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Preparation of highly oriented thin film exhibiting transparent conduction by the sol–gel process

K. NISHIO, S. MIYAKE, T. SEI, Y. WATANABE, T. TSUCHIYA
Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Science University of Tokyo, 2641 Yamazaki, Noda, Chiba 278, Japan

Highly oriented thin films exhibiting transparent conduction aluminium-doped ZnO (AZO), were prepared by a spin-coating method. The effects of the solvents on the preparation and electrical properties of the thin films were examined. The thin films were formed on quartz glass substrates by spin-coating into a selected solution and calcining at 700 °C for 5 h. The thin films had a resistivity of ρ (Ω cm) = 1.5 after heat treatment in an air atmosphere, and 1.5×10^{-3} Ω cm in a reducing atmosphere, and a transmission of about 85% in the visible light region. The differences in the high orientation and the conductivities were attributed to a chelate formation in the aluminium-doped ZnO due to the solvent effect.

1. Introduction

ZnO is an n-type semiconductor of a metal-excess type, that does not have absorption in visible light region, and has finds wide use as surface wave filters, fluorescence indication tubes and inflammability gas sensors because it is harmless and very stable to the atmosphere.

Indium tin oxide (ITO) (SnO_2-doped In_2O_3) and ZnO (Al_2O_3- or Ga_2O_3-doped ZnO) are well known for their transparency when made into thin films, and are expected to find wide use as transparent electrodes for many devices, such as Electrochromic (ECDs), Liquid crystal displays (ELs) and solar cells [1].

It was reported that the conductivity of aluminium-doped ZnO (AZO) increased with the orientation to the substrate in the *c*-axis direction [2]. Therefore, aluminium-doped ZnO (AZO) thin films oriented in the *c*-axis direction to the substrate, are prepared by vacuum deposition of an evaporated oxide, sputtering of an oxide or a metallic target [3, 4], and chemical vapour deposition (CVD) in which vapour of a metal oxide is deposited and thermally decomposed on a hot substrate [5, 6].

In general, the metal alkoxides are used as raw materials for the sol–gel process. But the preparation of a sol is tedious and the reagents of the metal alkoxide are very expensive. Therefore, many thin films have been prepared using metal salts as raw materials [7–9]. No report has been published on oriented thin films in the *c*-axis direction using metal salts as raw materials until now. In this study, the spin-coating process was employed, because of its favourable characteristics, to produce thin films of aluminium-doped ZnO (AZO) oriented to the *c*-axis direction which are expected to find application as transparent electrodes. In particular, an attempt was made to prepare highly oriented thin films when the metal salts were used as raw materials, and an alcanol amine or β-diketon was used solvent; the relationship between the solvent effect and the electrical properties was then measured.

2. Experimental procedure

2.1. Preparation of thin films

The thin films prepared in this study had the composition of $(100 - x)\,\mathrm{ZnO}\cdot x\mathrm{Al_2O_3}$, where $x = 0$–7. Zinc acetate, which was used as the zinc source, was very soluble in water and alcohol; aluminium nitrate was used as the aluminium source. Zinc acetate and aluminium nitrate were mixed to obtain the desired composition and dissolved in ethanol; then diethylenetriamine (solution A), diethanolamine (solution B), monoethanolamine (solution C) and acetylacetone (solution D) were added to prepare the dip-coating solution.

Transparent quartz glass plates were used as substrates. Thin films were prepared by spin-coating on the substrate. The coated substrate was dried at room temperature for 1 h, at 100 °C for 3 h, at 250 °C for 3 h, and then heat treated at a given temperature in an air atmosphere or hydrogen gas to form the thin film.

2.2. Analytical procedure

The thin film was analysed by an X-ray diffractometry, with copper as the target, equipped with a thin-film attachment and a carbon monochromator to identify the product crystalline phase. The thickness of the thin film was determined by an ellipsometer, the

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resistivity by a four-terminal type of analyser equipped with parallel electrodes, the transmittance by a two-wavelength double-beam self-recording type spectrometer, and the morphology of surface by scanning electron microscopy.

