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Low pressure chemical vapor deposition of fluorine-doped indium oxide films from an indium alkoxide complex

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Fluorine-doped indium oxide films are of interest as a transparent conducting material. Polycrystalline indium oxide films were deposited at 400–550 °C in a low-pressure chemical vapor deposition process from $In[OCMe(CF_3)_2]_3(H_2N\text{-}t\text{-}Bu)$ and O_2 precursors. The films deposited at $\leqslant$500 °C contained 2–3 atom% fluorine while the film deposited at 550 °C had no detectable fluorine incorporation (by X-ray photoelectron spectroscopy with sputtering). Films deposited on quartz ($\approx$1800 Å thickness) showed >85% transmittance in the 400–800 nm region and had band gaps of 3.65–3.75 eV. Resistivities of 1.25×10^{-2}–9.96×10^{-3} Ω cm were measured for the as-deposited films. The resistivities of films grown on silicon decreased markedly after annealing to values as low as 1.43×10^{-3} Ω cm.

Tin and indium oxides are members of an important class of compounds that uniquely combine the properties of electrical conductivity and transparency.[1–4] For applications, these oxides are made more conductive by doping with fluorine and tin, respectively. We reported recently the preparation of fluorine-doped tin oxide films from a new precursor, $Sn[OCH(CF_3)_2]_4(HNMe_2)_2$.[5] In this process, the source of fluorine in the films was the fluorinated alkoxide ligands. The incorporation of fluorine *via* the ligands circumvented the need to add a separate fluorine precursor, such as an organic fluorocarbon. As part of a study to examine the generality of this procedure, we report here on the preparation of fluorine-doped indium oxide by using the metal–organic compound $In[OCMe(CF_3)_2]_3(H_2N\text{-}t\text{-}Bu)$ and O_2 as precursors.

There have been only a few studies on the preparation of fluorine-doped indium oxide films despite the importance of transparent conducting oxide films in applications. In particular, only two processes involving chemical vapor deposition (CVD), which is the best method for large-scale applications, have been reported. Both of the published CVD procedures are by Maruyama and co-workers, who reported the preparation of fluorine-doped indium oxide thin films by atmospheric pressure processes from InF_3 and $In[O_2CCH(Et)(CH_2)_3CH_3]_3$,[6] and from the single-source precursor $In[O_2CCH(Et)(CH_2)_3CH_3]_2[O_2C(CF_2)_3CF_2H]$.[7] The latter example is related to the present study in that the fluorinated pentanoate ligand was found to serve as a source of fluorine dopant in the deposited films.

Experimental

Depositions

Depositions were carried out in a home-built hot-wall horizontal low-pressure chemical vapor deposition system equipped with mass flow controllers. Ultra high purity argon and extra dry oxygen were used as the carrier and reactive gases, respectively. During depositions, the precursor container was maintained at 45–50 °C while the temperature of the precursor feed lines ranged from 55 to 75 °C. The argon carrier gas flow rate through the precursor container was 350–450 sccm. The oxygen (200–300 sccm) was diluted in argon (500–650 sccm) before entering the reactor. The deposition pressure was 3.4–4.0 Torr. After the precursor supply was shut off for a given run, the films remained under the same deposition conditions for 1.5 h. Afterwards, they were cooled slowly to room temperature under an Ar/O_2 flow, which was decreased gradually from the composition used during deposition to a pure argon flow of 120 sccm. Selected films were annealed in an argon flow (80 sccm) for 2 h at 450 °C and 1 h at 550 °C, and then cooled slowly to room temperature under an argon flow. To prepare the silicon substrates for depositions, they were first degreased by rinsing them in hexanes and methanol before blow-drying with pre-purified nitrogen. Soda lime glass (Corning) and quartz (ChemGlass) substrates were degreased with soap, rinsed with deionized water, and finally rinsed with methanol before being blow-dried by a pre-purified nitrogen flow.

