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Electrical and Optical Properties of Cadmium Stannate Deposited by RF Magnetron Sputtering

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CTO (Cadmium Stannate) thin films, one of TCOs (Transparent Conducting Oxide) having a potential application for photovoltaic or display product, were prepared by using rf magnetron sputtering system. The lowest resistivity of CTO thin film deposited at room temperature was 6.6×10^{-4} ohm·cm with carrier mobility of 9.1 cm^2/Vs and carrier concentration of 10.4×10^{20} cm^{-3}. The average transmittance of CTO thin film was found to be over 80% regardless of deposition condition. The transmittance of the annealed CTO thin film at 600°C in air atmosphere, was found to increase upto more than 90%, but the film resistivity degraded by two order of magnitude due to the decreased carrier concentration with minor increase of carrier mobility.

Keywords Annealing; cadmium stannate; CTO; photovoltaic; sputtering; TCO; thin film solar cell

Introduction

Transparent conducting oxides (TCOs) are required to satisfy both of high transparency in the visible range of the light spectrum and high conductivity, which are traded off in most cases. Depending on the application, one or both of these properties must be optimized. Applications for TCOs include photovoltaic devices, flat panel displays, and gas sensors. In photovoltaic application, especially, TCO should be able to maximize the light transmittance within the absorption band width for higher short circuit current and electrical conductivity for lower material usage, which contribute to the cost reduction of module fabrication as well.

Since CdO as the first TCO was announced by Badeker in 1907, many materials including indium tin oxide (ITO), zinc oxide (ZnO), Tin Oxide (SnO_2) were examined [1]. Cadmium stannate (CTO) has not been widely used for TCO material. However, cadmium stannate has excellent capability in terms of electrical conductivity, thermal stability and optical transmission especially over 1 μm wavelength range, which should be absorbed effectively in most of solar cell system [2].

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Since the first cadmium stannate synthesized by using rf sputtering system was reported by Nozik in 1972 [3], the electrical performance of the films having high free carrier concentration of $10^{26}\,cm^{-3}$, hall mobility of $45\,cm^2V^{-1}$, are readily available [4]. The cadmium stannate thin films can be obtained by several techniques such as rf sputtering [2], dc reactive sputtering [4], ion beam sputtering [5], chemical vapor deposition [6], spray pyrolysis [7], and electroless deposition [8].

In this study, the high-quality cadmium stannate thin films were fabricated on glass substrates using rf magnetron sputtering system. The films were characterized to examine the electrical, optical, and structural properties according to process and anneaing conditions.

Experimental

Fabrication of Cd_2SnO_4

Cd_2SnO_4 thin films were prepared on both of glass and silicon at room temperature by rf magnetron sputtering system equipped with a tilted sputter gun. A single target of 3 inch diameter and 3 mm thickness was used. The base pressure was 1×10^{-6} torr, and working pressure was maintained at 3 mtorr. The substrate was rotated at 10 rpm for better uniformity of film thickness. The substrates were located on the concentric circle of the substrate holder because the film properties are heavily affected by the incidence angle of the sputtered target molecule [9]. CTO films of 200 nm thickness were prepared with various rf power. Some of the deposited CTO films were annealed in air atmosphere at 600°C.

Measurements

The thickness of CTO thin films was calculated from the reflectance spectrum (K-MAC, ST2000DLXn), and the electrical properties such as resistivity, hall mobility, and carrier concentration by hall effect measurement system (ECOPIA, HMS-5000). The optical transmittance was measured over the range of from 300 nm to 1100 nm by UV-Vis spectroscopy. The crystalline properties were characterized by X-ray diffractometer (PANalytical, Cu-Kα = 1.54178 Å).

Results and Discussion

Figure 1(a) shows variation of growth rate and electrical properties of the films deposited at different rf power. It is well known that the growth rate rises with increasing rf power due to higher power dissipation. The resistivity was found to increase over 150 W, where the minimum value is obtained. Under the room temperature deposition condition, the target molecules arriving at the surface can gain its energy from the impinging ions as shown in Figure 2. Therefore, when the growth rate is too high under fixed ion flux and energy, the ad-atoms cannot have enough energy to move and find a stable site so that the film would have lower density, which in turn is resulted in higher resistivity. As shown in Figure 1(b), below 150 W, the carrier concentration and the mobility shows a trade-off relation, however, both parameters decreased above 150 W. Therefore, the minimum resistivity

