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Homoleptic Tin and Silicon Amido Compounds as Precursors for Low-Temperature Atmospheric Pressure Chemical Vapor Deposition of Tin and Silicon Oxide Thin Films

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Tin oxide films doped with fluorine or antimony are transparent conductors used in optoelectronic devices and solar cells.[1] Silicon oxide thin films are used as diffusion barriers, passivation layers, and dielectric layers in the microelectronics industry.[2] Tin oxide thin films are commonly deposited in atmospheric pressure chemical vapor deposition (APCVD) processes by hydrolyzing $SnCl_4$ or by reacting tetramethyltin with oxygen.[3] The APCVD of silicon oxide films normally involves the reaction of ozone or oxygen with SiH_4 or tetraethylorthosilicate.[4]

Gordon et al. recently reported the use of main-group amido complexes and ammonia as precursors in the APCVD of main-group nitride thin films.[5] Because the amido precursors are volatile, easily synthesized, and relatively safe to handle, we decided to examine their use as precursors to main-group oxide thin films.[6,7] This paper reports the successful APCVD of tin and silicon oxide from homoleptic dimethylamido complexes, $M(NMe_2)_4$ (M = Sn, Si), and oxygen at deposition temperatures ranging from 250 to 400 °C.

The amido precursors $M(NMe_2)_4$ (M = Sn, Si) were prepared from MCl_4 and $LiNMe_2$ by literature methods.[5,8] The precursors, which are thermally stable and only moderately air sensitive, were distilled before use, and the purity (>99%) was checked by high-field NMR spectroscopy. Depositions were performed in an atmospheric pressure laminar-flow rectangular glass reactor that has been described elsewhere.[9] The liquid amido precursors were loaded in a stainless steel bubbler which was then connected to the CVD apparatus via VCO fittings. Ultrahigh-purity argon was used as carrier gas. The bubbler was heated to 55 °C for both $Sn(NMe_2)_4$ and $Si(NMe_2)_4$ in order to increase their vapor pressure ($Sn(NMe_2)_4$, bp 51 °C/15 mmHg; $Si(NMe_2)_4$, bp 74–75 °C/19 mmHg). Oxygen (extra dry grade) and argon flow rates were controlled with mass flow controllers. After the substrate was loaded, the system was heated and simultaneously flushed with a 1000 sccm flow of argon for 60 min prior to each deposition to remove adventitious water. Oxygen diluted with argon was flushed through the reactor for 5 min prior to opening the precursor bubbler. After deposition, the films were quickly cooled by placing the reactor on top of an insulating ceramic block for 5 min under a dilute oxygen flow. This was followed by a 15-min argon flush. The silicon, glass, and quartz substrates were cleaned by immersing them in H_2O_2:H_2SO_4 (1:4) for 10 min, rinsing in deionized water for 15 min, and drying under a stream of argon. Details concerning film characterization are given in a footnote.[10]

Table 1. Growth Rates and Stoichiometries for Selected SnO_2 and SiO_2 Thin Films Deposited by APCVD

film	temp (°C)	growth rate (Å/min)	O/M ratio[a]
SnO_2[b]	250	650	2.00
SnO_2[b]	350	10 000	1.97
SiO_2[c]	300	380	2.08
SiO_2[c]	350	900	2.10

[a] ±0.10. [b] Deposition by using a total flow of 1200 sccm, 43% oxygen in the stream. [c] Deposition by using a total flow of 1000 sccm, 30% oxygen in the stream.

Tin oxide thin films are deposited at substrate temperatures of 250–400 °C. [**Warning**: Extreme caution should be exercised to prevent buildup of unreacted organometallic precursor in the reactor because of the possibility of fire or explosion upon reaction with oxygen.] Film thicknesses, as estimated from Rutherford backscattering data, are up to 20 000 Å thick, and growth rates are 650–10 000 Å/min (Table 1). The growth rates increase with increasing temperature and with increasing oxygen flow rates. Our growth rates are comparable to those for the APCVD of SnO_2 from tetramethyltin and oxygen, which are reported to be 6000–60 000 Å/min.[3] The films show good adhesion (Scotch tape test) and are conductive with resistivities ranging from 10^{-1} to 10^{-3} Ω cm. The refractive indexes of the films (λ 632.8 nm) vary from 2.064 to 2.867.

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(10) Rutherford backscattering (RBS) analyses and elastic recoil spectroscopy (ERS) were performed using a 2.0-MeV $^4He^+$ beam, and the data were analyzed and modeled by using the program RUMP. Kapton ($C_{22}H_{10}N_2O_5$) foil was used as the ERS standard. Sheet resistivity was measured using a four-point probe and converted to local film resistivity using film thicknesses determined by ellipsometry. Depth profiling for Auger electron (AES) and X-ray photoelectron spectroscopy (XPS) measurements was performed using a 3.5-keV Ar^+ sputter gun. X-ray irradiation for XPS used a Mg source ($h\nu$ 1253.6 eV) with a spot size of 5 μm. Peak scans were obtained with a band pass of 25 eV and analyzer resolution of 1.6%. The XPS binding energies were referenced to a gold standard (Au $4f_{7/2}$ at 83.95 eV).