3. Results

3.1. Thickness of the thin films

The thin films, prepared on the substrate by the spin-coating method, were approximately 0.09 μm (for solution A), 0.08 μm (for solution B), 0.06 μm (for solution C) and 0.03 μm (solution D) in thickness by one spin-coating. Fig. 1 shows the relationship between the thickness of the heat-treated film and the number of spin-coatings. The film thickness increased linearly with the number of spin-coatings, implying that the thickness could easily be controlled by the number of spin-coatings.

3.2. X-ray diffraction analysis and SEM observation

The conventional powder X-ray diffraction analysis produced no diffraction pattern, except the halo pattern of the glass substrate. However, when equipped with a thin-film X-ray diffraction apparatus, the analyser produced the diffraction patterns shown in Fig. 2 for thin films prepared from solution D of $95ZnO \cdot 5Al_2O_3$ heat treated at each temperature for 5 h. The crystallization of a thin film started from 300 °C when prepared from solution A, and from 200 °C when prepared from solutions B, C, and D. Remarkably, it was observed that only the (0 0 2) plane grew rapidly from 400 °C for thin films prepared from solutions C and D. This indicated that the crystals grown in the direction of the *c*-axis were predominant. The growth in the direction of the *c*-axis was preferentially in the neighbourhood of 600 °C for thin film prepared from solution B. However, the thin film prepared from solution A was homogeneously grown in all peaks and no preferential growth was observed. In order to analyse the orientation of the thin film to the substrate, the following methods were used. One method was X-ray diffraction analysis by rotation in θ–2θ of a goniometer, and the other was the rocking curvature measurement. For the former measurement, the thin films prepared from solutions C and D were rapidly grown on only the (0 0 2) plane by heat treatment from 400–500 °C and, furthermore, the large peak was observed from the measurement of fixed θ. On the other hand, the thin film prepared from solution D grew rapidly on only the (0 0 2) peak from 600 °C and was almost unchanged by the measurement of fixed θ. From these results, the thin films prepared from solutions C and D were found to exhibit enhanced orientation in the *c*-axis direction with increasing heat-treatment temperature.

3.3. Measurements of TG–DTA and FT–IR

The results of Fourier transform–infrared spectroscopy FT–IR agreed with the results of X-ray diffraction measurements. The Zn–O peak was observed in the neighbourhood of 400 cm^{-1} for the thin film prepared at 300 °C from solution B, and was observed at a temperature 100 °C higher than that prepared from solutions C and D. From TG–DTA measurements,

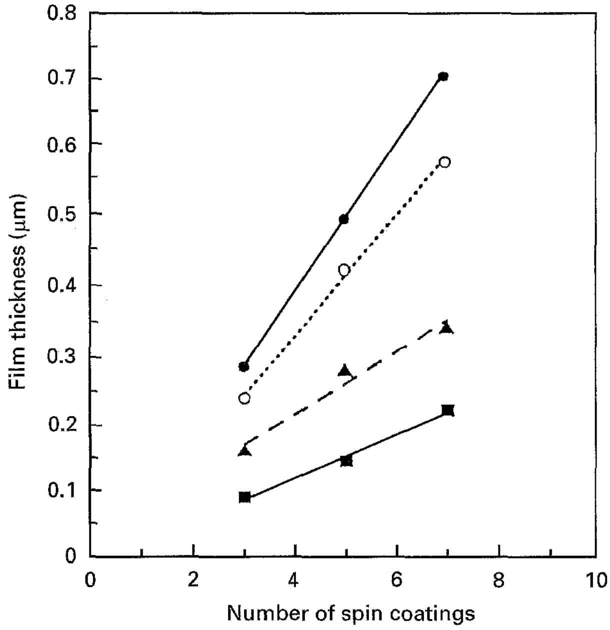

Figure 1 Film thickness versus number of spin coatings. (●) Diethylenetriamine, (○) diethanolamine, (▲) monoethanolamine, (■) AcAc.