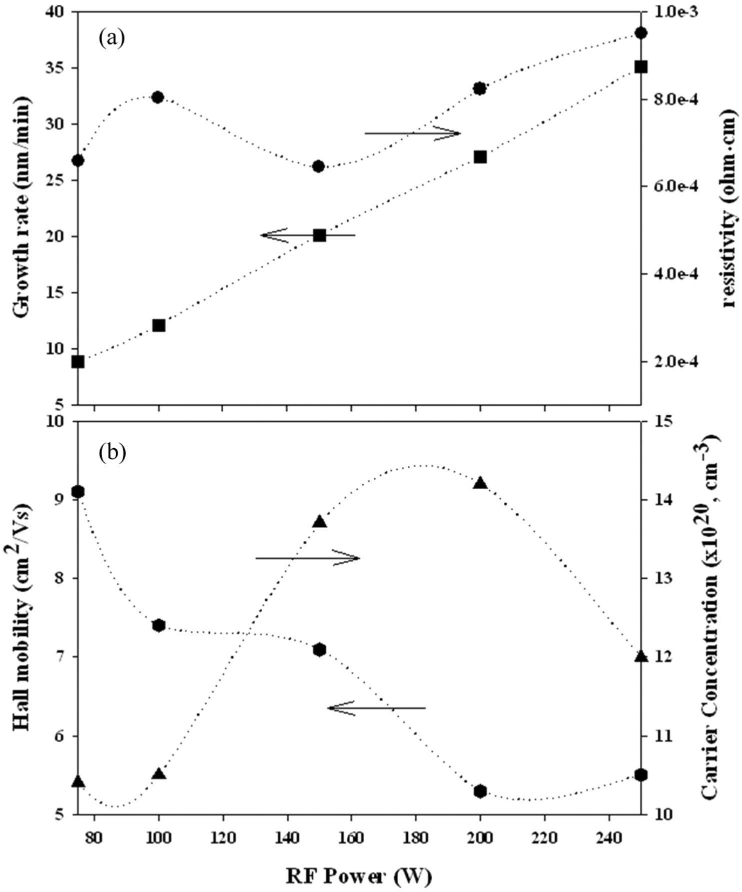

Figure 1. The variation of electrical property of CTO thin film as a function of variety rf power.

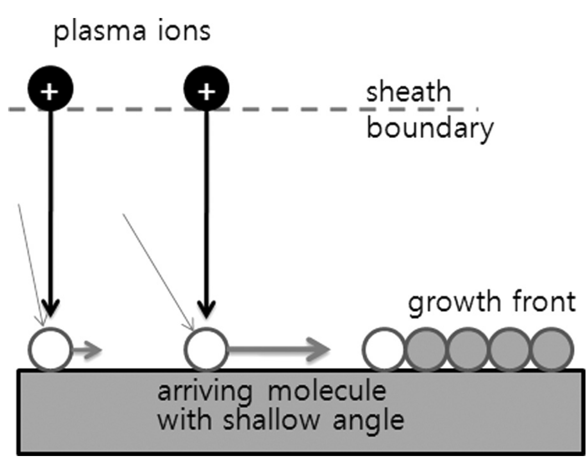

Figure 2. Schematic diagram for the events taking place during the film growth.

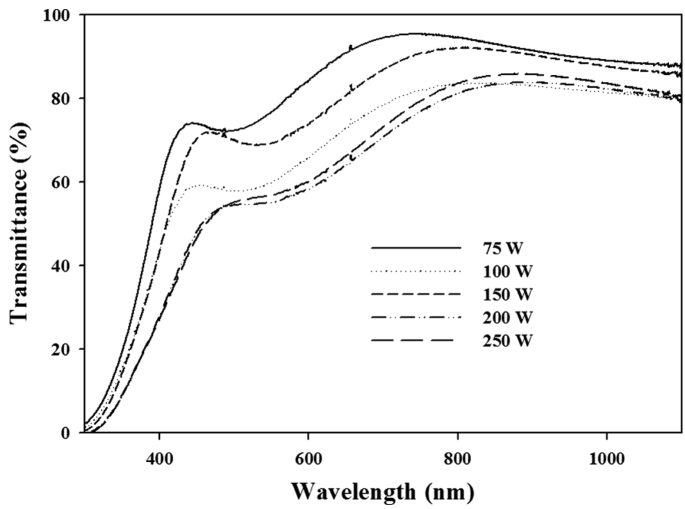

Figure 3. Transmittance curve of CTO thin film as function of variety rf power.

is obtained at 150 W condition due to the improved carrier concentration and mobility.

Figure 3 shows the transmittance curves of the film deposited at various rf power. The maximum transmittance showed a similar trend with the resistivity, where the resistivity minima corresponds to the higher transmittance. The maximum transmittance over 90% is readily obtained from the films deposited between 75 W and 150 W. This result did not behind property of transmittance and electrical as compared to AZO (Al doped Zinc Oxide) and FTO (F doped Tin Oxide) that is on the latest development instead of ITO (In doped Tin Oxide).

