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The X-ray single crystal structure of $[Me_2In(acac)]_2$ and its use as a single-source precursor for the deposition of indium oxide thin films

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Crystalline dimethyl(pentane-2,4-dionato)indium(III), $[Me_2In(acac)]_2$, has been prepared by the reaction of dimethylindium methoxide and pentane-2,4-dione in toluene. An X-ray structure determination shows that in the solid state, the complex is dimeric. $[Me_2In(acac)]_2$ has been used as a single-source precursor for the deposition of cubic In_2O_3 thin films by low pressure metal–organic chemical vapour deposition (LP-MOCVD) at temperatures ranging from 350 to 450 °C, on borosilicate glass, Si(100) and GaAs(111) substrates. All the as-deposited indium oxide films are single phase, cubic-In_2O_3.

1. Introduction

Doped and undoped indium oxide thin films are attractive materials for use as transparent conductors, in applications such as display panels and solar cell windows.[1] Undoped indium oxide has found use in industrial and technological applications due to both its transparency and conductivity and has a direct band gap of 3.75 eV[2] for single crystals and 3.65 eV[3] for thin films. Indium oxide can be doped with other metals to enhance its electronic properties; Sn-doped indium oxide (ITO) can be prepared and its band-gap and resistivity values vary with its level of doping.[4] Indium oxide films are generally polycrystalline with the same cubic structure as the bulk material (a = 10.118 Å).[5] Some single-source precursors have been used to prepare thin films of indium oxide including the homoleptic β-diketonates $[In(acac)_3]$[6] (acac = pentane-2,4-dionate) and $[In(tmhd)_3]$[7] (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate), Me_3In[8] and $[In\{O_2C(C_7H_{15})\}_3]$.[9] Reich *et al.*[7] reported the preparation of indium oxide using $[In(tmhd)_3]$ by plasma-enhanced chemical vapour deposition (PECVD). The films were deposited at temperatures between 250 and 400 °C. Maruyama and Kitamura[8] also deposited In_2O_3 at 330 °C from Me_3In and O_2 by PECVD. The related dibutylindium compounds, $^nBu_2InL$ [L = O^{t}Bu, OPh, acac, O_2CEt, $O_2CCH(Et)(CH_2)_3Me$], have been used with dibutyltin oxide to prepared indium tin oxide. The ITO films were prepared at 400–450 °C by the pyrolysis of solutions of the precursors spread onto glass substrates.[10]

Here, we report the synthesis of the dialkylindium β-diketonate complex, $[Me_2In(acac)]_2$, and its characterisation by spectroscopic and structural methods. Further, we report the use of $[Me_2In(acac)]_2$ as a single-source precursor for the deposition of indium oxide thin films by low pressure MOCVD onto borosilicate glass, Si(100) and GaAs(111) substrates.

2. Experimental section

Dimethylindium methoxide was a gift from Epichem Ltd. Toluene (BDH) was distilled over Na-benzophenone and degassed prior to use. Pentane-2,4-dione (acetylacetone, acacH) was used as purchased from Aldrich. All manipulations and reactions were carried out in an inert atmosphere using Schlenk techniques and a vacuum line. Low-pressure growth experiments were carried out at *ca.* 10^{-2} Torr and the films were deposited on borosilicate glass, silicon(100) or gallium arsenide(111) substrates by LP-MOCVD. Growth experiments were carried out in a low-pressure cold-walled reactor without carrier gas, as has been described elsewhere.[11]

Preparation and characterisation of dimethyl(pentane-2,4-dionato)indium(III), $[Me_2In(acac)]_2$

