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Electrical Conductivities of Mn-Doped Indium Oxide Thin Films in Moist Air

Yasutaka TAKAHASHI, Radhouane BEL HADJ TAHAR, Kimiko SHIMAOKA,
Takayuki BAN and Yutaka OHYA

Faculty of Engineering, Gifu University,
Yanagido, Gifu 501-11, JAPAN

Mn-doped indium oxide thin films, prepared on glass plates by dip-coating method from a sol have been found to rapidly decrease in the electrical conductivity at room temperature by about three orders of magnitude when brought into contact with moist air, although the conductivities of non-doped indium oxide films were almost independent of moisture. Thus, the Mn-doped films can be applied as a humidity sensor. The film thickness had no substantial effects on the sensing properties, probably due to the porous nature of the sol-gel oxide films. In order to examine the effects of film morphologies, a comparison between the humidity sensing properties of the films prepared from the organic and aqueous sols was also made.

1. Introduction

Indium oxide is one of the key materials for transparent, electrically conductive films. In particular, tin-doped In_2O_3 (ITO) are widely used as transparent electrodes for opto-electric devices such as display and solar batteries. ITO films with high transparency and low electrical resistivity of 10^{-4} $\Omega \cdot cm$ order of magnitude have been prepared by sputtering technique and some other conventional preparation methods. Our group has been studying on the preparation of excellent ITO films by dip-coating method using a sol derived from diethanolamine(DEA)-indium acetate mixture. In the course of this investigation we have found that doping In_2O_3 with a few mol% of Mn ions increased the resistivity by several orders of magnitude at room temperature in dry atmosphere. The resistivity of Mn-doped In_2O_3 films decreased rapidly when brought into contact with moist air. This property prompted us to investigate a possible use of these films as humidity sensors. Detailed study of these films prepared from both aqueous and organic sols by dip-coating process has been made focusing on their response time, stability, sensitivity and hysteresis characteristics. Particular emphasis has been placed on the relationship between the sensing behaviors of the films and the nature of the sols used in their preparation.

2. Experimental

2.1. Thin film preparation

Aqueous [1] and organic sols used for the fabrication of the films were prepared as described elsewhere [2]. The organic sol was composed of an isopropanol solution of indium acetate-diethanolamine (DEA) mixture (molar ratio of DEA/In=2). Manganese chloride ($MnCl_2$, $4H_2O$) and manganese(II) acetate tetrahydrate ($Mn(CH_3COO)_2$, $4H_2O$) were used for introducing Mn in the aqueous and organic sols respectively. The films were coated two times on glass substrates (corning # 7059) by dip coating process, dried at 110°C for 10min and fired in air at 600°C for 30min for each coating. The withdrawal speed was fixed at 6cm/min. Indium ion concentration in organic and aqueous sols was almost 0.3M.

2.2. Measurement

The crystallite size was evaluated from the line broadening in XRD pattern as per Debye-Scherrer equation and directly measured from transmission electron microscopy (TEM) micrographs. The film thickness was estimated from the interference bands in the visible spectra and confirmed by direct measurement from TEM images of the film cross section.

Particle size and morphology were determined by TEM and the surface morphology of the films by SEM. The electrical resistivity was measured at room temperature between two gold electrodes separated by 5mm which were vacuum evaporated on the films. These electrodes were connected to a digital ampere metre and DC voltage supplier through platinum wires. The relative humidity (RH) was controlled by mixing wet air (water vapor saturated air) with dry air in a given ratio. The sensitivity (S) was defined as the ratio of the resistivity in dry air (ρ_a) to that in 90 %RH air (ρ_{90}), that is ρ_a / ρ_{90}.

