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Preparation of Al doped ZnO thin films by Liquid-Delivery MOCVD

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Al doped ZnO thin films were prepared by a liquid-delivery MOCVD (Metal Organic Chemical Vapor Deposition) method using the complexes whose solubility to organic solvents is high as precursors. The influence of the oxygen flow rate, the reactor pressure and the kind of precursors in film deposition on the metal composition in films, the surface roughness and the resistivity of the obtained films was investigated. In the optimized deposition conditions, the resistivity and transparency of the 230 nm-thick film prepared on glass substrate at 550°C were $3\times10^{-3}\Omega$cm and more than 90% in the visible range, respectively.
Key words: ZnO, transparent conductive oxide, metalorganic precursor, β-diketonate, MOCVD

1. INTRODUCTION

Al doped ZnO (AZO) films have been investigated for application to the transparent conductive films for organic light-emitting devices and liquid-crystal displays because they are highly conductive and less expensive than In_2O_3-SnO_2 (ITO). If AZO films can be fabricated by MOCVD method, which has advantages such as high deposition rate and good step coverage, more applications will be realized. In preparation of AZO films by conventional MOCVD method, alkyl metals such as $ZnEt_2$ and $AlMe_3$ and acetylacetonates such as $Zn(acac)_2$ and $Al(acac)_3$ were used as precursors(1)(2). Alkyl metals such as $ZnEt_2$ and $AlMe_3$ have higher volatility than β-diketonates such as $Zn(acac)_2$ and $Al(acac)_3$. It is difficult, however, to control the vapor phase reaction and the surface morphology of films because the alkyl metals are highly reactive with oxygen. Moreover, the acethylacetonato complexes, which are generally used for preparing oxide films, cannot be vaporized below the decomposition temperature by a bubbling method, which is one of the methods to vaporize precursors with a constant rate, because of their low thermal stability and high melting point. In the case that solid precursors are used, a liquid-delivery method can be adopted as the appropriate method to vaporize precursors. In this method, the solution prepared by dissolving solid precursors into organic solvent, is introduced by a fixed flow rate and completely vaporized in the vaporizer. Thereby a constant vaporization rate of precursors is obtained. However, the solubility of the acetylacetonato complexes in organic solvents was too low to be used as precursors for

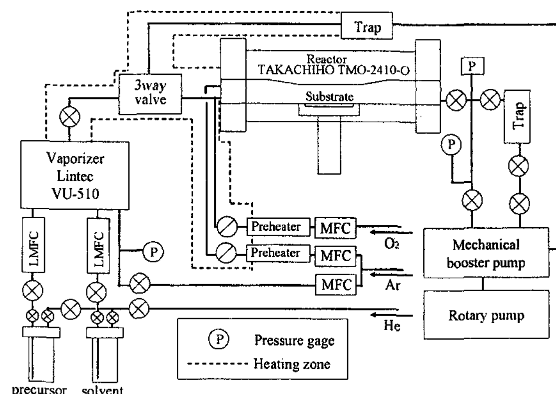

Fig. 1 Schematic diagram of the liquid-delivery MOCVD apparatus.

