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Preparation and properties of transparent electrical conductive thin film by sol-gel process with metal salts

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Indium tin oxide(ITO) and zinc aluminum oxide(AZO) thin films were prepared by a sol-gel process using metal salts and organic solvents. Metal chloride, acetate and nitrate were used as raw materials. Effects of the organic solvents on the electrical properties of those films were examined. Obtained ITO and AZO thin films had high transmittance in the visible range. After reduction in hydrogen atmosphere, the AZO thin film containing 5mol% Al_2O_3 showed a resistivity of ρ=3.6x10^{-2}[Ωcm] at room temperature. The ITO thin film containing 12mol% SnO_2 showed the minimum resistivity of ρ=1.2x10^{-3}[Ωcm], carrier concentration N=1.2x10^{20}[cm^{-3}] and mobility μ_H=7.0[cm^{2}V^{-1}s^{-1}] at room temperature.

1. INTRODUCTION

Indium tin oxide (ITO) (SnO_2 doped In_2O_3) and Zinc aluminum oxide (AZO) (Al_2O_3 doped ZnO) are expected to use widely as transparent electrodes for many devices, such as ECDs, ELs and solar cells[1]. These thin films are prepared from many processes such as sputtering[2,3], and chemical vapor deposition (CVD)[4,5], and sol-gel process[6]. In general, metal alkoxides are used as raw materials for the sol-gel process. But it is difficult to control the hydrolysis ratio of each alkoxide. And the reagent of the metal alkoxide are very expensive. Therefor we prepared many thin films by use of metal salts as raw materials[7,8,9]. Several organic solvents may be formed stabilized metal ions in solution. We investigated the relationship between stability of starting solution and electrical properties of the thin films.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of thin films

(a) Solution for AZO thin films

The thin films prepared in this study had the composition of (100-x)ZnO・xAl_2O_3, where x=0-7. Zinc acetate and aluminum nitrate were dissolved in ethanol; then diethylenetriamine (solution A), diethanolamine (solution B), monoethanolamine (solution C) or acetylacetone (solution D) was added to prepare four kinds of coating solution. Thin films were prepared on transparent quarts glass substrates. The coated substrates were heat-treated in air. Then the films were reduced in hydrogen atmosphere at 500℃.

(b) Solution for ITO thin films

The thin films prepared in this study had the composition of (100-x)In_2O_3・xSnO_2, where x=0-20. Indium chloride was used as the indium source, tin chloride was used the tin source. Indium chloride was dissolved in acetylacetone and the solution was refluxed at 60℃. Tin chloride was dissolved in ethanol and this solution was mixed with the refluxed solution. Thin films were prepared on the transparent quartz glass substrates. The coated substrates were heat treated at a given temperature in air to form the thin film.

2.2 Analytical procedure

IR spectra of these solutions were measured in the range of 400 to 2000cm^{-1} at room temperature. Differential thermal analysis and thermo-gravimetric analysis were performed at a heating rate of 3℃/min.

Crystalline phases of those films were identified by using a X-ray diffractmetor with a thin film attachment. Electrical resistivity of those films were measured by means of the four terminal method. Hall coefficients of those films were measured by means of Van Der Paw method. Transmittance of those films were measured by using an UV-spectrophotometer.

3. RESULTS

3.1 AZO thin films

3.1.1 X-ray diffraction analysis

The crystallization of AZO started at about 300℃ in the case of A and 200℃ in the case of B, C and D. The peak intensity increased with increasing temperature up to 700℃. The thin films prepared from solution C and D were found that the orientation of c-axis heightened with increasing heat-treatment temperature.

3.1.2 Hall effect measurement

The Hall coefficient(Rh), carrier concentration(n) and mobility(μ) were calculated from the Hall voltage(Hv) and resistivity(ρ) of the film sintered in air at 700℃. Fig. 1 shows the relationship of resistivity, mobility and carrier concentration for the films prepared from each solution(A, B, C and D). The mobility and carrier concentration increased in the order of A, B, C, D, simultaneously. The thin film prepared from solution D showed the largest carrier concentration($22.6x10^{17}cm^{-3}$) and mobility ($1.49cm^2/Vsec$) by the heat-treatment in air at 700℃.

The film was heated in hydrogen atmosphere to increase carrier concentration. Then it showed the resistivity of $3.6x10^{-2}$[Ωcm].

