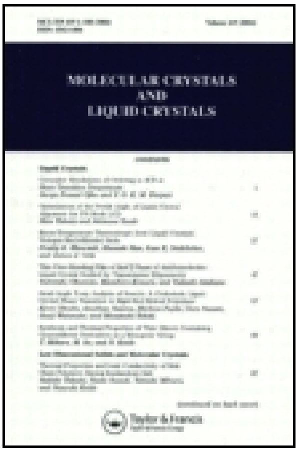

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Electrical and Optical Properties of Cd_2SnO_4 Thin Film Depending on its Chemical Bond

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Cd_2SnO_4(CTO) thin film was made using RF magnetron sputtering and a single (CTO) target. Among various deposition variables, the effect of changes in plasma power on the electrical and optical properties of the film was investigated. It was observed, as plasma power grows, specific resistivity of the thin film increases while transmittance considerably decreases. It was found that such a phenomenon occurred because of the density of the thin film reduced by increased deposition speed. Another noteworthy result obtained through the X-ray photoelectron spectroscopy analysis is that Sn has metallic bond in the case of the thin film deposited under high power. It seems that existence of such metal was another cause of the reduced transmittance of the thin film.

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

Introduction

Transparent conductive oxide(TCOs) is a material that has high transmittance over a wide wavelength range as well as high electrical property. There are a lot of research data about TCOs and they are widely used in many industrial fields. It is also used as an important material for various products such as photovoltaic devices, LCD products, gas sensor, and architectural materials.

TCOs, the transparent electrode, requires high optical transmittance and high electrical conductivity as n-type semiconductor. Currently, materials such as tin oxide(SnO_2), indium tin oxide (ITO, In_2O_3:Sn), zinc oxide (ZnO), cadmium stannate (CTO, Cd_2SnO_4), aluminum zinc oxide (AZO, ZnO:Al) are widely used as transparent electrode. [1]

It is well known that mobility of charge carrier within the transparent conductive oxide film considerably influences the electro-optic property of the thin film. High mobility over 100 cm2/Vsec is required to obtain high electric conductivity and transmittance. This is to minimize the absorption loss due to free carriers within the infrared spectral range.

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The electrical conductivity of a material is directly proportional to the carrier concentration multiplied by carrier mobility. Therefore, electrical conductivity can be increased by raising carrier concentration or carrier mobility. As carrier mobility and carrier concentration become higher, resistivity of TCO becomes lower. However, simply increasing carrier concentration may increase carrier absorption and the absorption spectrum range will lean to the short wave side. With excessive high concentration, yellowing may occur to the thin film. Therefore, it seems that increasing mobility is desirable to improve electric conductivity and to minimize absorption of free carrier.

In general, materials such as ITO, ZnO, and AZO are widely used as transparent electrode. In the meantime, it is known that, CTO, which has higher carrier mobility compared to existing TCOs, has good electrical and optical properties. [2]

Haacke made Cd_2SnO_4 which has much higher conductivity than AZO. [3] CTO thin film is made by several methods such as rf sputtering [4], dc reactive sputtering [5], ion beam sputtering [6], chemical vapor deposition [7], spray pyrolysis [8], and electroless deposition [9].

In this study, CTO thin film synthesis was tried by magnetron sputtering on glass substrate. It was observed that, in the optimizing process of thin film property, particularly transmittance is considerably affected by rf power. In this study, electrical, optical, and chemical properties of thin film depending on changes in rf power are compared to find the cause of the change in transmittance and to come up with countermeasures.

Experimental

Fabrication of Cd_2SnO_4

Cd_2SnO_4 thin film was made using RF Magnetron Sputtering system which can adjust the tilt-angle of sputter-gun. Three inch CTO single target which is 3mm thick was used. Base pressure was set at 1×10^{-6} torr and working pressure was kept at 3 mtorr using Ar gas. Substrate was rotated by 10 rpm in order to improve the film uniformity. The substrate was located at the center of substrate holder in order to keep the incidence angle of sputtering molecules same when they reach the substrate. The incidence angle of the target elements reaching the substrate is about 59° against the surface normal. [11] CTO thin film whose thickness is fixed at 200mm was deposited under various RF power conditions.

Measurements

For the thickness of CTO thin film, α-step and optical interferometry (K-MAC, ST2000DLXn) were used. Meanwhile, for electrical property such as resistivity, carrier mobility, and carrier concentration, the Hall effect measurement system (ECOPIA, HMS-5000) was used. Optical transmittance was measured using UV-Vis spectroscopy over the range of 300 to 1100 nm. And, XPS (X-ray photoelectron spectroscopy) analysis was performed to examine the correlation between transmittance of thin film and process variable of plasma.