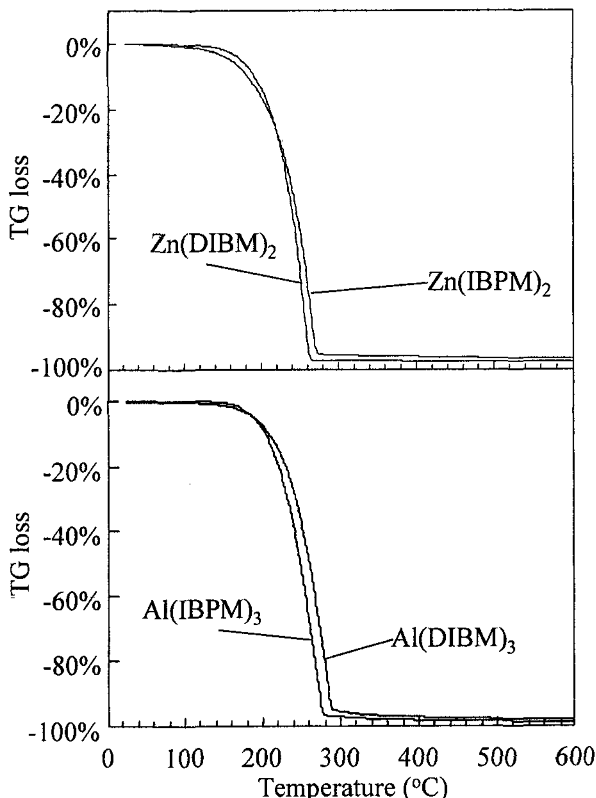

Fig. 2 TG curves of Zn and Al complexes.

liquid-delivery (LD)-CVD. On the other hand, the complexes which have high solubility in organic solvents can be obtained by using some β-diketones except acetylacetone as ligands, e.g., diisobutyrylmethane (DIBM) and isobutyrylpivaloylmethane (IBPM). Therefore, the complexes of Zn and Al with these ligands were synthesized and AZO thin films were prepared by liquid-delivery MOCVD method.

2. EXPERIMENTAL

Zn and Al complexes with DIBM and IBPM ligands were synthesized by a known method[3]. The volatility and thermal stability of those complexes were confirmed by thermogravimetric analysis (TGA) in argon flow atmosphere at the rate of 200 ml/min, and the solubility in the solvents generally used in LD-MOCVD was investigated. Preparation of AZO thin films was carried out by means of the liquid-delivery MOCVD apparatus shown in Fig. 1. The apparatus consists of a vaporizer (Lintec Co., Ltd., VU-510) and a cold-wall type reactor (Takachiho Trading Co., Ltd., TMO-2410-O). The precursor solutions were prepared by mixing 0.02 mol/kg toluene solution of the Zn complexes and 0.02 mol/kg toluene solution of Al complexes with various ratios. The flow rates of precursor solution, carrier gas and oxygen gas were 0.5 g/min, 200 ml/min and 209-557 ml/min, respectively. The vaporizer temperature was fixed at 160°C. Corning 1737 glass of 3 inch diameter was selected as a substrate. The substrates were heated at 550°C and rotated at 4 rpm. The reason why the substrate temperature was fixed at 550°C is that both good surface morphology and high deposition rate were obtained in ZnO film preparation. The reactor pressure was set at 10 torr(1.3 kPa) or 30 torr(4 kPa). The amounts of Zn and Al in the obtained films were determined by inductively coupled plasma spectrometry (ICP).

3. RESULTS AND DISCUSSION

The TG curves of the synthesized complexes were shown in Fig. 2. Any complex vaporized completely below 300°C. Those volatilities were relatively high in all the β-diketonates. Table I shows the solubility of the complexes in some organic solvents. The solubility of any complex was high enough to be utilized as a precursor for LD-CVD. To optimize deposition conditions, oxygen flow rate and reactor pressure were varied. The ratio of Al complex to the sum of Zn and Al complexes in precursor solution was fixed at 1 mol%. The dependence of the deposition rate of Zn on oxygen flow rate was shown in Fig. 3. The deposition rate of Zn at 10 torr increased independent of the kind of precursors by increasing oxygen flow rate, but the effect of oxygen flow rate on the deposition rate of Zn was not observed at 30 torr. The Al content in the films obtained at 10 torr decreased by increasing oxygen flow rate but that at 30 torr was unchanged.

The root mean square (RMS) of surface roughness in 4 μm×4 μm area measured by AFM (Atomic Force Microscopy) was shown in Fig. 4. The effect of oxygen flow rate on the surface roughness of the films prepared at 30 torr was not observed but the surface roughness of the films prepared at 10 torr was inclined to increase by increasing oxygen flow rate. Moreover, the RMS values of the films obtained from IBPM precursor solutions was more than that from DIBM precursor solutions.