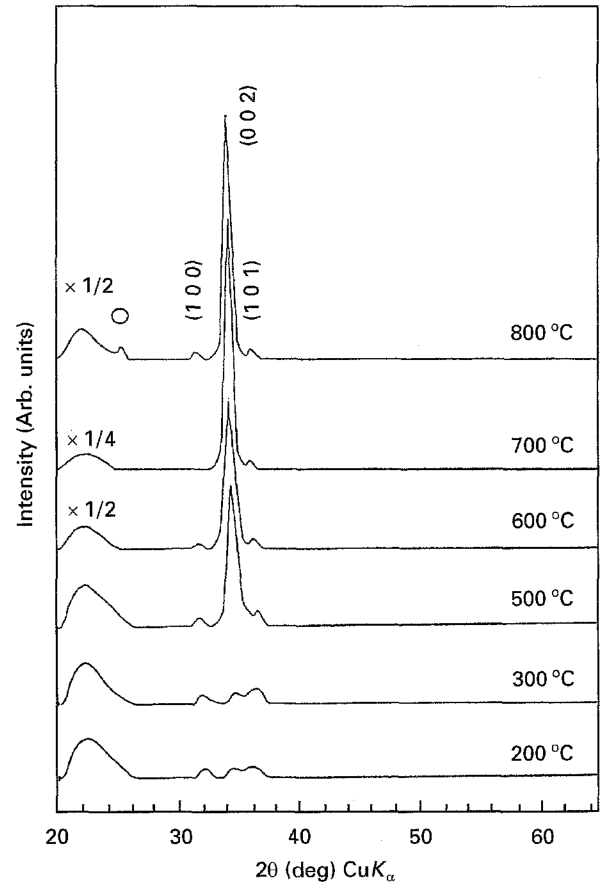

Figure 2 X-ray diffraction patterns of AZO thin film prepared at various heat-treatment temperatures prepared from solution D. (○) Unknown.

a large exothermic peak with large weight loss was found at about 460 °C for solution A, about 510 °C for solution B, about 390 °C for solution C, about 340 and 400 °C for solution D. These results are thought to be due to the difference in the burning temperatures of the organic solvents.

3.4. Resistivity

Fig. 3 shows the heat-treatment temperature dependence of resistivity. The resistivity decreased with increasing crystallization and the orientation of thin films. The lowest resistivity (1.54 Ω cm) was observed in the thin film prepared by heat treatment at 700 °C from solution D.

3.5. Hall-effect measurement

The Hall voltage was measured in the thin film prepared by heat treatment at 700 °C. The Hall coefficient, *Rh*, carrier density, *n*, and mobility, μ, were calculated from the Hall voltage, *Hv*, and resistivity, ρ. Fig. 4 shows the relationship of resistivity, mobility and carrier density with the films prepared from each solution (A, B, C and D). The increase and decrease of mobility and carrier density corresponded to that of resistivity. The thin film prepared from solution D showed the largest carrier density (22.6×10^{17} cm^{-3}) and mobility (1.49 cm^2 V^{-1} s^{-1}) by heat treatment in an air atmosphere.

3.6. Lattice constant of AZO

Fig. 5 shows the heat-treatment temperature dependence of the lattice constants of the *a*- and *c*-axes. The

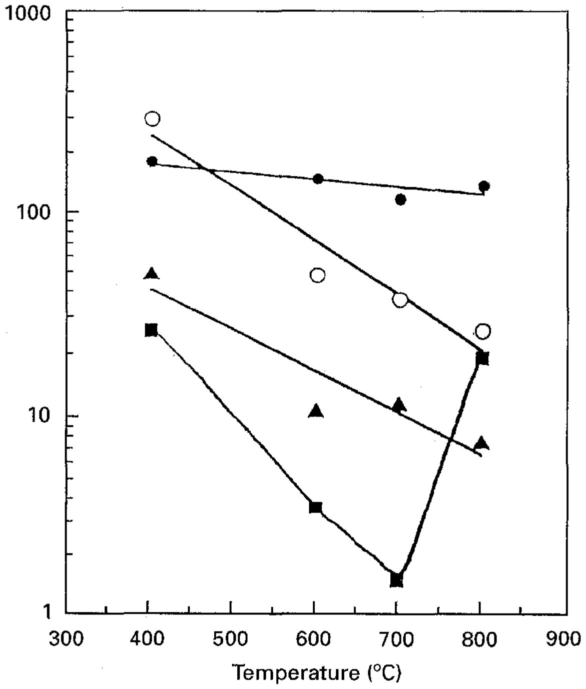

Figure 3 The dependence of resistivity on heat-treatment temperature of the thin films prepared from each solution. (●) Diethylenetriamine, (○) diethanolamine, (▲) monoethanolamine, (■) AcAc.