Results and Discussion

The electrical, optical, structural, chemical analysis was carried out for the Cd_2SnO_4 thin film which has identical thickness by changing plasma power in the RF magnetron sputter system.

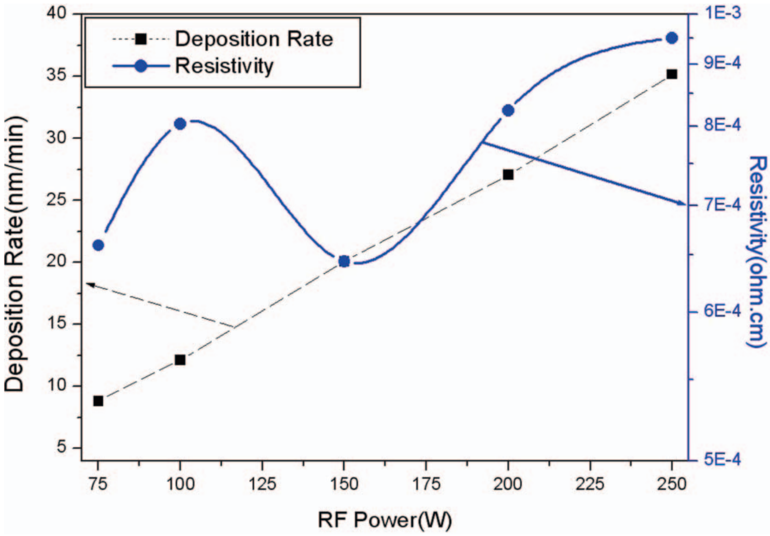

Figure 1. The variation electrical property of Cd2SnO4 films deposited at various rf power.

As shown in Fig. 1, deposition rate increased linearly due to the increase of plasma power and the resistivity of thin film slightly increased accordingly. Usually, when it comes to thin films made at room temperature, as growth speed is higher, the harder to make dense films because the surface mobility of the ad-atoms arriving at the surface is low. On the other hand, as plasma power grows, the increase of surface mobility by ion bombardment could be expected. However, it seems that the effect was not big enough in this experiment.

The behavior of resistivity depending on plasma power can be explained by the changes of carrier concentration and carrier mobility. As shown in Fig. 2, as plasma power grows, carrier concentration increases while carrier mobility decreases. That is, due to reduced density of the thin film mentioned above, carrier mobility is limited and hence the film resistivity increases. It was found that the CTO thin film deposited under high plasma power is considerably affected in resistivity property as well as optical property. Figure 3 shows the changes in transmittance and optical bandgap depending on plasma power. As the power grew, transmittance decreased not only in visible ray but also in infrared ray range. The thin film with a low transmittance showed translucent metallic gray color. Figure 3 shows the absorption coefficient, α, which was obtained by calculating the transmittance values. The absorption coefficient can be defined by the following equation.

$$I = I_0 \exp(-\alpha t)$$

Where, I and I_0 indicate transmittance and incidence angle each. α is absorption coefficient and t is thickness of the thin film. Since the I/I_0 is the optical transmittance given in Fig. 3 and the thin film thickness, t, is also given, the absorption coefficient α depending on hv, the optical energy, can be calculated. As one can know with Fig. 3, α^2 is becoming almost linear for $h\nu$. For such interband transition, following equation can be applied [13].

$$\alpha^2 = A(h\nu - E_g)$$

Where, A is a constant. If α^2 is extrapolated, the optical energy, $h\nu$, becomes E_g of the thin film.