Table I Melting point and solubility of Zn and Al complexes.

complexes	m.p. (°C)	solubility		
		toluene	n-butyl acetate	THF
$Zn(IBPM)_2$	<20	A	A	A
$Zn(DIBM)_2$	80	S	A	S
$Al(IBPM)_3$	188	C	E	B
$Al(DIBM)_3$	152	A	D	A

S:>1mol/l A:1-0.5mol/l B:0.5-0.33mol/l C:0.33-0.25mol/l D:0.25-0.2mol/l E:<0.2mol/l

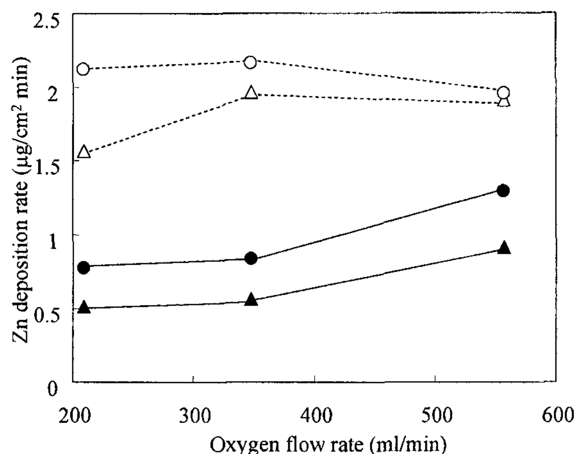

Fig. 3 Dependence of Zn deposition rate on oxygen flow rate.

10 torr;▲$Zn(DIBM)_2$-$Al(DIBM)_3$, ● $Zn(IBPM)_2$-$Al(IBPM)_3$
30 torr;△$Zn(DIBM)_2$-$Al(DIBM)_3$, ○ $Zn(IBPM)_2$-$Al(IBPM)_3$

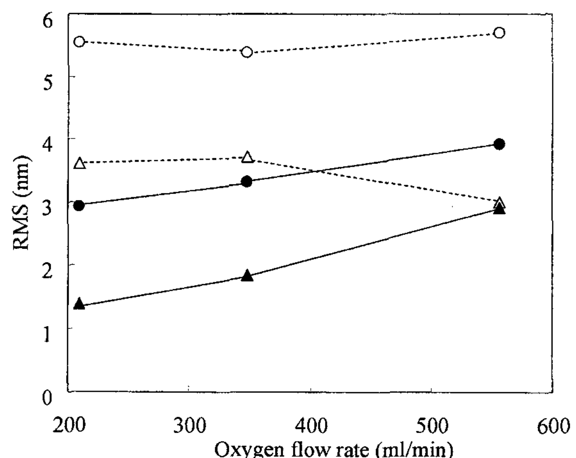

Fig. 4 Dependence of RMS on oxygen flow rate.

10 torr;▲$Zn(DIBM)_2$-$Al(DIBM)_3$, ● $Zn(IBPM)_2$-$Al(IBPM)_3$
30 torr;△$Zn(DIBM)_2$-$Al(DIBM)_3$, ○ $Zn(IBPM)_2$-$Al(IBPM)_3$

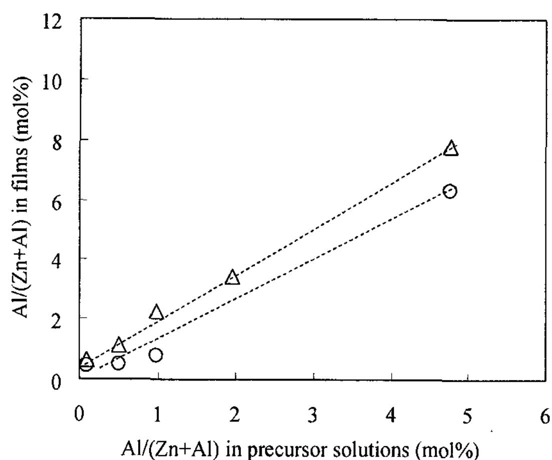

Fig. 5 Relationship between Al content in precursor solutions and in films.

30 torr; Δ $Zn(DIBM)_2$-$Al(DIBM)_3$, O $Zn(IBPM)_2$-$Al(IBPM)_3$.

