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Evaluation of Some Indium β-Diketonates as a Precursor for Preparing In_2O_3 Thin Films by MOCVD

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Some indium β-diketonates such as tris(dipivaloylmethanato)indium ($In(DPM)_3$), tris(diisobutyrylmethanato)indium ($In(DIBM)_3$), tris(isobutyrylpivaloylmethanato)indium ($In(IBPM)_3$) and tris(2,2,6,6-tetramethyl-3,5-octanedionato)indium ($In(TMOD)_3$) were synthesized and evaluated as MOCVD precursors. Though In_2O_3 films could be obtained at the substrate temperature of 500°C using each indium compound as a precursor, the films were deposited with only $In(acac)_3$ and $In(DIBM)_3$ in the temperature lower than 350°C. The resistivity of the film with $In(acac)_3$ deposited over 440°C was the order of 10^{-3} Ω cm and the same resistivity was obtained in the film with $In(DIBM)_3$ over 400°C

Key words: MOCVD, indium oxide, thin film, precursor, β-diketonate

1. INTRODUCTION

Indium oxide (In_2O_3) films which have good transparency and conductivity are suitable for applications such as transparent electrodes of liquid crystal and solar cells. Generally, In_2O_3 films are fabricated by sputtering or vacuum evaporation. If In_2O_3 films can be fabricated by MOCVD, they will be adopted for more applications. However, the films fabricated by MOCVD are inferior to the films by sputtering.

When In_2O_3 thin films were fabricated by MOCVD, alkoxide[1], β-diketonate[2,3], carboxylate[4], chloride[5] and alkyl[6] indium compounds were used as precursors. In those compounds, β-diketonates are one of the most popular precursors for fabricating oxide thin films because of their thermal and chemical stability. β-diketonates have a lot of kinds but only dipivaloylmethanato (DPM) complex and acetylacetonato (acac) complex were used as MOCVD precursors in previous studies of fabricating In_2O_3 films.

In this study, we synthesized some indium β-diketonates and evaluated In_2O_3 thin films fabricated using them by MOCVD process.

2.EXPERIMENTAL

Five indium complexes, tris[dipivaloylmethanato] indium ($In(DPM)_3$), tris[2,2,6,6-tetramethyl-3,5-octanedionato]indium ($In(TMOD)_3$), tris[isobutyrylpivaloylmethanato]indium ($In(IBPM)_3$), tris[diisobutyrylmethanato]indium ($In(DIBM)_3$) and tris[acetylacetonato] indium ($In(acac)_3$), were evaluated as MOCVD precursors for fabrication of In_2O_3 thin films. Their molecular structures are shown in Figure1. They were synthesized from indium nitrate hydrate and sodium β-diketonate. The obtained complexes were characterized by FT-IR, ^{1}H-NMR and indium content analysis. The volatility and the stability to heat and oxidation were expected from thermogravimetry (TG) and differential thermal analysis (DTA) data. Both measurements are undertaken in argon and dry air flow atmosphere.

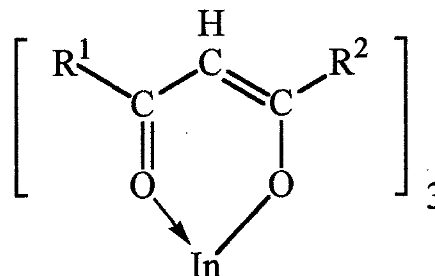

Fig.1 Molecular structures of indium β-diketonates; R^1=R^2=*t*-Bu:$In(DPM)_3$;R^1=*t*-Bu,R^2=$C(CH_3)_2C_2H_5$:$In(TMOD)_3$;R^1=*t*-Bu,R^2=*i*-Pr:$In(IBPM)_3$,R^1=R^2=*i*-Pr:$In(DIBM)_3$;R^1=R^2=CH_3:$In(acac)_3$.

Table I Deposition conditions.

Source temperature	140°C
Ar carrier gas flow rate	100ccm
O_2 gas flow rate	100ccm
Reactor pressure	30torr
Substrate temperature	320-500°C
Substrate	Si(100)
Deposition time	1h

Table II Characterization of indium β-diketonates.