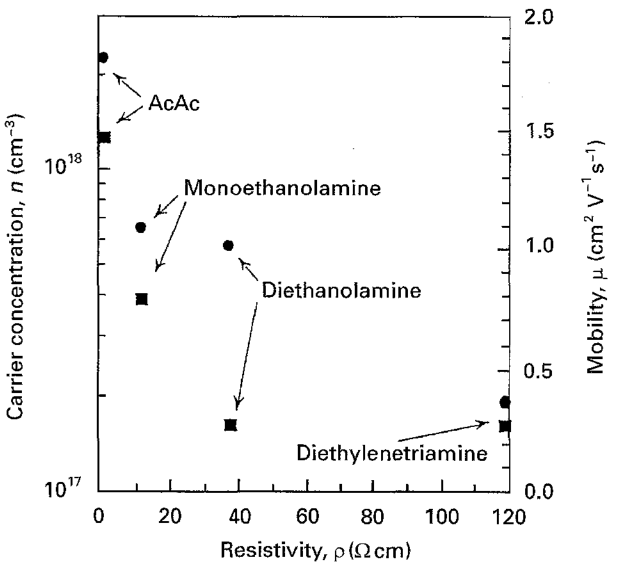

Figure 4 Relationship between resistivity, and (■) mobility and (●) carrier density of the thin films prepared from each solution.

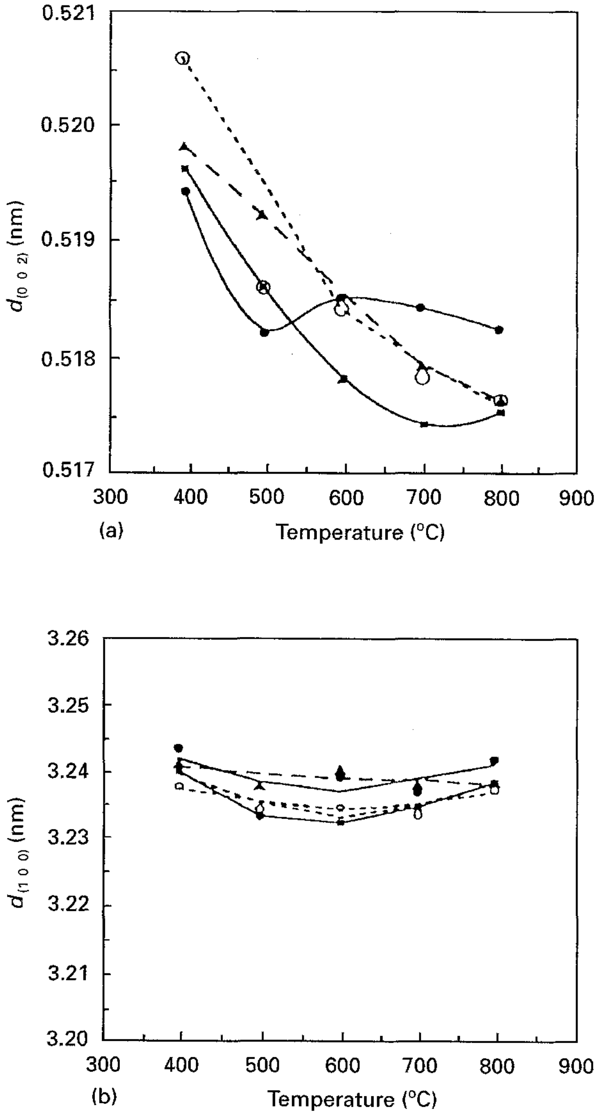

Figure 5 The dependence of lattice constants of the *a*-axis (1 0 0) and *c*-axis (0 0 2) on the heat-treatment temperature for thin films prepared from each solution: (a) *c*-axis direction, (b) *a*-axis direction. (●) Diethylenetriamine, (○) diethanolamine, (▲) monoethanolamine, (■) AcAc.