3.1.3 Measurement of IR spectra

Fig. 2 shows IR spectra of the following solution. (a) zinc acetic acid dissolved in H_2O, (b) aluminum nitrate dissolved in H_2O, (c) AcAc mixed with ethanol and (d) the coating solution. The C=O peaks

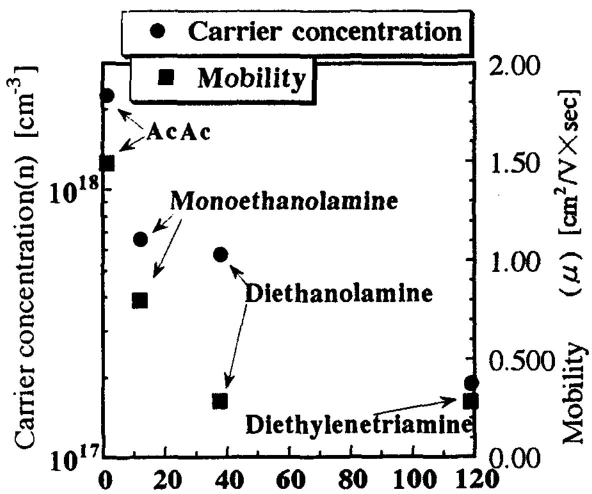

Fig. 1 Relation of carrier concentration and mobility to resistivity of AZO thin films

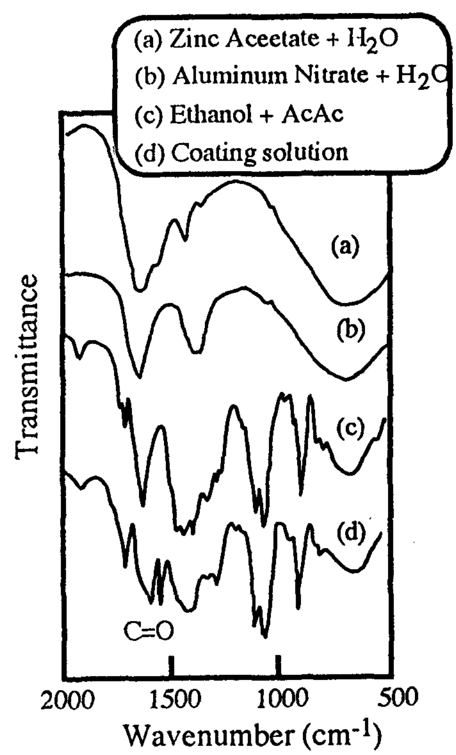

Fig. 2 IR spectra of AcAc solutions

of keto and enol with proton type were found at $1700cm^{-1}$ and $1620cm^{-1}$. The new peaks were found at $1600cm^{-1}$ (C=O peak of enol with metal ion) and $1540cm^{-1}$ (C-C peak) for the coating solution.

3.1.4 Surface observation by SEM

The grain size increased with increasing heat-treatment temperature in the case of C and D solution. And the c-axises of AZO crystals were preferentially oriented perpendicularly to the substrate.

The AZO film prepared at 700℃ from solution B showed a very smooth surface. On the other hand, the film prepared from A showed a rough one having many pin holes.

3.1.5 Transmittance of AZO film

AZO thin film containing 5mol% Al_2O_3 prepared from solution B(0.4μm thickness), solution C(0.3 μm) and solution D(0.15μm) showed transmittance of above 85%.

3.2 ITO thin films

3.2.1 X-ray diffraction analysis

We investigated the crystallization process of ITO thin films containing 10mol% SnO_2 by XRD. Peaks of indium oxide already appeared at 400℃, and the intensity increased with increasing temperature up to 600℃. These results suggest that these films begin crystallization at 400℃ and are fully crystallized at 600℃.

3.2.2 Hall effect measurement

Fig. 4 shows compositional dependence of resistivity, mobility and carrier concentration in the system of (100-x)In_2O_3 · xSnO_2. The carrier concentration of the thin films increased, and resistivity of the thin films decreased with increasing SnO_2 content up to 12mol%.