Complex	Melting Point(°C)	NMR(d,ppm C_6D_6)	IR $\nu_{C=O}$ (cm^{-1})	In content (%) calcd.	In content (%) found
$In(DPM)_3$	167	1.17(54H,s), 5.85(3H,s)	1551	17.3	17.3
$In(TMOD)_3$	110	0.75(9H,s), 1.06(27H,s), 1.21(18H,t), 1.61(6H,q),	1553	16.2	16.2
$In(IBPM)_3$	99	1.10(18H,d), 1.18(27H,s), 2.30(3H,m), 5.51(3H,s)	1560	18.4	19.1
$In(DIBM)_3$	92	1.10(36H,d), 2.25(6H,m), 5.35(3H,s)	1568	19.8	20.4
$In(acac)_3$	190	1.56(18H,s), 5.50(3H,s)	1576	27.9	27.6

In_2O_3 thin films were fabricated by the MOCVD apparatus with a hot-wall type reactor. A 15×15 mm Si(100) was used as a substrate. The substrate was placed on the susceptor which inclined at 15 degrees in the gas flow in the chamber. Deposition conditions are shown in Table I. The film thickness was measured by fluorescent X-ray (XRF) and scanning electron microscopy (SEM).The crystallinity of the film was analyzed by using X-ray diffractometer (XRD). The electric resistivity was measured by the van der Pauw method.

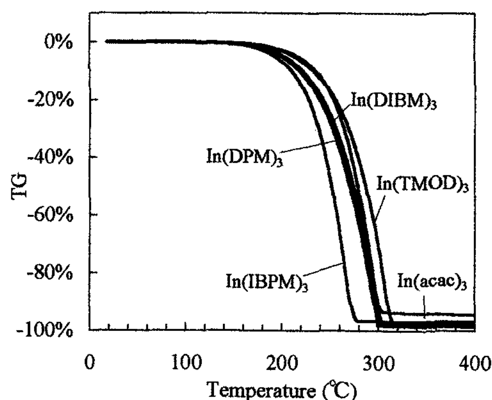

Fig.2. TG curves of indium β-diketonates.

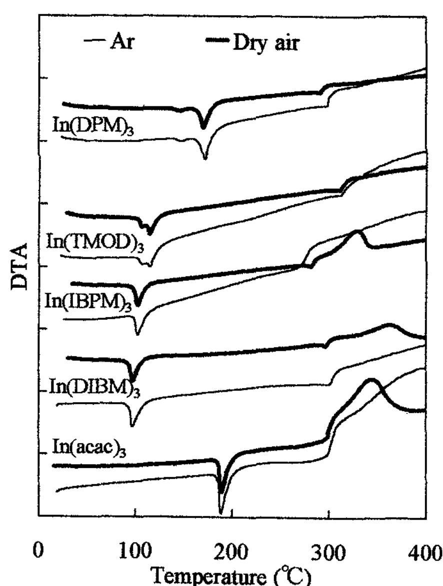

Fig.3. DTA curves of indium β-diketonates measured under argon and dry air flow atmosphere.

3.RESULTS AND DISCUSSION

3.1 Properties of indium complexes

As shown in Table II, the results of FT-IR, 1H-NMR and indium content analysis indicates that the desired complexes were formed.

The TG curves of the indium β-diketonates are shown in Figure.2. Their TG weight loss finished by 300°C. The volatility of the indium β-diketonates is relatively high as compared to the other metal β-diketonates. Figure 3 shows the DTA curves measured under argon and dry air flow atmosphere. Since the obvious difference between the curves in argon and those in dry air were not observed, it is found that these indium complexes have high stability to oxygen.

3.2 Deposition of In_2O_3 thin films

Figure 4 shows the XRD patterns of the obtained films. The deposition of In_2O_3 thin films was carried out using each indium complex as a MOCVD precursor on Si(100) at 500°C of the substrate temperature. It is confirmed that all the films are preferentially a-axis oriented In_2O_3.

The dependence of the film thickness measured by XRF on the substrate temperature is shown in Figure5. When the substrate temperature was lowered, no film was obtained at less than 400°C using $In(DPM)_3$ as a precursor and at less than 380°C using $In(IBPM)_3$ and $In(TMOD)_3$. In the case of using $In(acac)_3$ and $In(DIBM)_3$, the films could be obtained at temperatures above 320°C and 340°C, respectively. This indicates $In(acac)_3$ and $In(DIBM)_3$ have higher reactivity to oxygen than the other three complexes. The difference of the reactivity seems to be attributable to the strength