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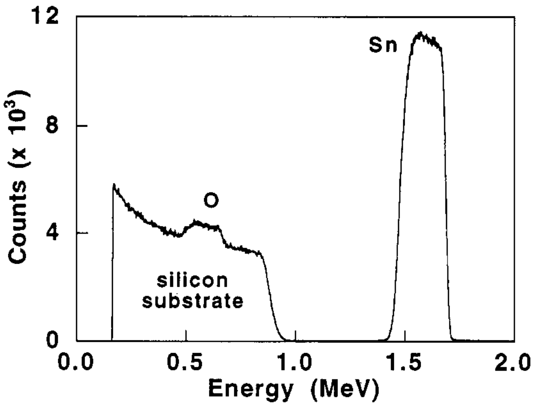

Figure 1. RBS spectrum of a 4300-Å SnO_2 film deposited on silicon at 350 °C.

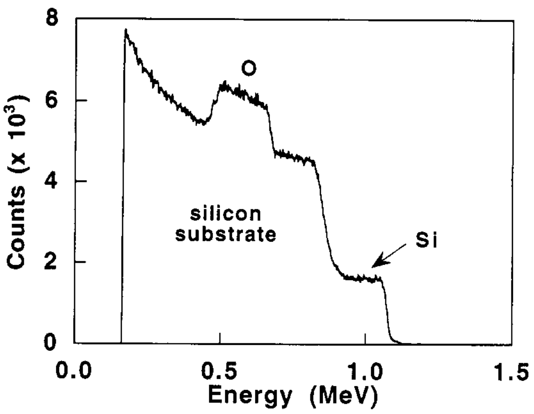

Figure 2. RBS spectrum of a 6100-Å SiO_2 film deposited on silicon at 350 °C.

X-ray diffraction for a film deposited at 350 °C gives a cassitterite pattern with some (101) orientation. The average grain size, as estimated from the diffraction study, is around 70 Å.[11] Scanning electron microscopy (SEM) for a film 8800 Å thick deposited at 350 °C shows surface roughness with nodular growth indicative of a three-dimensional island growth mechanism[4] and no obvious cracks or fissures. Films of tin oxide deposited at 250 °C are amorphous by X-ray diffraction and featureless by scanning electron microscopy.

Rutherford backscattering data (e.g., Figure 1) give O/Sn ratios averaging 2.0. No hydrogen was detected in three films examined by ERS. Auger electron spectroscopy depth profiling for a film deposited at 350 °C indicates the sample has uniform composition, consistent with the RBS results. X-ray photoelectron spectroscopy survey scans indicate the samples contain <1 atom % C and <0.3 atom % N. The XPS binding energy of the Sn $3d_{5/2}$ and the O 1s electrons in the bulk are 486.9 and 530.6 eV, respectively. The reported value for the Sn $3d_{5/2}$ electron is 486.4 eV.[12]

Thin films of silicon oxide are deposited on silicon and quartz at temperatures ranging from 300 to 400 °C.[7] The film deposited at 350 °C is amorphous by X-ray diffraction and featureless by SEM. Film thicknesses, determined by ellipsometry and RBS, are up to 6100 Å, and growth rates range from 380 to 900 Å/min (Table 1). The growth rates, which were not optimized, depend on temperature and oxygen flow rates with a highest observed growth rate of 900 Å/min at 350 °C with 30% O_2 in the stream. This growth rate is less than the rates observed in the APCVD of SiO_2 from SiH_4 and oxygen (2000–5000 Å/min).[4] The films show good adhesion (Scotch tape test), and they are etched by HF or concentrated KOH. The refractive indexes of the films (λ 632.8 nm) are 1.458 ± 0.003, which is in agreement with the typical value of 1.46 reported for SiO_2.[13]

Auger electron spectroscopy depth profiling indicates the silicon oxide films have uniform composition. The carbon and nitrogen contents estimated from XPS survey scans are less than 0.2 and 0.3 atom %, respectively. The XPS binding energies for the Si 2p and O 1s electrons in the bulk are 106.1 and 535.6 eV, respectively. These energies are higher than the reported values of 104 and 531 eV,[13] which may be due to sample charging during data collection.

Rutherford backscattering spectra were routinely obtained for SiO_2 films greater than 2000 Å thick (e.g., Figure 2). The spectra indicate that the films have an average O/Si ratio of 2.0. Elastic recoil spectra indicate that there may be a small amount of uniformly distributed hydrogen in the films ($<9 \pm 5$ atom %) as well. Transmittance IR spectra have characteristic Si–O absorbances at 1070 and 810 cm^{-1} and a peak at 926 cm^{-1}, which may be due to Si–OH, although the peak is shifted 14 cm^{-1} from the reported frequency (940 cm^{-1}).[14] A broad peak around 3500 cm^{-1} may be the corresponding OH stretch. Further work is in progress to determine the source of hydrogen in the films.

In conclusion, we have demonstrated that tin and silicon amido complexes are promising precursors for the deposition of tin and silicon oxide thin films at low substrate temperatures. The process gives stoichiometric tin and silicon oxide with moderate growth rates. The mechanism by which the films are deposited is not known, but presumably insertion of dioxygen into the $M-NMe_2$ bond is a key step. This study further illustrates that main-group amido complexes are reactive sources of the main-group elements for CVD processes[15] on par with main-group hydrides, halides, and alkyls.

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