3. Results and discussion

The XRD patterns as well as the visible spectra of Mn-doped In_2O_3 (5mol%Mn) and pure In_2O_3 thin films fired at 600°C in air are shown in Figs. 1 and 2 respectively. Both pure and Mn-doped In_2O_3 films had very sharp XRD patterns corresponding to cubic crystal structure. The presence of phases other than In_2O_3 were not recognized. Refractive indices of both films estimated from the corresponding visible spectrum are in the range 1.8~1.9 which is lower than the value (2.1) reported in literature indicating the porous nature of these films. The refractive indices of Mn-doped films were somewhat lower than those of pure In_2O_3 films as shown in Table 1. Fig.3 shows log(ρ) vs relative humidity relationship for

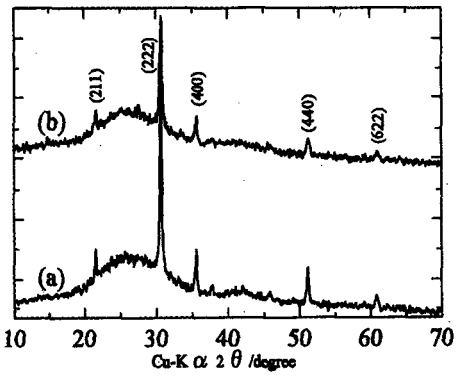

Figure 1. XRD patterns of thin films of (a) pure In_2O_3 and (b) Mn-doped In_2O_3 (5 mol%Mn).

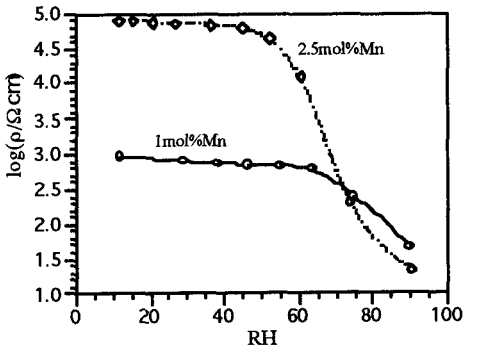

Figure 3. Humidity-sensitivity characteristics at 20°C in air for the In_2O_3 thin films doped with 1 and 2.5 mol%Mn.

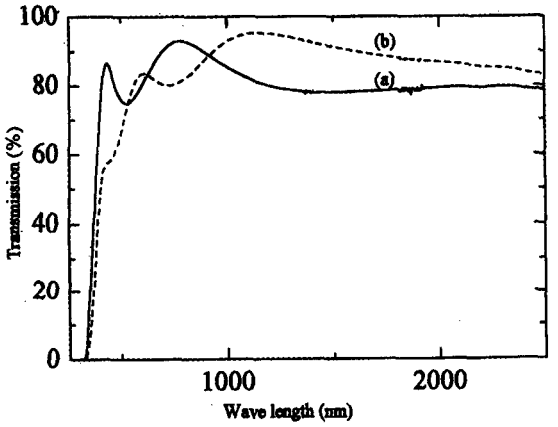

Figure 2. Visible spectra of thin films of (a) pure In_2O_3 and (b) Mn-doped In_2O_3 (5 mol%Mn).

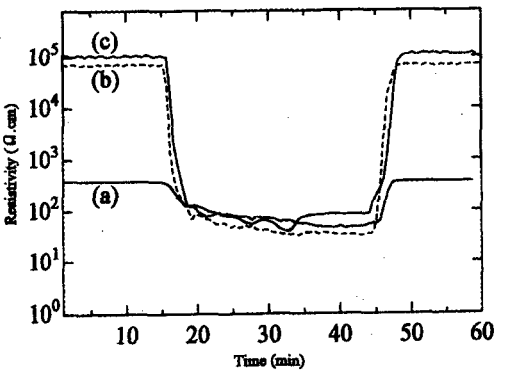

Figure 4. Response of In_2O_3 thin films doped with (a) 1mol%Mn, (b) 2.5mol%Mn and (c) 3mol%Mn when RH changed from 10 to 90% and from 90 to 10%.

Table 1

Sensing properties of In_2O_3 thin films coated two times doped with different Mn mol%.

	mol%Mn	resistivity in dry air (Ω cm)	sensitivity	refractive index*	thickness (nm)
0	(A)**	1.3	—	1.84	42
0	(O)**	5.10^{-2}	—	1.95	40
0.5	(A)	28	4	—	—
1	(A)	941	20	—	—
2	(A)	2500	50	—	—
2.5	(A)	8.10^4	3600	—	60
3	(A)	4.10^5	17000	—	—
5	(A)	inaccessible	—	1.75	63
5	(O)	$1.1.10^4$	2000	—	—

* Evaluated from 10 time dipped films.