lattice constants of the *a*- and *c*-axes were calculated from (1 0 0) and (0 0 2) peaks of hexagonal closest packing. The lattice constant of the *a*-axis was not observed to change for the film prepared from solutions A, B, C and D. But the lattice constant of the *c*-axis decreased with increasing heat-treatment temperature, except for the thin film prepared from solution A.

3.7. Surface observation by SEM

Fig. 6 shows scanning electron micrographs of the thin film prepared from solutions A, B, C and D. The grain size increased with increasing heat-treatment temperature for thin films prepared from solutions C and D, and was observed to be oriented in the direction perpendicular to the substrate. No crystal particles were observed at a heat-treatment temperature of 700 °C for the thin film prepared from solution B. However, crystal particles were observed at a heat-treatment temperature of 400 °C for the thin film prepared from solution A, and exhibited a rough surface structure having pin holes.

3.8. Measurement of infrared spectra

Fig. 7 shows infrared spectra from the following solutions: (a) zinc acetic acid dissolved in H_2O, (b) aluminium nitrate dissolved in H_2O, (c) AcAc mixed in ethanol, and (d) the coating solution. The C=O peaks of keto- and enol-type were found at 1700 and 1620 cm^{-1}. The new peaks were found at 1600 and 1540 cm^{-1} for the coating solution (d). It was expected that the state of AcAc would be changed by dissolution of the raw materials.

4. Discussion

4.1. Orientation of thin films

The crystal growth in the *c*-axis direction was observed in the temperature range 400–500 °C for thin films prepared from solution D. The growth of the (0 0 2) plane was more remarkable for θ–2θ measurements than that of fixed θ measurement. It was considered that the orientation in the *c*-axis direction against the substrate was heightened.

4.2. Resistivity and lattice constant

In general, the grain boundary produced a larger effect on the electrical properties. The grain boundary decreased with increasing crystallization for thin films prepared from solutions C and D, and the resistivity decreased due to the increase in crystallization and orientation with increasing heat-treatment temperature. It was considered that the carrier mobility was