3.2.3 Measurement of IR spectra

Fig. 5 shows IR spectra of acetylacetone (a), a mixture of acetylacetone and iso-propanol (b), and indium chloride dissolved in the mixture of acetylacetone and iso-propanol (c). The position of C=O stretching peak of keto is very close to that of

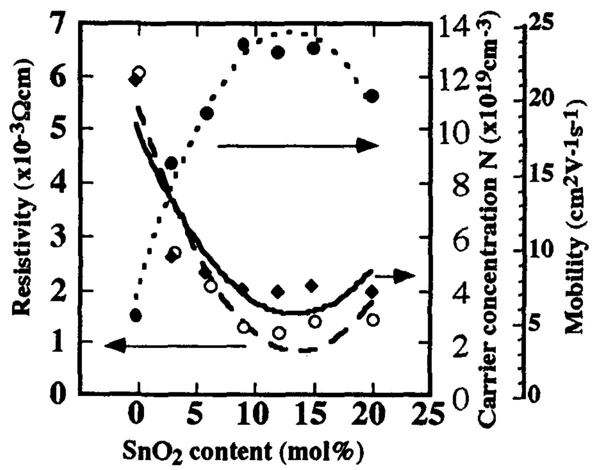

Fig. 3 Relation of carrier concentration and mobility to resistivity of ITO thin films
—O— Resistivity —◆— Mobility
-●- Carrier concentration

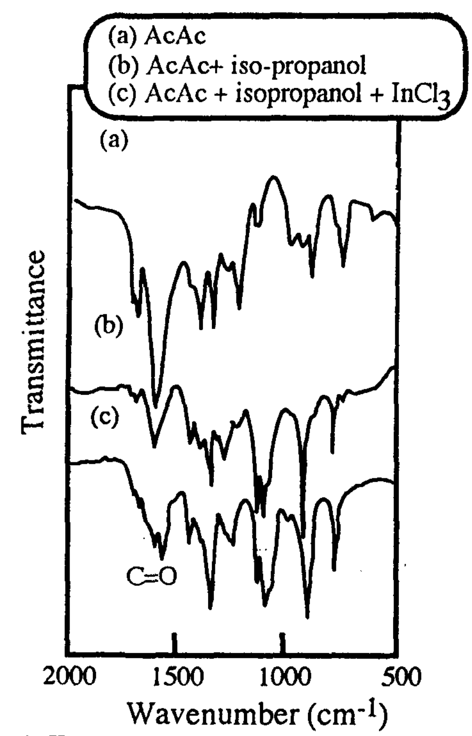

Fig. 4 IR spectra of indium AcAc solutions

enol with proton. In (a) and (b) solutions, the C=O stretching vibrations appeared at 1640cm^{-1}. In (c) solution, they are widely separated and appeared at 1600 and 1630cm^{-1}. The stretching vibration of enol with metal ion is lower than that of enol with proton.

3.2.4 Transmittance of ITO film

ITO thin film containing 10mol% SnO_2 has high transmittance above 80% over the visible range.

4. DISCUSSION

The difference of the orientation and the resistivity are considered to be due to the difference of the coordination power and the boiling point of the solvents. The boiling point of the solvents are as follows, diethanolamine(271℃) > diethylene-triamine(207.1℃) > monoethanolamine(171.1℃) > AcAc(140℃). Thin films prepared from another solution begin crystallization at 200℃, but diethanolamine begin at 300℃. Remaining diethanolamine prevented the crystallization of AZO at 200℃, Thin films prepared from high boiling point solvent showed rough surface having many pin holes because of the rapid firing of the remaining solvent at high temperature.

Monoethanolamine have one N and one O atom and AcAc have two o atoms in each molecule. In general, the coordination power of O atom stronger than that of N. Two Zn-O bond or In-O bond may be formed in the solution by use of AcAc due to the chelate formation shown in Fig. 2 and Fig. 4.

The oxygen-metal-oxygen bond is considered to be good for the low temperature crystallization of AZO and ITO.

5. CONCLUSION

1) Al doped ZnO(AZO) and Sn doped In_2O_3(ITO) thin films were prepared by the sol-gel process with metal salts and organic solvents.

2) Acetylacetone formed chelate complexes with metal in the solutions.

3) The minimum resistivity of the AZO thin film heat-treated in air was 1.54[Ωcm], and then it showed the resistivity of $3.6x10^{-2}$[Ωcm] by heat-treatment in hydrogen atmosphere at 500℃ for 1h.

4) The ITO thin film showed a resistivity of $1.2x10^{-3}$[Ωcm].

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