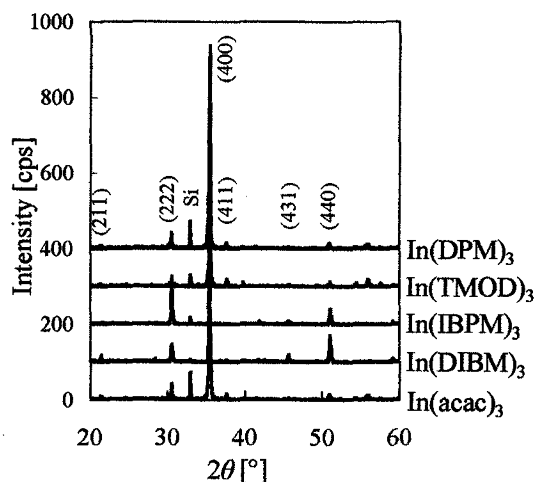

Fig.4. XRD patterns of In_2O_3 films deposited at 500°C.

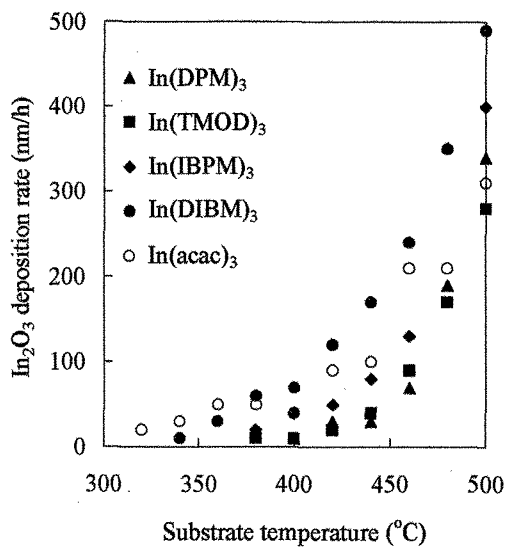

Fig.5. Dependence of deposition rate on the substrate temperature.

of the bond between indium and ligands. The order of wave number of C=O stretching vibration shown in Table II corresponds to that of the depositable substrate temperature. As the wave number increased, the depositable substrate temperature decreased. The more wave number of C=O stretching vibration indicates that the length of the C=O bond is shorter. The shorter C=O bond indicates O-In bond is longer and the strength of the O-In bond is weaker. Weaker O-In bond causes decomposition of the complex at lower temperature. It can be presumed that the oxygen including In_2O_3 films came from not their ligands but oxygen gas used as an oxidant from the above discussion.

Figure 6 shows the electric resistivities of the In_2O_3 films using $In(acac)_3$ and $In(DIBM)_3$ as precursors as a function of substrate temperature. The resistivity of the

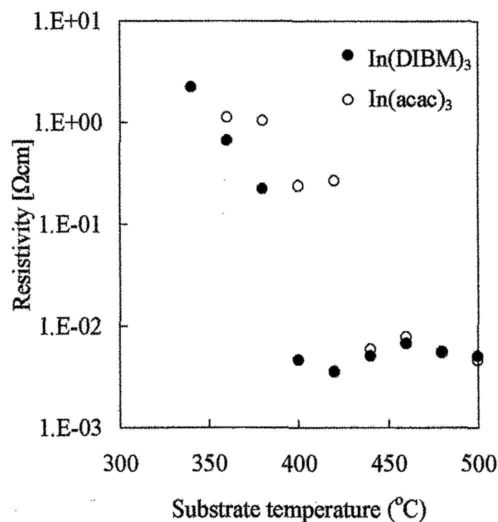

Fig.6. Dependence of the electric resistivity of the films deposited using $In(DIBM)_3$ and $In(acac)_3$ on the substrate temperature.

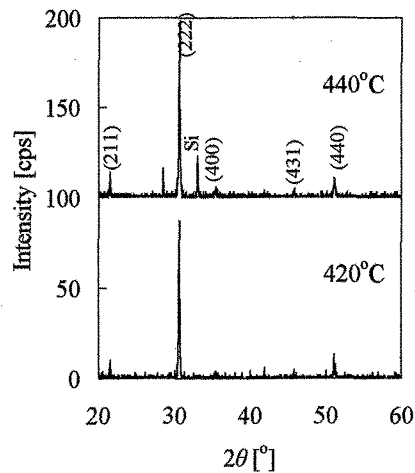

Fig.7. XRD patterns of the In_2O_3 films deposited with $In(DIBM)_3$ at 420°C and 440°C.