** (A) and (O) refer to the films from aqueous and organic sols respectively.

the films doped with 1 and 2.5 mol%Mn as representative examples which were derived from aqueous sol. The resistivity abruptly decreases about three orders of magnitude for the film doped with 2.5mol%Mn above 60%RH. It remains almost constant at lower RH conditions. The conductivity enhancement is due to chemisorption, physisorption, and/or capillary condensation of water within the pore structure[3]. Possible use of these films for the detection of high humidity was investigated. The time response of the films doped with 1, 2.5 and 3mol%Mn obtained in rapid humidity change from 10 to 90 %RH and from 90 to 10 %RH is shown in Fig. 4. These curves were reproducible with excellent reversibility and without any further thermal desorption treatment which adds design complexity and cost. Although the resistivity of the films increased with the doping amount in dry atmosphere, it decreased nearly to the same value at high RH. Taking into account the time required to evacuate the residual air(dry or wet) from the chamber, that is about 2

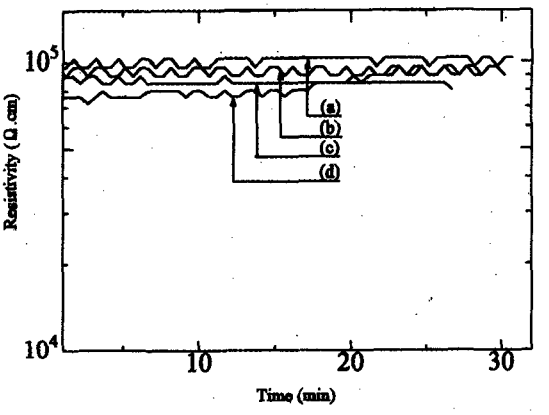

Figure 5. Sensitivity characteristics of Mn-doped In_2O_3 thin films (5mol%Mn) to various test gases: (a) CH_4, (b) methyl-2-butene, (c) H_2 and (d) CO_2.

minutes, the response time of the films to the humidity change is estimated to be within a few tens seconds. The quick response is attributed to the rapidity in the rate of adsorption and desorption of water molecules at the film surface. The resistivity in dry air, sensitivity, refractive index and thickness of the films doped with 0.5~5mol%Mn are listed in Table 1. The Mn-doped In_2O_3 thin films exhibit high sensitivity to humidity which increases proportionally to the doping amounts of Mn. Comparing with pure In_2O_3, the increase in thickness accompanying the decrease in refractive index of the Mn-doped films as a result of doping may explain their porous structure. Table 1. also shows the difference in refractive indices, resistivities and sensitivities of the films derived from organic and aqueous sols. Generally it can be observed that the films derived from organic sols have higher density and; hence, lower resistivity than those derived from aqueous sols.

Fig.5 shows the sensitivity characteristics of Mn-doped In_2O_3 thin films to various test gases including inflammable gases which would affect the electrical properties of n-type oxide semiconductors. The film doped with 3mol%Mn was chosen as a typical sample. As shown in Fig.5 this film responded only to humidity and gave no response to the tested gases such as CH_4, 1%H_2 air, CO_2 and methyl-2-butene. Thus, the Mn-doped In_2O_3 films have been found to selectively detect the humidity in various atmospheres: air, CH_4 and reducing gases which indicates their stability and reliability in aggressive environments. Beside Mn^{2+} the doping effect of other metal ions such as Co^{2+} and Ni^{2+} has been examined. These divalent ion-doped films were found to behave similarly to Mn-doped films. Therefore, it can be concluded that raising the resistivity of In_2O_3 films by doping metal ions should be a key factor to make the oxide films useful as humidity sensor. At present the reason why In_2O_3 showed rapid adsorption and desorption of water vapor at their surface even at room temperature remains unclear.

4. Conclusion

Mn-doped In_2O_3 films prepared by dip coating can be used as humidity sensor with high selectivity and sensitivity. It is found that doping with divalent metal ions like Mn or Ni increases the resistivity of films which plays a key role in the humidity sensing characteristics. The porosity of the films was also found to affect the sensing property. Due to their higher porosity the films from aqueous sol show better sensitivity to moisture than those from organic sol.

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