Dimethylindium methoxide (5.50 g, 32.3 mmol) was placed in a flask with dry toluene (~20 ml) and cooled to 0 °C. Pentane-2,4-dione (2.92 mL, 30.0 mmol) was slowly added to the mixture, which was stirred for 1 hour at room temperature. A white crystalline solid formed on the addition of the β-diketone, which was subsequently isolated by removal of the solvent *in vacuo*. Yield = 98% (based on acacH); mp 133 °C. ^{1}H NMR (δ, C_6D_6, 400 MHz): 0.11 [6H, s, In–CH_3]; 1.70 [6H, s, C–CH_3]; 4.97 [1H, s, C–H]. ^{13}C NMR (δ, C_6D_6, 100 MHz): −3.75 [In–CH_3]; 28.20 [CH_3]; 100.64 [C–H]; 192.00 [C–O]. Microanalysis: Calculated for $[C_7H_{13}InO_2]_2$: C, 34.46; H, 5.37%. Found: C, 34.38; H, 5.17%. IR (Nujol mull, cm^{-1}): 538, 662, 723, 791, 922, 1020, 1163, 1252, 1520, 1595, 1948, 2301, 2735. Mass spectrum: *m/z* (significant peaks, L = acac) 473, $[LMe_2In_2Me_2OCMeCHCO]^+$; 443, $[LMe_2In_2MeOCCHCO]^+$; 359, $[LMe_2In_2]^+$; 245, $[LMe_2In]^+$; 215, $[Me_2InOCCHCO]^+$.

Physical measurements

NMR spectra were recorded using a Bruker AM400 pulsed Fourier-transform spectrometer. Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer as Nujol mulls between potassium bromide plates. X-Ray powder diffraction

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analysis was performed with a Siemens D500 automated diffractometer. Samples were mounted flat, and scanned from 10–60° in steps of 0.2°, with a count time of 10 s. Electron microscopy and energy dispersive analytical X-ray analysis (EDAX) was carried out on a JEOL J535CM scanning electron microscope with a LINK QX2000 energy dispersive X-ray analysis unit. Microanalyses were carried out by the service at Imperial College. Melting points were recorded in sealed tubes with an electrothermal melting point apparatus.

Single crystal X-ray diffraction

Crystal data for $[Me_2In(acac)]_2$: $C_{14}H_{26}In_2O_4$, $M = 487.99$, triclinic, space group $P\bar{1}$, $a = 8.581(5)$, $b = 8.507(6)$, $c = 8.033(6)$ Å, $\alpha = 108.39(5)$, $\beta = 112.48(5)$, $\gamma = 101.46(5)°$, $V = 478.9(6)$ Å^3, $Z = 1$, $D_c = 1.692$ g cm^{-3}, μ(Mo-Kα) = 2.416 mm^{-1}, $F(000) = 240$, $T = 293$ K; monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, ω–2θ-scans, 1671 independent reflections. The structure was solved by direct methods using the DIRDIF-96[12] program package, and refined anisotropically by full-matrix least-squares based on F^2 using SHELXL-97[13] to give $R_1 = 0.0190$, $wR_2 = 0.0501$ for 1671 independent observed reflections and 101 parameters. The ORTEP 3 program[14] was used for drawing the structure. Selected interatomic distances and angles are given in Table 1.

CCDC reference number 161738. See http://www.rsc.org/suppdata/jm/b1/b102212l/ for crystallographic data in CIF or other electronic format.

3. Results and discussion

The complex, dimethyl(pentane-2,4-dionato)indium(III), $[Me_2In(acac)]_2$, was prepared by the reaction of dimethylindium methoxide with a stoichimetric quantity of pentane-2,4-dione in toluene. The reaction of a dialkylindium alkoxide and a β-diketone is a novel route for the preparation of such complexes which avoids the use of pyrophoric or highly air-sensitive reagents. $[Me_2In(acac)]_2$ was recrystallised in toluene to give colourless crystals. The complex is sparingly soluble in most organic solvents, and surprisingly showed little or no tendency to decompose when left in air for extended periods of time.