Film analysis

Ion beam data were collected by Dr Yongqiang Wang at the Ion Beam Analysis Facility, University of Minnesota. The beam was 2 MeV $^4He^+$ ions, and the total charge collected for the spectrum was 10 μC at 10 nA. The Rutherford backscattering spectrometry (RBS) detector (FWHM = 18 keV, Ω = 4.16 msr) was located at 165°. X-Ray diffraction (XRD) studies were carried out using a Siemens diffractometer (Model D5000; Cu-K_α radiation; 0.01° step size). X-Ray photoelectron spectroscopy (XPS) studies were carried out by using a Physical Electronics PHI 5700 ESCA system equipped with a 5 keV Ar^+ sputter gun. The electron energy analyzer was referenced to the Au $4f_{7/2}$ line at 84 eV. The base pressure was 2×10^{-8} Torr during sputtering. After sputtering into the bulk, spectra were collected using a monochromatic Al source at a pass energy of 11.75 eV. The base pressure was below 10^{-9} Torr.

Sheet resistances were measured for films deposited on silicon (the substrate resistivity was 30 Ω cm), glass and quartz by using a four-point probe configuration (Signatone Model S-301). A series of 3–4 measurements were taken on each film and the measurements were averaged to give the final reported value. Typically, variations of ±3% in the individual measurements were observed. A JEOL JSM-6330F field emission instrument was used to gather scanning electron microscopy (SEM) images. Film thicknesses were obtained from SEM cross-sectional views (tilt angle of 40°). Transmittance spectra were collected on a Varian Cary UV-Vis spectrophotometer.

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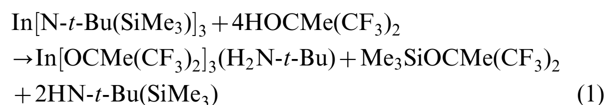
Results and discussion

The metal–organic complex $In[OCMe(CF_3)_2]_3(H_2N\text{-}t\text{-}Bu)$ was used as the indium precursor in this study. It was synthesized according to eqn. (1) following the procedure of Mîinea *et al.*,[8] and isolated in 52% yield as colorless crystals from a cold ether–toluene solution. At the precursor container temperatures typically used in this study (45–50 °C), the complex was a sticky solid and at slightly higher temperatures (>55 °C), it liquefied.



$$In[N\text{-}t\text{-}Bu(SiMe_3)]_3 + 4HOCMe(CF_3)_2 \rightarrow In[OCMe(CF_3)_2]_3(H_2N\text{-}t\text{-}Bu) + Me_3SiOCMe(CF_3)_2 + 2HN\text{-}t\text{-}Bu(SiMe_3) \quad (1)$$

$In[OCMe(CF_3)_2]_3(H_2N\text{-}t\text{-}Bu)$ and O_2 reacted to produce shiny adherent films at substrate temperatures of 400–550 °C in a low pressure CVD process. Analyses of Rutherford backscattering spectra (*e.g.*, Fig. 1) of films deposited at 400 and 500 °C on silicon gave O/In ratios of 1.56 and 1.44, respectively, which is within experimental error (±3–5%) for this method of the required ratio for stoichiometric In_2O_3. Carbon, nitrogen and fluorine peaks were not observed in the spectra indicating low levels of these elements in the films. X-Ray photoelectron spectra for films deposited on silicon at 400, 450, 500, and 550 °C had In $3d_{5/2}$ and O 1s peaks at 445.0–445.6 eV and 530.5–531.1 eV, respectively. These values are close to the values of 444.5–444.9 eV for In $3d_{5/2}$ and 530.1–530.6 eV for O 1s in bulk In_2O_3;[9,10] 444.80–444.85 eV for In $3d_{5/2}$ and 530.25–530.40 eV for O 1s in In_2O_3 fims prepared by sputter deposition[11] and reactive ion plating;[12] 444.7±0.2 for In $3d_{5/2}$ and 530.6±0.1 eV for O 1s in oxidized indium foil surfaces;[9] and 445.1 eV for In $3d_{5/2}$ and 530.6 eV for O 1s in undoped In_2O_3 deposited by low pressure CVD.[13] There appear to be no detailed XPS studies on fluorine-doped indium oxide.