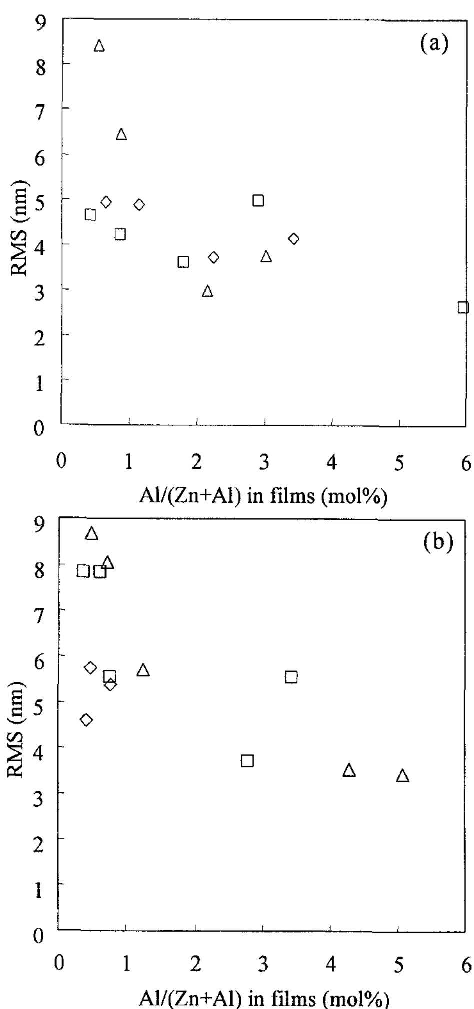

Fig. 6 Dependence on RMS on Al content in films.
(a) $Zn(DIBM)_2$-$Al(DIBM)_3$
(b) $Zn(IBPM)_2$-$Al(IBPM)_3$

O_2 flow rate (ml/min); ◇ 209, □ 348, △ 557.

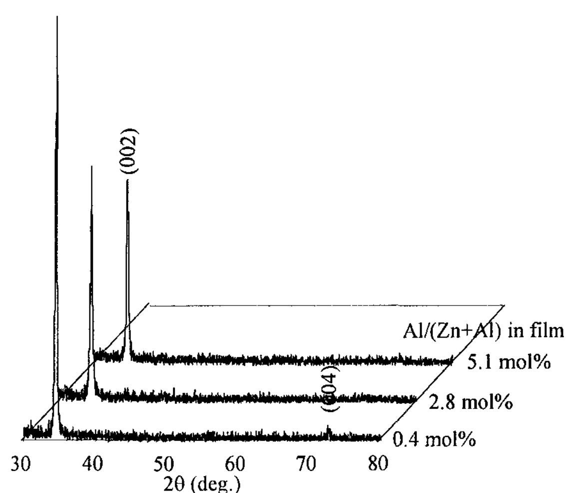

Fig. 7 Dependence of intensity on Al content in films.

Sub. Temp; 550°C
Precursors; $Zn(IBPM)_2$-$Al(IBPM)_3$
Reactor pressure; 30 torr

The relationship between Al contents in precursor solutions and in films was shown in Fig. 5. The reactor pressure was fixed at 30 torr because of high deposition rate and low influence of oxygen flow rate on deposition rate and RMS. When the Al contents in the precursor solutions increased, the Al contents in the films also increased on both of the precursor solutions. When the precursor solutions which have the same Al contents were used, the Al contents in the films prepared from DIBM precursor solutions were higher than that from IBPM precursor solutions.

Figure 6 shows the dependence of surface roughness (RMS) on the Al contents in films. When the Al contents in the films increased, RMS values were decreased independent of the kind of precursor solutions. As shown in Fig. 7, since the intensity of observed peaks became smaller by increasing the Al contents in films, it is found that the existence of Al as an impurity inhibited the growth of ZnO crystal.

The dependence of resistivity of the films on Al contents in films was shown in Fig. 8. When the oxygen flow rate was high, the resistivity was inclined to be low. The lowest resistivity of the films obtained from IBPM and DIBM precursor solutions was observed in the ranges of 0.5-1mol% and 1-2mol% of Al contents in films, respectively. However, the lowest resistivity was $10^{-2}\Omega$cm order, which is higher than the resistivity of conventional transparent conductive films by two orders of magnitude. Therefore, annealing in vacuo was carried out in order to generate oxygen vacancies in films. The annealing condition was heating at 550°C for 1 hour in vacuo. As the result, the resistivity after annealing lowered by one to two orders of magnitude and the influence on the oxygen flow rate in deposition conditions disappeared.