Single crystal X-ray structure of $[Me_2In(acac)]_2$

The complex is dimeric and centrosymmetric, each indium atom is coordinated to three oxygen atoms and two methyl-group carbons (Fig. 1). The acetylacetonate groups of the complex twist away from the alkyl substituents on the metal centres. The coordination geometry at the indium centre is trigonal bipyramid with O(2) and O(1a) in the approximately axial positions [O(2)–In(1)–O(1a), 155.64°] and O(1), C(6) and C(7) lie close to the equatorial plane. The geometry at the bridging oxygen atoms is near to trigonal planar with O(1) lying 0.0085 Å out of the In(1), C(1) and In(1a) plane. There are three types of In–O interactions. The first is to O(2), on each β-diketonate ligand which coordinates to a single indium, In(1), [In(1)–O(2), 2.253(2) Å]. The second and third involve O(1) in a distinctively asymmetric mono-molecular bridge between the two indium atoms [In(1)–O(1), 2.194(2) Å and In(1a)–O(1), 2.606(3) Å]. The third and longest In–O contact may be viewed as that which holds the dimer together. The breaking of this bond is likely to be the first step in the decomposition of the dimer.

Table 1 Selected interatomic distances (Å) and angles (°) for $[Me_2In(acac)]_2$

In(1)–C(6)	2.125(4)	C(2)–C(3)	1.248(4)
In(1)–C(7)	2.126(4)	C(1)–C(2)	1.365(4)
In(1)–O(1)	2.194(2)	C(1)–C(4)	1.504(4)
In(1)–O(2)	2.253(2)	C(2)–C(3)	1.405(5)
O(1)–C(1)	1.295(3)	C(3)–C(5)	1.504(4)
C(6)–In(1)–C(7)	147.12(19)	O(1)–C(1)–C(2)	126.4(3)
C(6)–In(1)–O(1)	106.10(14)	O(1)–C(1)–C(4)	114.8(3)
C(7)–In(1)–O(1)	105.14(15)	C(2)–C(1)–C(4)	118.8(3)
C(6)–In(1)–O(2)	96.83(15)	C(1)–C(2)–C(3)	128.8(3)
O(7)–In(1)–O(2)	96.80(14)	O(2)–C(3)–C(2)	125.3(3)
C(1)–In(1)–C(2)	83.14(10)	O(2)–C(3)–C(5)	116.4(3)
C(1)–O(1)–In(1)	127.99(18)	C(2)–C(3)–C(5)	118.3(3)
C(3)–O(2)–In(1)	128.3(2)		

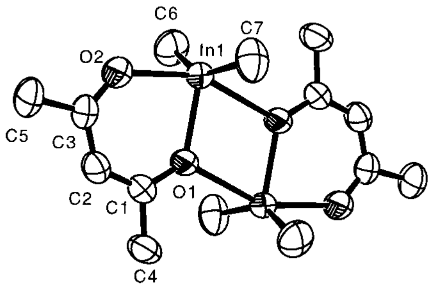

Fig. 1 X-Ray single crystal structure of $[Me_2In(acac)]_2$.

Five coordinate indium centres as observed in this complex are not seen in the related $[Me_2In(O_2CMe)]_n$ complex reported by Einstein *et al.*, prepared by the reaction of trimethylindium and acetic acid[15] for which a linear polymer was observed, and the indium was six coordinate, with very long In–O bonds to adjacent acetate groups [2.600(5) Å]. The shorter In–O contact [2.371(5) Å] was from a chelating acetate group; these contacts are longer than those found for the analogous In–O bonds in $[Me_2In(acac)]_2$. The acetato complex is similar to the thioacetato(dialkyl)indium complexes of Hausen *et al.* In their study the distance between In–O (chelate), [2.582(15) Å] was also much longer than the In–O contacts in $[Me_2In(acac)]_2$.[16] Hausen also reported the structures of an acetato(dialkyl)-indium complex.[17] All of these complexes demonstrate a tendency for the indium atoms to adopt coordinatively saturated environments by oligomerisation. In a very recent paper Baum and coworkers reported the crystal structure of $Me_2In(hfac)$ and used it as a precursor for the deposition of Cu–In alloys.[18] In the structure, through long-range interactions within the crystal lattice, two indium molecules formed weakly associated dimers. The bond length between In–O(2a) [2.869(2) Å] holding the two molecules together in $Me_2In(hfac)$ is much longer than that found in this work.