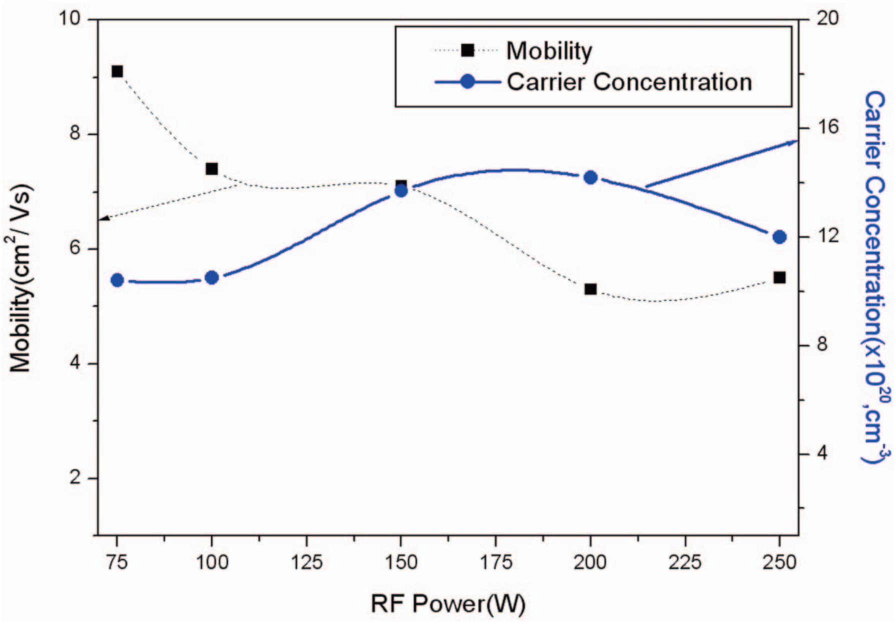

Figure 2. The variation of electrical property of CTO thin film as a function of rf power.

The optical bandgap of the thin film deposited under 250 W was 2.7 eV and it was measured to be very low compared to CTO (bandgap energy = 3.1 eV). Considering that the bandgap energy of CdO and SnO2 consisting of CTO is 2.4 eV and 3.75 eV each, there is a high possibility that the CTO deposited under high power could be CdO-rich thin film. [12]

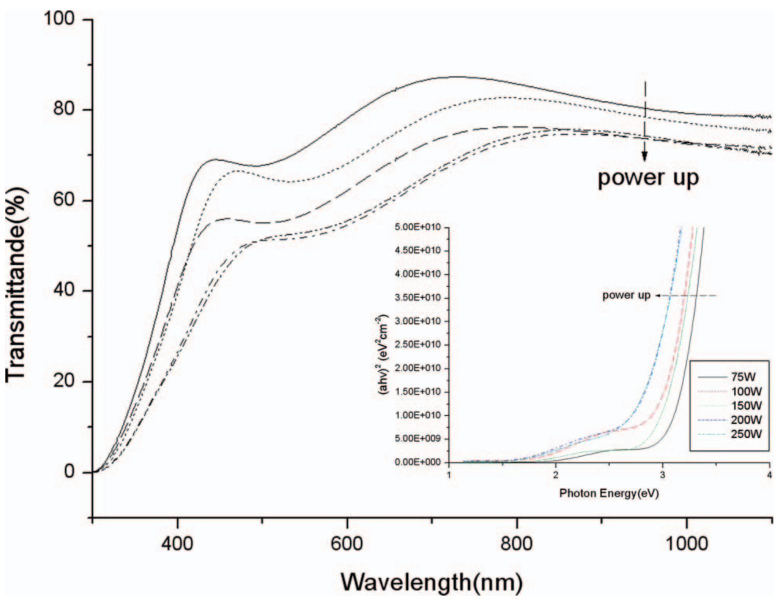

Figure 3. Transmittance curve and bandgap of CTO thin film as a function of rf power.