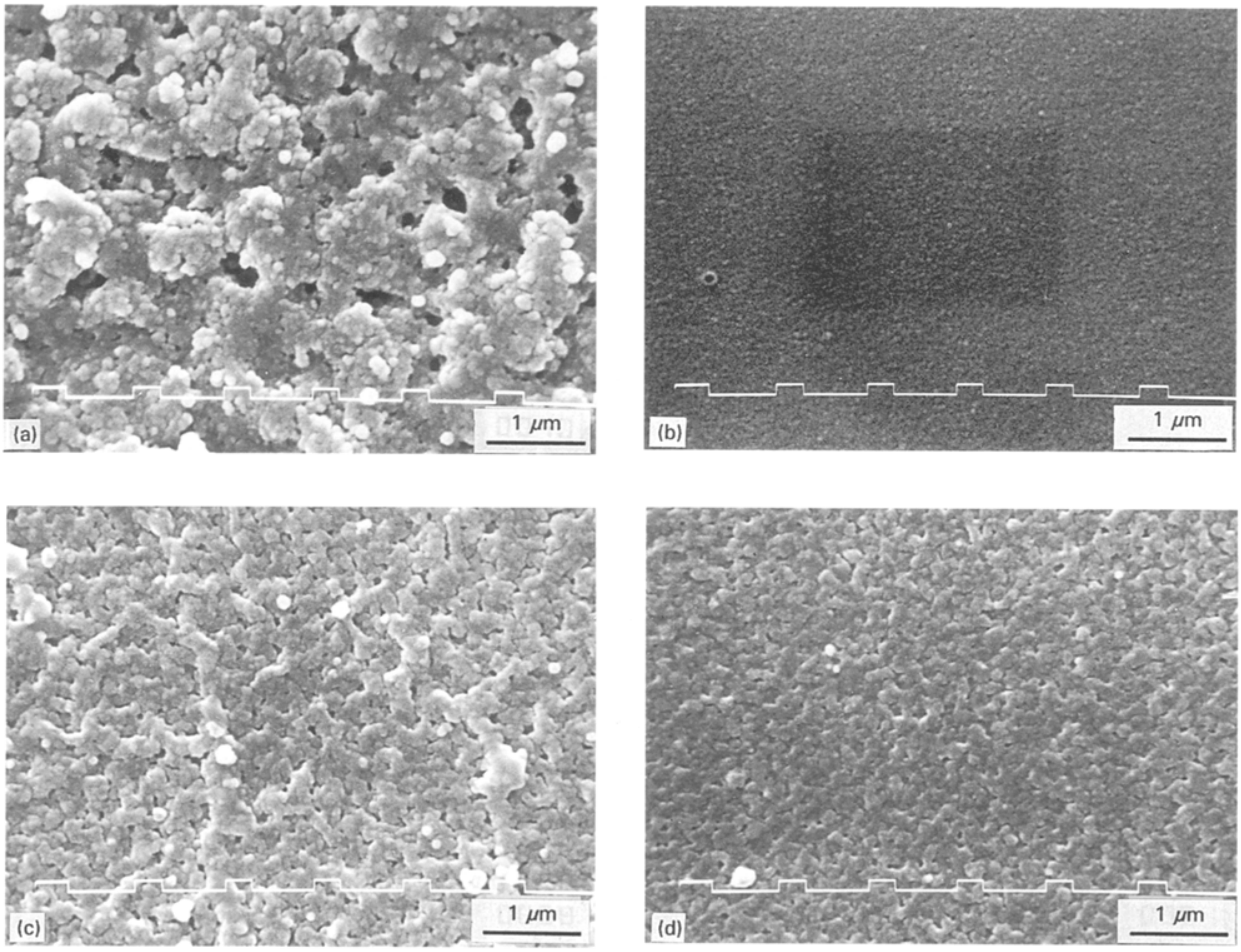

Figure 6 Scanning electron micrograph of the thin films prepared from each solution (heat treatment at 700 °C for 5 h); (a) solution A, (b) solution B, (c) solution C, and (d) solution D.