Deposition of thin films

Thin films of indium oxide have been grown using $[Me_2In(acac)]_2$ as a single-source precursor. Thermogravometric analysis (TGA) showed the complex to sublime between 130 and 210 °C with a 6.2 wt% final residue at 210 °C. Deposition was attempted at substrate temperatures of 350–450 °C, and *ca.* 200 mg of the precursor used for each experiment, whilst the precursor temperature was maintained at 150 °C. The films obtained were shiny and yellow at lower temperatures, and dark brown at higher temperatures, and adhered to the glass substrate surface (Scotch tape test) but could be removed by scratching the surface with a scalpel. The SEM images of indium oxide grown at 350 °C showed the thicknesses of the films to be up to *ca.* 3 μm on glass, silicon wafer(100) or GaAs(111) substrates (Fig. 2). The growth rate at 350 °C was *ca.* 6 μm h^{-1} for In_2O_3. The surface of all these films tended to be featureless.

EDAX analyses of the as-deposited films showed the presence of only indium peaks (the EDAX instrument used in this study could not detect oxygen). All the films obtained were composed of cubic crystalline In_2O_3 and the XRD patterns showed strong reflections for the (222) plane (Fig. 3 and Table 2). All the indium oxide films grown at 350–450 °C

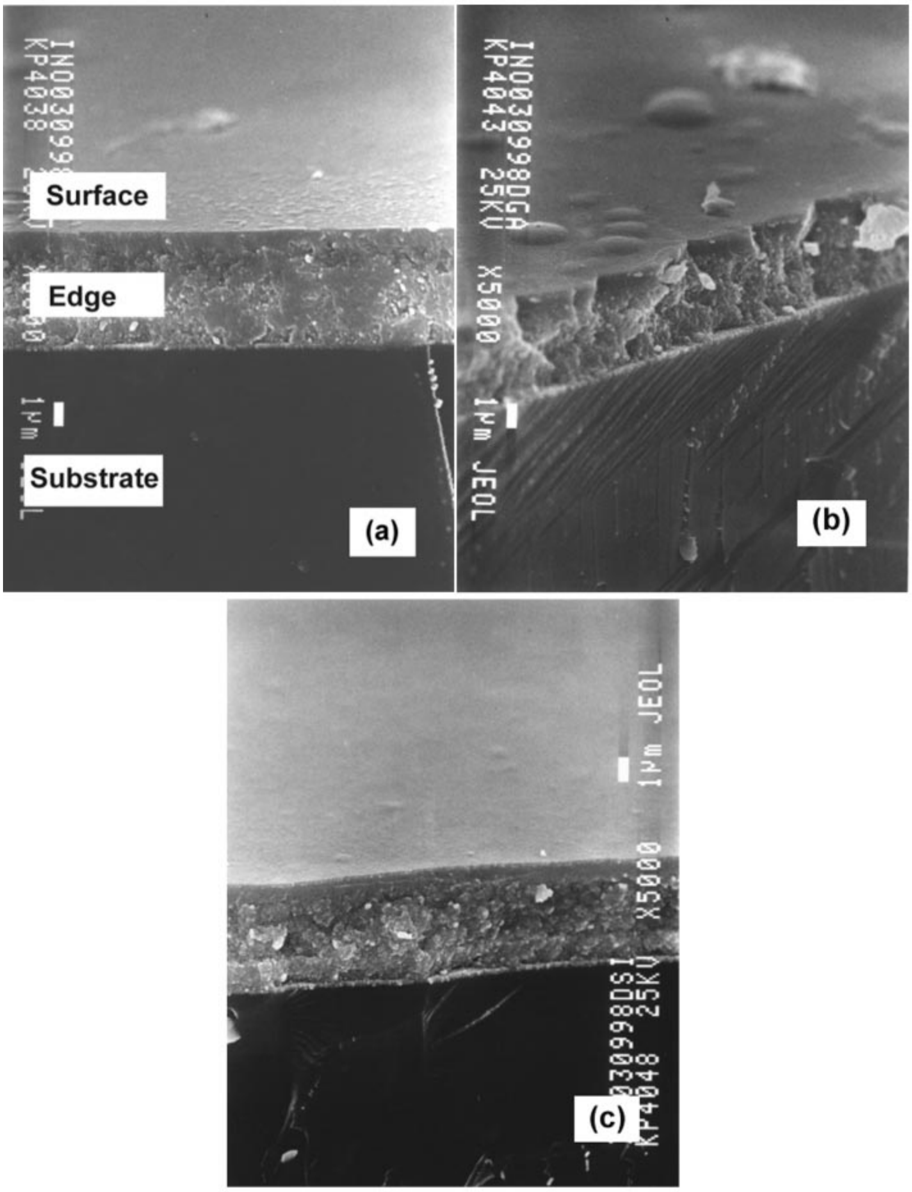

Fig. 2 SEM micrographs of cubic-In_2O_3 grown at 350 °C on glass (a), GaAs(111) (b) and Si(100) (c).

showed only single phase cubic-In_2O_3. In general, indium oxide films are polycrystalline with a cubic structure in the bulk material, and a preferred orientation along the (222) plane is common. However dopants (*e.g.* F or Sn) can promote other orientations in indium oxide. Maruyama *et al.