XPS depth profiles (*e.g.*, Fig. 2) for films deposited at 400 and 500 °C on silicon gave O/In ratios in the bulk averaging 1.25 and 1.11 (±0.10), respectively, and showed no detectable nitrogen and little or no carbon contamination. Reported O/In ratios determined by the same method for other indium oxide films are 1.24–1.37.[11,12] The atom ratios obtained by RBS, which suggest the films are stoichiometric In_2O_3, are probably better indicators of the true compositions since possible preferential sputtering and sputtering induced reduction processes make the O/In ratios obtained by XPS suspect. The F/In ratios from the XPS depth profiles averaged 0.068 (3.1 atom%) and 0.055 (2.4 atom%) for the films deposited at 400 and 500 °C, respectively, but no fluorine was detected by XPS in the film deposited at 550 °C. The apparent decrease in fluorine incorporation as the temperature of deposition is increased is in agreement with data reported by Maruyama and Fukui for their fluorine-doped indium oxide films prepared by CVD.[6]

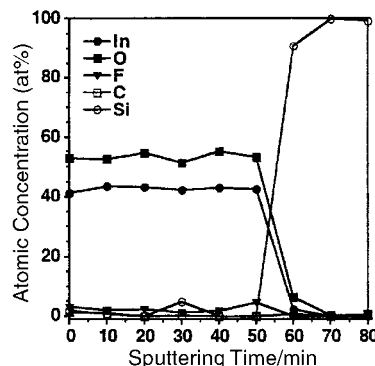


Fig. 2 XPS depth profile for a fluorine-doped indium oxide deposited on silicon at 400 °C.

The film growth rates, which were calculated from the film thicknesses obtained by cross-sectional SEM, were <20 Å min^{-1}. When the temperature of the precursor container was increased from 45 (the temperature used primarily in this study) to 50 °C, while keeping the substrate temperate (400 °C) and gas flow rates constant, the growth rate increased about two-fold (from 10 to 19 Å min^{-1}). A further increase in container temperature to 55 °C produced a poor quality film that had a dull brown appearance and adhered poorly to the substrate. Maruyama and Fukui reported growth rates of about 8–50 Å min^{-1} at deposition temperatures of 325–425 °C for fluorine-doped indium oxide thin films prepared by atmospheric pressure CVD from InF_3 and $In[O_2C\text{-}CH(Et)(CH_2)_3CH_3]_3$.[6]

X-Ray diffraction studies for films deposited on glass at 400–550 °C indicated the films were polycrystalline cubic indium oxide with a (100) preferred orientation (*e.g.*, Fig. 3).[14] For a given deposition temperature, the films were more oriented as their thickness increased, suggesting a buffering effect. A comparison of films of similar thickness grown at 400 and 550 °C indicated that the latter film was more randomly oriented (Fig. 4). The more random orientation for the 550 °C deposited film, which had no fluorine incorporation according to the XPS analysis, compared to the 400 °C deposited film, which had F/In = 0.068, is consistent with an observation by Maruyama and Fukui who found that an increase in fluorine content caused the films to favor the (100) orientation.[6]

Scanning electron micrographs for 1000–2200 Å films deposited at 400, 450, 500, and 550 °C on silicon indicated that the films had a columnar grain structure (*e.g.*, Fig. 5). Thicker films gave grains with a larger average diameter (about 2×) than thinner films if all other deposition parameters were kept constant.