Finally, the transparency of a film was measured by UV-VIS spectrometry. The average transparency of

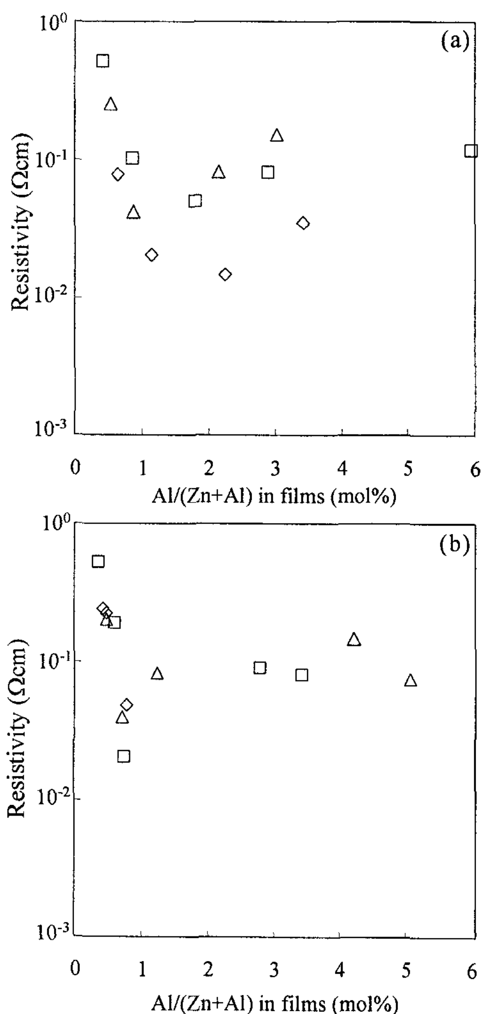

Fig. 8 Dependence of resistivity on Al content in films.
(a) $Zn(DIBM)_2$-$Al(DIBM)_3$
(b) $Zn(IBPM)_2$-$Al(IBPM)_3$
O_2 flow rate (ml/min); ◇ 209, □ 348, △ 557

about 230nm-thick film in the range of 400-800 nm was more than 90% as shown in Fig. 9. This transparency

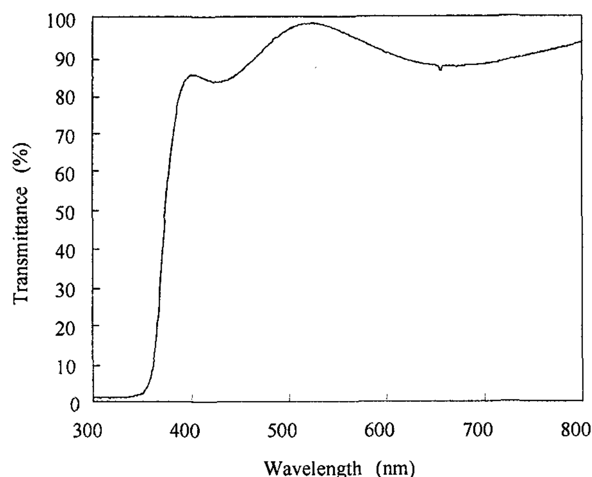

Fig. 9 Transparency of Al doped ZnO thin films.
$Zn(DIBM)_2$-$Al(DIBM)_3$
Film thickness; 229nm
Al/(Zn+Al); 0.8mol% in the film

was high enough to be used as a transparent conductive film.

4. CONCLUSIONS

Al doped ZnO thin films were prepared by a liquid-delivery MOCVD method using the complexes whose solubility to organic solvents is high as precursors. IBPM complexes of Zn and Al resulted in higher deposition rate than DIBM complexes but the resistivity of films was $3\text{-}5\times10^{-3}\Omega$cm independent of the kind of precursors.

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