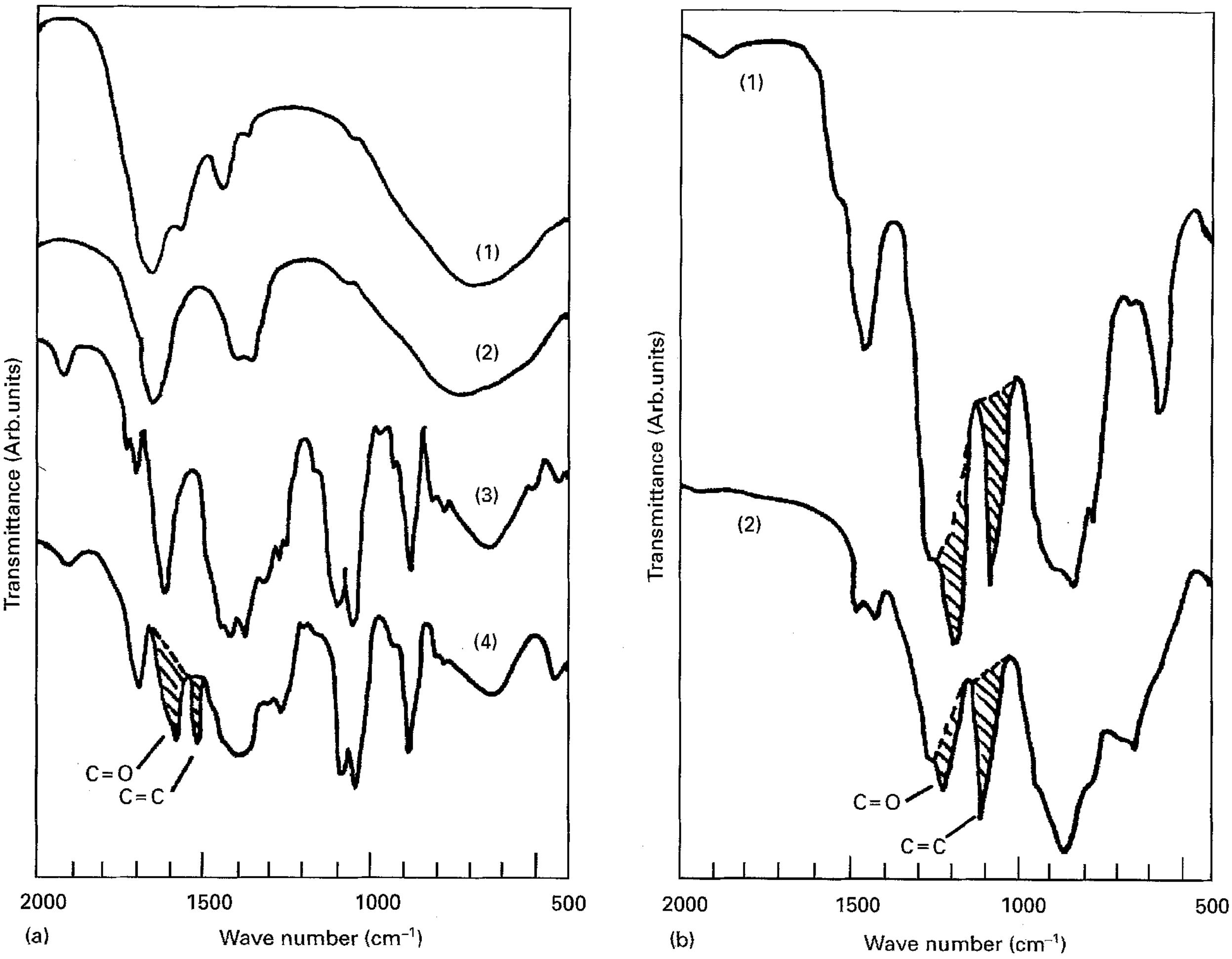

Figure 7 Infrared spectra obtained from the following solutions: (a) (1) zinc acetate + H_2O, (2) aluminium nitrate + H_2O, (3) ethanol + AcAc, (4) spin-coating solution. (b) (1) Zinc acetate + AcAc, (2) aluminium nitrate + AcAc.

larger with the alignment of the orientation of the crystals. On the other hand, the thin film prepared from solution A shows a higher resistivity due to the lower crystallization and orientation. The decrease in resistivity due to the atomic valence control mechanism, by a substitution of aluminium for zinc sites in ZnO for AZO thin films, and the lattice constant, are changed with increasing substitution. ZnO has a wurtzite structure and the Zn^{2+} ionic size is 0.071 nm and the Al^{3+} ionic size is 0.057 nm. Therefore, the lattice constant of the *c*-axis becomes distorted and smaller whilst that of the *a*-axis remains virtually unchanged by a binding due to the dense closest packing of oxygen. The lattice constant of the *a*-axis was found to remain almost unchanged for all solutions A–D, but the lattice constant of the *c*-axis decreased with increasing heat-treatment temperature. It was considered that the substitution of Al^{3+} to Zn^{2+} progressed with increasing heat-treatment temperature; the carrier density also increased.

4.3. Chelate formation of AcAc

Chelates of the ring type are formed by the reaction of AcAc and metal ions in the solution because the C=O peak at 1600 cm^{-1} is due to the incorporation of metal ions in coating solution D, and the C–C peak at 1540 cm^{-1} appeared owing to the formation of the ring-type structure. The optimum pH is 5.5–7 for zinc and 4 for aluminium for the formation of chelates of AcAc. The formation of the chelate was expected because the measured pH of the solution was 5.