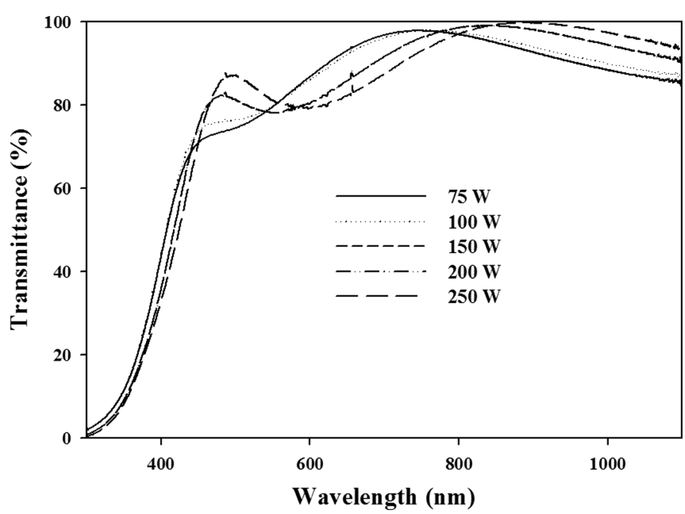

Figure 4. Transmittance curve of CTO thin film as function of variety rf power after anneal.

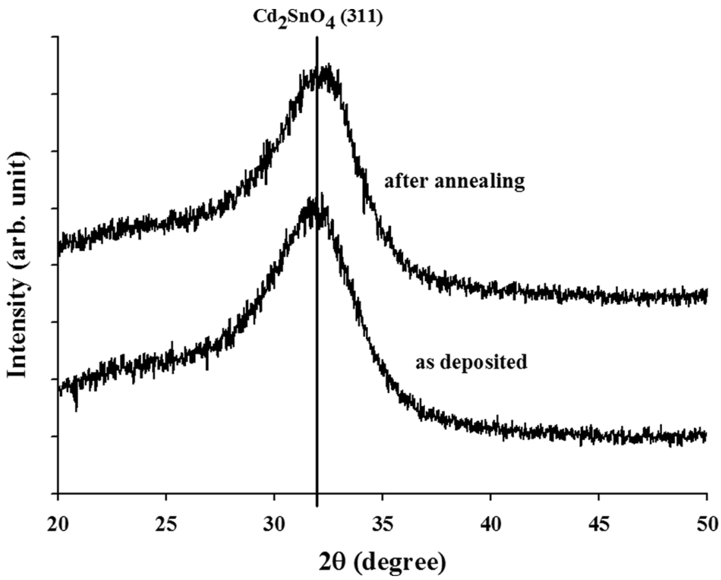

Figure 5. X-ray diffraction pattern for CTO thin film, deposited and after anneal.

Figure 4 shows transmittance curves of CTO thin film annealed in air atmosphere for 30 min at 600°C. Compared to the previous results of Figure 3, the transmittance was greatly improved after the heat treatment. The properties of thin film can be improved by heat treatment due to either recrystallization or further reaction within the material. We measured X-ray diffraction of thin film after and before annealing, which results are shown in Figure 5. Over the wide angle diffraction analysis between 20° to 80°, only the Cd_2SnO_4 (311) peak was found with same diffraction intensity and full-width half-maximum, which means that the crystallinity doesn't change with the annealing. The electrical properties of the films after annealing is summarized in Table 1. Together with the transmittance results shown in Figure 4, it is suggested that further reaction took place rather than film recrystallization. Usually, addition of oxygen in a thin film increases transmittance but degrades electrical property. Since the conductivity of CTO film stems from high oxygen vacancy concentration, the film annealed in an oxygen environment would have lower carrier concentration.

Table 1. The variation of electrical properties of annealed CTO thin film

	Resistivity (ohm · cm)	Hall mobility (cm^2/Vs)	Carrier concentration ($\times 10^{20}$, cm^{-3})
CTO	6.6E-04	9.1	10.4
Annealed-CTO	2.4E-02	13.5	0.19

Conclusions

In this study, Cd_2SnO_4 as an alternative TCO was fabricated by sputtering system at room temperature and annealed in air atmosphere. The resistivity of 6.6×10^{-4} ohm · cm, hall mobility of 9.1 cm^2/Vs, and carrier concentration of 10.4×10^{20} cm^{-3} were achieved when prepared at rf power of 75 W at room temperature. The transmittance was more than 90% from as-deposited film and over 95% from annealed film.

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