400 nm thick. It can be seen that crystallization starts at about 580 °C, and the intensity of the crystalline peaks increases with annealing temperature, while the intensity of the amorphous CTO peak decreases. This indicates a higher degree of crystallinity in films annealed at higher temperatures. Grain size measurements by TEM have not yet been made. Fig. 3 shows that both mobility and carrier concentration of CTO films increase with increasing integrated intensity of the (311) Cd_2SnO_4 peak in the XRD

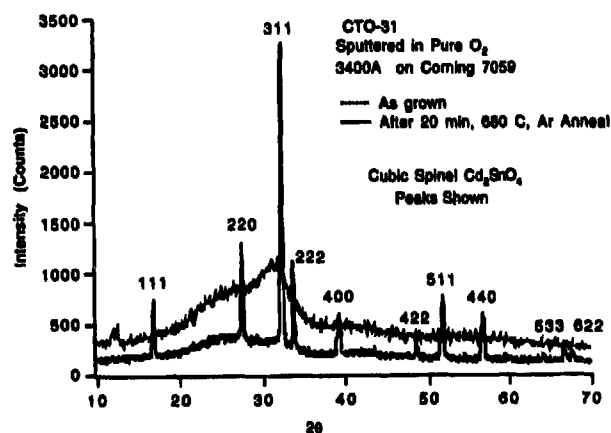


Fig. 1. X-ray diffraction pattern for CTO-31, as-deposited and after anneal.

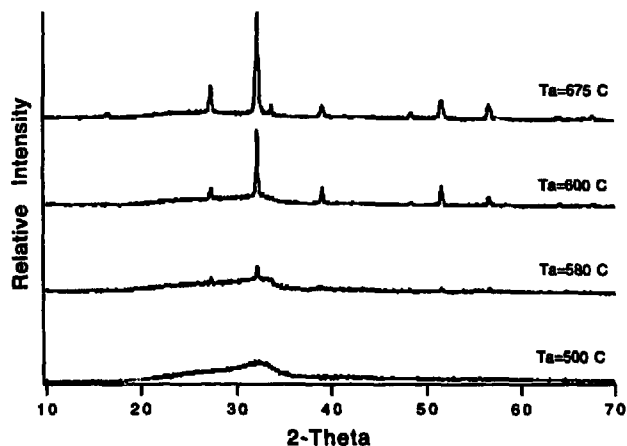


Fig. 2. X-ray diffraction pattern for CTO-45 annealed at different temperatures.

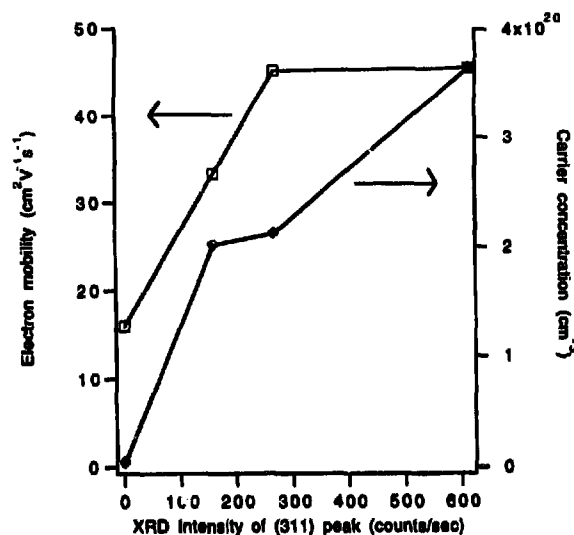


Fig. 3. Mobility and carrier concentration vs. integrated intensity of the (311) XRD peak of c-spinel Cd_2SnO_4 for CTO45, annealed at different temperatures.

pattern, that is, as the ratio of spinel phase to amorphous phase increases in the films.