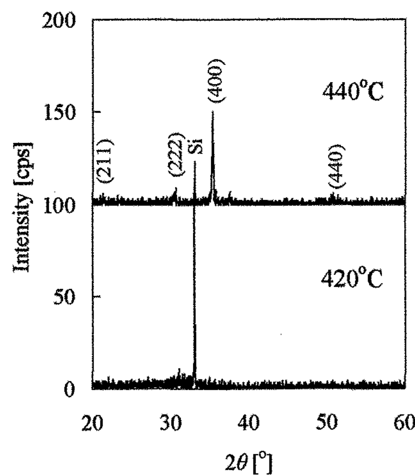

Fig.8. XRD patterns of the In_2O_3 films deposited with $In(acac)_3$ at 420°C and 440°C.

films deposited with $In(acac)_3$ over 440°C was the order of 10^{-3}ohmcm, and the similar resistivity was obtained in the film with $In(DIBM)_3$ over 400°C.

The XRD patterns of the In_2O_3 films deposited at 420°C and 440°C are shown in Figures 7 and 8. Both patterns of the films deposited with $In(DIBM)_3$ at 420°C and 440°C indicate the films were crystallized with no orientation. In case of $In(acac)_3$, the pattern of the film deposited at 440°C indicates the film was crystallized with preferential a-axis orientation, while no peak was observed from the film deposited at 420°C.

The SEM images of the In_2O_3 films deposited at 420°C and 440°C are shown in Figures 9 and 10. It is observed that crystal grains were grown with a columnar structure in the films deposited with $In(DIBM)_3$ at 420°C and 440°C and with $In(acac)_3$ at 440°C. However, obvious crystal grains were not observed in the film deposited with $In(acac)_3$ at 420°C. This supports the results of the XRD patterns shown in Figures 7 and 8. Furthermore, the thickness of the film deposited with $In(acac)_3$ at 420°C measured from its cross-sectional SEM image was much larger than that measured by XRF. This indicates the film has low density.

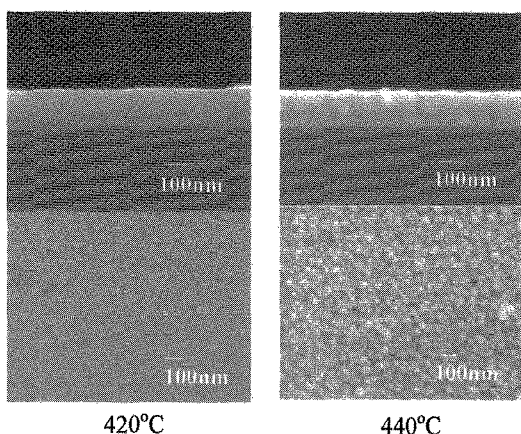

Fig.9. SEM images of the In_2O_3 films deposited with $In(DIBM)_3$ at 420°C and 440°C. upper: cross section, lower: surface.

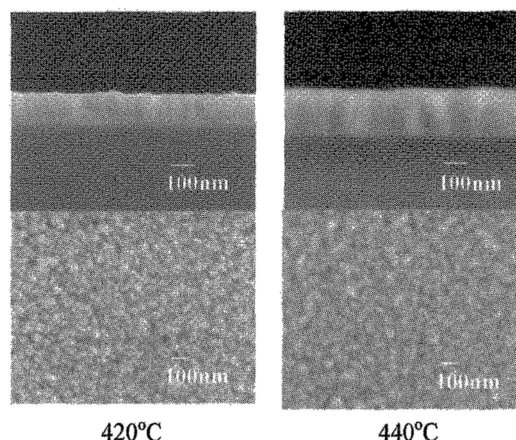

Fig.10. SEM images of the In_2O_3 films deposited with $In(acac)_3$ at 420°C and 440°C. upper: cross section, lower: surface.

4.CONCLUSION

Five indium *β*-diketonates were synthesized and evaluated as MOCVD precursors. In_2O_3 films could be deposited with only $In(acac)_3$ and $In(DIBM)_3$ in the temperature lower than 350°C. The resistivity of the film with $In(acac)_3$ deposited over 440°C was the order of 10^{-3} Ωcm and the same resistivity was obtained in the film with $In(DIBM)_3$ over 400°C. It was confirmed that the crystalline In_2O_3 films could be obtained using $In(DIBM)_3$ at lower temperature than using $In(acac)_3$.

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