Transmission spectra for ≈1800 Å films grown on quartz are shown in Fig. 6. The films showed >85% average transmit-

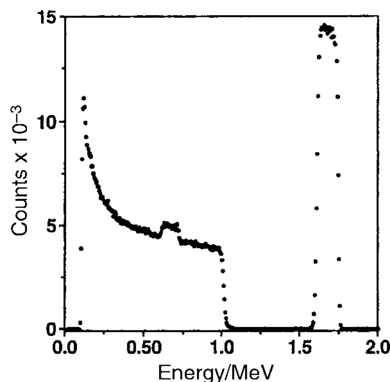


Fig. 1 Backscattering spectrum of a fluorine-doped indium oxide deposited on silicon at 500 °C.

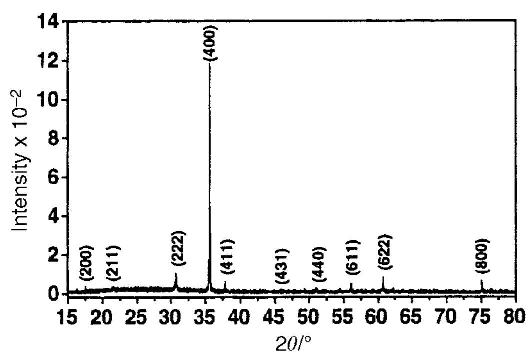


Fig. 3 X-Ray diffraction pattern for a fluorine-doped indium oxide deposited on glass at 500 °C.

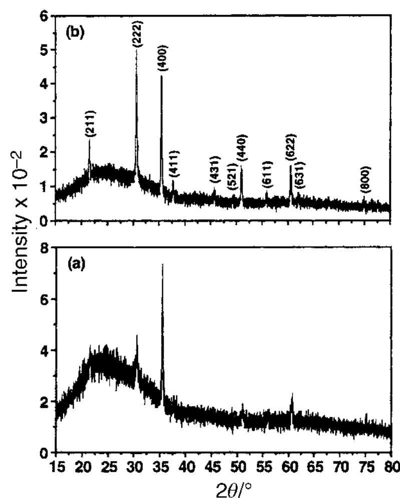


Fig. 4 X-Ray diffraction pattern for 936 (a) and 1021 Å (b) films deposited on glass at 400 and 550 °C, respectively.

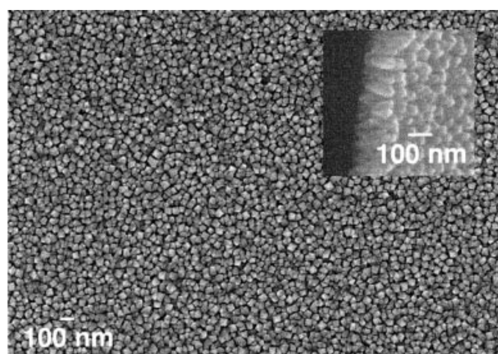


Fig. 5 SEM top and cross-sectional (inset; 40° tilt angle) views of a 1200 Å film deposited on silicon at 450 °C.

tance in the 400–800 nm region. Comparable transmittance values were reported for a 980 Å film deposited at 380 °C from $In[O_2CCH(Et)(CH_2)_3CH_3]_2[O_2C(CF_2)_3CF_2H]$ in a nitrogen atmosphere,[7] and for a 578 Å film deposited at 400 °C from $In[O_2CCH(Et)(CH_2)_3CH_3]_3$ and InF_3.[6] Band gaps were calculated from the absorbance data by plotting $(\alpha\Delta d)^2$ *vs.* E and extrapolating the linear portion of the curve to $(\alpha\Delta d)^2 = 0$, where α is the absorption coefficient, Δd is the film thickness and E is the photon energy.[15] For the films deposited at 400, 450, 500 and 550 °C the band gaps were 3.75, 3.66, 3.65, and 3.66 eV, respectively. These values are in the range reported for fluorine-doped indium oxide deposited by CVD (3.50–3.72 eV)[6,7] and spray pyrolysis (3.55–3.82 eV),[16,17] and for undoped indium oxide deposited by reactive sputtering (3.50–3.70 eV).[2]

The resistivity vaues for 1000–2200 Å films deposited on silicon at 400–550 °C ranged from 1.25×10^{-2} to 9.96×10^{-3} Ω cm (Table 1). The resistivity decreased with