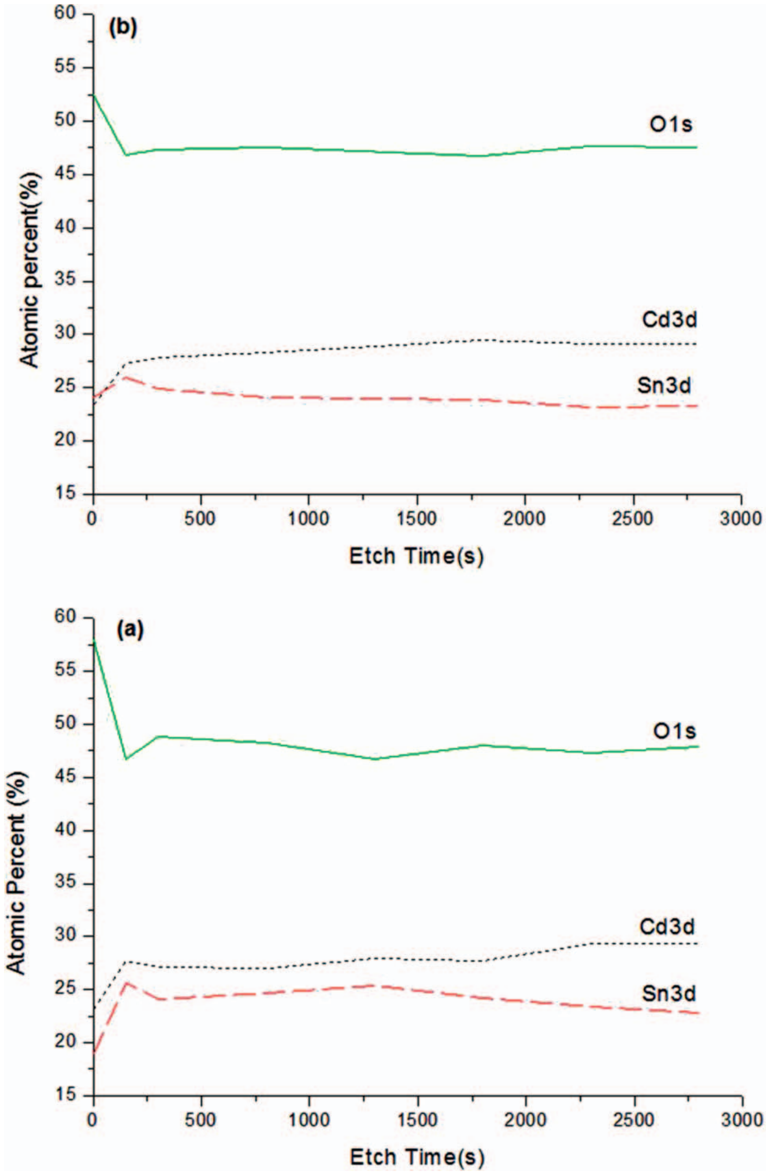

Figure 4. Comparison of XPS depth profile of Cd2SnO4 thin films deposited at different RF Power (a)75 w, (b)200 w).

In order to examine such a possibility, the CTO thin film deposited under 75 W and 200 W was analyzed with XPS. Figure 4 shows the results of depth profile for each thin film and the 75W film seems to have slightly higher Cd content. However, the content itself seems insufficient to prove whether it is Cd-rich. Fur the more both thin films show values far from the stoichiometry of Cd:Sn:O = 2:1:4. That is because proper reference materials were not used when XPS was measured. What is clearly different in the two films is the chemical bonding status of Sn as shown in Fig. 5. Regarding Sn3d binding energy values, metallic Sn is reported to be located at $Sn3d_{3/2}$ 484.9 eV, and $Sn3d_{5/2}$ 493.3 eV.

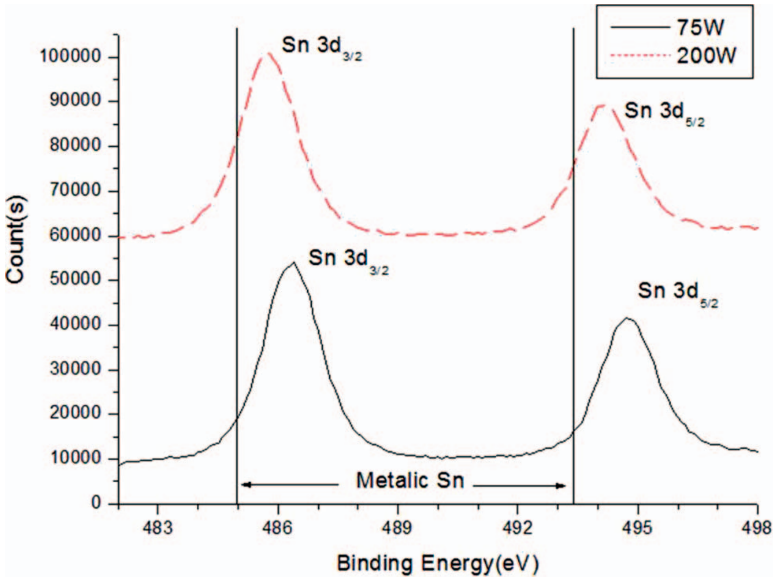

Figure 5. Comparison of narrow scan XPS spectra of Sn $3d_{3/2}$ and $Sn3d_{5/2}$ of the Cd2SnO4 thin films.

[10] Meanwhile, in the case of the thin film deposited under 200 W, Sn3d peak was found to be at $Sn3d_{3/2}$ 485.8 eV, $Sn3d_{5/2}$, and 494.2 eV which are the bonds closer to metallic Sn compared with the 75 W film. Also the metallic Cd bonds not bonded with oxygen was found. Therefore, it is judged that, as plasma power increases for deposition, contents of metallic components increase and thus the transmittance of thin film deceases. In order to remove such metallic components, the CTO synthesis, where plasma chemistry adopting a mixed gas(Ar:O2), will be tried to improve transmittance.

Conclusions

Concerning the Cd_2SnO_4 synthesizing using RF magnetron sputtering, the effect that the changes in plasma power have on the electrical and optical properties and the bond of components was examined. It was found, as plasma power increases, the electrical property as well as optical transmittance of thin film considerably deteriorated. It seems that such phenomenon occurred because the density of thin film was reduced due to the increase of deposition speed. Regarding the thin film deposited under high plasma power, the bond of Cd and Sn was found close to metallic compound. And, it was found that such mixture of metallic component contributed to the reduced transmittance. In order to improve transmittance, metallic component should be removed and using gas mixture containing oxygen seems reasonable.

Acknowledgment

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