*[19] reported the XRD pattern of tin-doped indium oxide in which the pattern had a significant peak for the (400) plane. The full widths at half-maximum of the (222) plane suggest the crystallite sizes are in the range 15–20 nm at deposition temperatures of 350–450 °C. The average lattice constant of cubic-In_2O_3 was found to be 10.133 Å in this work, close to the accepted value, 10.118 Å,[20] for bulk In_2O_3.

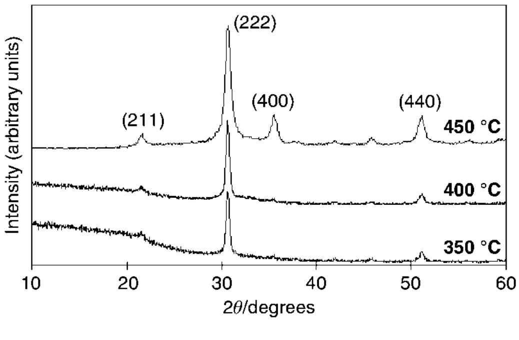

Fig. 3 X-Ray pattern of indium oxide from $[Me_2In(acac)]_2$ grown on glass substrates (note: temperatures indicate deposition temperatures).

4. Conclusions

$[Me_2In(acac)]_2$ has been prepared and characterised by various techniques, and used as a single-source precursor for the deposition of cubic In_2O_3 by LP-MOCVD without a separate oxygen source. The films were oriented and could be deposited

Table 2 X-Ray diffraction data, indices (*hkl*) and *d*-values, for cubic-In_2O_3 films deposited on glass in these studies (% = intensity)

JCPDS (6-416) *d*-spacing (*hkl*) (%)	350 °C *d*-spacing (%)	400 °C *d*-spacing (%)	450 °C *d*-spacing (%)
4.130 (*211*) (14)	4.117 (10)	4.125 (7)	4.114 (13)
2.921 (*222*) (100)	2.911 (100)	2.911 (100)	2.910 (100)
2.529 (*400*) (30)	2.531 (4)	2.534 (3)	2.555 (27)
2.385 (*411*) (8)	N/A	2.383 (1)	N/A
1.984 (*431*) (10)	1.975 (3)	1.978 (2)	1.980 (10)
1.788 (*440*) (35)	1.784 (14)	1.785 (12)	1.784 (27)
1.525 (*622*) (25)	N/A	1.523 (6)	N/A

in a relatively short time period (*ca.* 30 min) compared to other growth techniques for indium oxide deposition. Analyses of the as-deposited films showed that only cubic-In_2O_3 was deposited at all growth temperatures. Our continuing studies in this area will focus on the preparation of good quality indium oxide films at lower deposition temperatures.

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