4.4. Solvent effect and orientation

The differences in the orientation and resistivity are considered to be due to the differences in the coordination power and the boiling points of the solvents. The ligands of the solvent are nitrogen and oxygen atoms. The diethylenetriamine has three nitrogen atoms, diethanolamine has one nitrogen atom, monoethanolamine has one nitrogen atom and one oxygen atom and AcAc has two oxygen atoms. In general, the coordination power of the oxygen atom is stronger than that of the nitrogen atom. The boiling points of the solvents are as follows; diethanolamine (271 °C) > diethylenetriamine (207.1 °C) > monoethanolamine (171.1 °C) > AcAc (140 °C). The two Zn–O bonds may be formed at the lower temperature in the solution due to the ring type chelates formed by AcAc. The orientation to the substrate increased at the relatively low temperature of 200 °C and then increased with increasing heat-treatment temperature. As a result, the resistivity decreased with increasing high orientation in the direction of the *c*-axis.

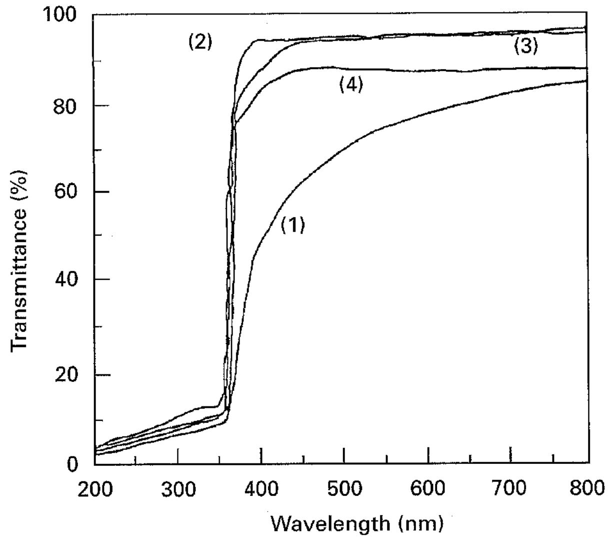

Figure 8 Visible spectral transmittance of AZO thin films prepared from each solution. (1) Diethylenetriamine, (2) diethanolamine, (3) monoethanolamine, (4) AcAc.

4.5. Transmittance

The thin film prepared from solution B (0.4 μm thick), solution C (0.3 μm thickness) and solution D (0.15 μm thickness) showed a transmittance of above 85% (Fig. 8). In particular, the films prepared from solutions C and D were considered to be very useful as transparent conductive thin films.

5. Conclusions

1. Aluminium-doped ZnO (AZO) transparent thin films were prepared by the sol–gel process from four types of solution (A, B, C and D).

2. Aluminium-doped ZnO (AZO) thin films prepared from solutions C and D were found to be orientated in the direction of the *c*-axis of the substrate when zinc acetate and aluminium nitrate were used as raw materials and monoethanolamine (solvent C) and AcAc (solvent D) were used as solvents.

3. The highly orientation thin films prepared from solutions C and D were attributed to a chelate formation in the aluminium-doped ZnO (AZO) by the solvent effect.

4. The resistivity of the thin films prepared from solution D was 1.54 Ω cm after heat treatment at 1 atm and 1.54×10^{-3} Ω cm under a reduced atmosphere.

5. The thin films prepared from solutions C and D showed a transmittance in excess of 85%.

References

1. Y. SAWADA, *Mater. Forum* **6** (1986) 15 (in Japanese).
2. D. J. GOYAL, CHITRA AGASHE, M. G. TAKWALE and V. G. BHIDE, *J. Mater. Res.* **8** (1993) 1052.
3. T. SUZUKI, *J. Mater. Sci. Lett.* **7** (1988) 79.
4. *Idem, ibid.* **6** (1987) 1086.
5. N. SRINIVASA MURTY, *Thin Solid Films* **92** (1982) 347.
6. G. FRANK, *ibid.* **77** (1981) 107.
7. T. TSUCHIYA, T. EMOTO and T. SEI, *J. Non-Cryst. Solids* **178** (1994) 327.
8. E. KATO, T. SEI and T. TSUCHIYA, *J. Ceram. Soc. Jpn* **102** (1994) 818.
9. *Idem, ibid.* **178** (1994) 333.

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