Fig. 4 shows the optical transmittance, reflectance and absorbance vs. wavelength of the highest conductivity sample. It can be seen that absorbance in the visible is less than 5%, even at a carrier concentration of $9 \times 10^{20} \text{ cm}^{-3}$. Atomic Force Microscopy (AFM) has also been performed and indicates that the films are very smooth; the average surface roughness over a $1 \mu\text{m}^2$ area is only $\pm 1.3 \text{ nm}$. The specular reflectance of these CTO films is high due to their smooth surface. Characterization by Fourier Transform InfraRed (FTIR) spectroscopy shows that reflectance for CTO films

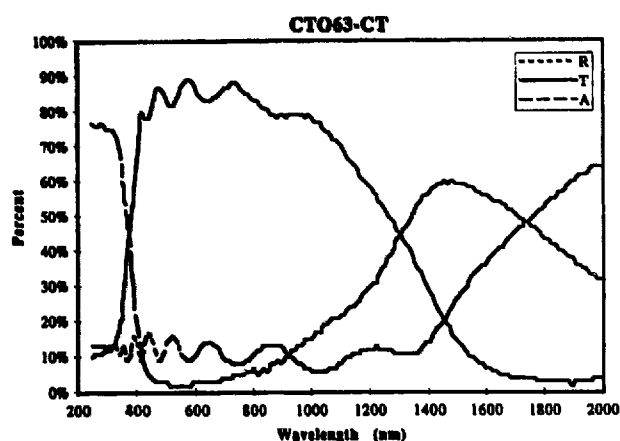


Fig. 4. Transmission, reflectance and absorbance vs. wavelength of CTO63-CT.

increases steeply for wavelengths greater than $1.3 \mu\text{m}$ and reaches 92% near $5 \mu\text{m}$.

It is well known that substrate temperature is an important deposition parameter in RF sputter deposition. We have studied deposition onto substrates heated as high as 570°C . XRD patterns indicate that these as-deposited films are mostly amorphous, with no evidence for the formation of crystalline Cd_2SnO_4 . Furthermore, after annealing in argon, films deposited on heated substrates show broader and less intense cubic spinel peaks and electrical properties inferior to those sputtered onto water-cooled substrates. These results are inconsistent with previous work by Haacke [4], who found that as-deposited crystalline Cd_2SnO_4 films were obtained when substrates were heated above 450°C , and that room-temperature-deposited films that were amorphous did not crystallize upon subsequent annealing. We suspect the differences may be related to the lower power environment of magnetron sputtering, compared to conventional RF diode sputtering, which was used by Haacke.

TCO conductivity can be improved either by increasing carrier concentration or by increasing electron mobility. Recently, we have proposed that there are advantages to increasing mobility compared to increasing carrier concentration [11], so our study has focused on optimizing the electron mobility. Electron mobilities as high as $65 \text{ cm}^2 (\text{Vs})^{-1}$ at a carrier concentration of $2 \times 10^{20} \text{ cm}^{-3}$ have been achieved. Even at a carrier concentration of $9 \times 10^{20} \text{ cm}^{-3}$, the mobility is still as high as $54.5 \text{ cm}^2 (\text{Vs})^{-1}$.

The resistivity of $1.28 \times 10^{-4} \text{ ohm}\cdot\text{cm}$ is the lowest reported for any CTO film and, to the best of our knowledge, for any TCO material prepared by sputtering. Reproducibility of resistivity is excellent, and the electron mobilities of most samples were greater than $50 \text{ cm}^2 (\text{Vs})^{-1}$. The unusually high mobility of CTO at high carrier concentration may be due to the small effective mass of the electrons, as originally

suggested by Nozik, but may also be due to higher quality material and longer carrier relaxation time. Annealing increases the free electron concentration from about 10^{18} cm^{-3} to approximately 10^{21} cm^{-3} . Free carriers probably result from an oxygen deficiency in the films, accommodated either as oxygen vacancies or cadmium interstitials, or a combination of both [4]. As shown in Fig. 3, mobility increases with increasing film crystallinity. This may explain why annealing in a reducing atmosphere not only raises the free electron concentration, as expected, but also increases electron mobility.

In addition to their high conductivity, high transmittance in the visible, and high reflectance in the IR, CTO thin films are nearly colorless and are easily patternable (films can be etched by HCl or HF). We have also found that CTO films are very durable and are stable at elevated temperatures. Because of these attributes, we believe that CTO warrants further investigation and, perhaps, commercialization, despite concerns about the toxicity of cadmium. We also plan to investigate nontoxic alternatives, such as the cubic spinel phase of Zn_2SnO_4 .

In conclusion, we have developed a reproducible process to obtain single-phase cadmium stannate thin films with high conductivity and high transparency. A film resistivity of $1.28 \times 10^{-4} \text{ ohm}\cdot\text{cm}$ has been obtained which, to the best of our knowledge, is the lowest value ever attained for a CTO material prepared by sputtering. Cadmium stannate is an exceptional TCO material due to its high mobility at high carrier concentration and has the potential to outperform existing TCOs in many applications.

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