Table 1 Resistivities for films deposited on silicon from $In[OCMe(CF_3)_2]_3(H_2N\text{-}t\text{-}Bu)$ and O_2 before and after annealing

Deposition temperature/°C	Film thickness/Å	Resistivity[a]/Ω cm
400	1702	1.25×10^{-2} 7.35×10^{-3}
450	1191	2.33×10^{-2} 1.72×10^{-3}
500	1872	1.62×10^{-2} 1.43×10^{-3}
550	1021	9.96×10^{-3} 2.07×10^{-3}

[a]Top value, before annealing; bottom value, after annealing.

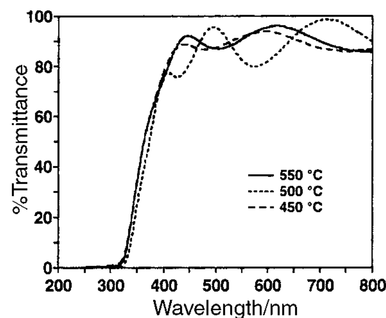


Fig. 6 Transmittance spectra for films deposited on quartz at 450, 500 and 550 °C.

increasing deposition temperature. These values are higher than those for fluorine-doped indium oxide films prepared by Maruyama *et al.* who reported 4.4×10^{-4} Ω cm for a 3200 Å film grown at 380 °C from $In[O_2CCH(Et)(CH_2)_3CH_3]_2[O_2C(CF_2)_3CF_2H]$ in a nitrogen atmosphere, and 2.89×10^{-4} Ω cm for a 578 Å film grown at 400 °C from $In[O_2CCH(Et)(CH_2)_3CH_3]_3$ and InF_3.

Selected films grown on silicon were annealed under an argon flow by heating at 450 °C for 2 h and then at 550 °C for 1 h. The resistivity after annealing decreased by up to an order of magnitude (Table 1); for example, the resistivity of a film deposited at 500 °C on silicon decreased from 1.62×10^{-2} Ω cm to 1.43×10^{-3} Ω cm after annealing. A similar decrease in resistivity after annealing was reported by Asikainen *et al.*[18] for films obtained by implanting fluorine in indium oxide films that had been grown by atomic layer epitaxy. They explained the decrease in resistivity as being due to replacement of oxygen in the lattice by the anionic dopant.

After annealing the films, shifts of 0.025 to 0.059 eV in the band gaps towards higher energies were observed. These shifts are comparable to those reported by Singh *et al.* for their annealed films.[19] The shifts to higher energy suggest an increase in the carrier concentration, which is in agreement with the observed decrease in the resistivity with annealing.[20]

Conclusion

Low-pressure chemical vapor deposition using $In[OCMe(CF_3)_2]_3(H_2N\text{-}t\text{-}Bu)$ and O_2 precursors gave polycrystalline indium oxide films at substrate temperatures of 400–550 °C. According to XPS studies, the films deposited at ⩽500 °C contained 2–3 atom% fluorine while the film deposited at 550 °C had no detectable fluorine incorporation. X-Ray photoelectron spectroscopy showed that the films contained virtually no carbon or nitrogen, and RBS spectra were consistent with an In_2O_3 stoichiometry. X-Ray diffraction studies showed that the films containing fluorine had a (100) preferred orientation. Resistivities of 1.25×10^{-2}–9.96×10^{-3} Ω cm were measured for the as-deposited films. The resistivity of films grown on silicon decreased markedly after annealing to values as low as 1.43×10^{-3} Ω cm. Films deposited on quartz (1800 Å thickness) showed >85% average transmittance in the 400–800 nm region and band gaps of 3.65–3.75 eV.

This study shows that under the limited CVD conditions examined, the fluorinated alkoxide ligands in $In[OCMe(CF_3)_2]_3(H_2N\text{-}t\text{-}Bu)$ are not a good source of active fluorine dopant.

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