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CHEMICAL VAPOR DEPOSITION OF GROUP 14 OXIDE
FILMS

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LOW TEMPERATURE ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION OF GROUP 14 OXIDE FILMS

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ABSTRACT

Depositions of high quality SiO_2 and SnO_2 films from the reaction of homoleptic amido precursors $\text{M}(\text{NMe}_2)_4$ ($\text{M} = \text{Si}, \text{Sn}$) and oxygen were carried out in an atmospheric pressure chemical vapor deposition reactor. The films were deposited on silicon, glass and quartz substrates at temperatures of 250 to 450 °C. The silicon dioxide films are stoichiometric ($\text{O}/\text{Si} = 2.0$) with less than 0.2 atom % C and 0.3 atom % N and have hydrogen contents of 9 ± 5 atom %. They are deposited with growth rates from 380 to 900 Å/min. The refractive indexes of the SiO_2 films are 1.46, and infrared spectra show a possible Si-OH peak at 950 cm^{-1} . X-Ray diffraction studies reveal that the SiO_2 film deposited at 350 °C is amorphous. The tin oxide films are stoichiometric ($\text{O}/\text{Sn} = 2.0$) and contain less than 0.8 atom % carbon, and 0.3 atom % N. No hydrogen was detected by elastic recoil spectroscopy. The band gap for the SnO_2 films, as estimated from transmission spectra, is 3.9 eV. The resistivities of the tin oxide films are in the range 10^{-2} to 10^{-3} Ω cm and do not vary significantly with deposition temperature. The tin oxide film deposited at 350 °C is crystalline cassiterite with some (101) orientation.

INTRODUCTION

Doped tin oxide, a transparent conductor, and silicon oxide, a dielectric, are important materials in the microelectronics industry [2,3]. In atmospheric pressure chemical vapor deposition (APCVD) processes, silicon oxide is prepared from silane and oxygen or by pyrolysis of tetraethylorthosilicate. Tin oxide is typically deposited by reacting oxygen with tetramethyltin or by hydrolysis of tin tetrachloride. These processes sacrifice quality and/or growth rates at low deposition temperatures.

Homoleptic metal amido complexes, in combination with ammonia, are known to be excellent precursors to nitride films at low temperatures [4]. They are also potential precursors to oxide films because they contain reactive metal-nitrogen bonds as possible sites for oxygen insertion [5,6]. Herein we report the atmospheric chemical vapor deposition of SiO_2 and SnO_2

from the reaction of oxygen with $\text{Si}(\text{NMe}_2)_4$ and $\text{Sn}(\text{NMe}_2)_4$, respectively, at temperatures of 250–450 °C [7].

EXPERIMENTAL

The amido precursors $\text{Si}(\text{NMe}_2)_4$ and $\text{Sn}(\text{NMe}_2)_4$ were prepared using literature methods [8]. Depositions were carried out in an atmospheric-pressure rectangular glass reactor as described previously [7]. Ultra-high purity argon was used as carrier gas, and extra-dry grade oxygen was used directly from the cylinder. The substrates were cleaned by immersing them in $\text{H}_2\text{O}_2\text{:H}_2\text{SO}_4$ (1:4) for 10 minutes, rinsing in deionized water for 15 minutes, and drying under a stream of argon. Total flow rates through the system ranged from 1000–1200 sccm. Rutherford backscattering (RBS) analyses and elastic recoil spectroscopy (ERS) were performed using a 2.0 MeV $^4\text{He}^{2+}$, and the data was analyzed and modeled by using the program RUMP. Kapton ($\text{C}_{22}\text{H}_{10}\text{N}_2\text{O}_5$) foil was used as the ERS standard. Nuclear reaction analyses (NRA) were performed using a 1.26 MeV $^2\text{H}^+$ beam with graphite as a standard. Sheet resistivity was measured with a 4-point probe and converted to local film density using film thicknesses obtained by ellipsometry or RBS. Depth profiling for Auger electron (AES) and X-ray photoelectron spectroscopy (XPS) measurements was carried out 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 microns. The XPS binding energies were referenced to a gold standard ($\text{Au } 4f_{7/2}$ at 83.95 eV).

RESULTS

Silicon oxide films are deposited from $\text{Si}(\text{NMe}_2)_4$ and oxygen on silicon and quartz at substrate temperatures of 300 to 400 °C. No deposition is observed when the amido precursor is pyrolyzed in the absence of oxygen. The SiO_2 films are stoichiometric with O/Si ratios of 2.00 ± 0.10 as determined by RBS. The carbon and nitrogen contents, estimated from XPS survey scans, are less than 0.2 atom % and 0.3 atom % respectively. The hydrogen content determined by ERS is $< 9 \pm 5$ atom % and is uniformly distributed throughout the film. Transmittance IR spectra have characteristic Si–O absorbances at 1070 and 810 cm^{-1} and a peak around 950 cm^{-1} , which may be due to Si–OH (reported at 940 cm^{-1}) [9]. The O–H group is observed as a broad band around 3500 cm^{-1} .

Auger electron spectroscopy depth profiling indicates the silicon oxide films have uniform composition, consistent with the RBS data. 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 [10], which may be due to sample charging during data collection. The growth rates of SiO_2 varied with flow rates and temperature. The conditions were not optimized, but the highest rate was observed at a deposition temperature of 350 °C (700

Å/min) when the bubbler containing the organometallic was heated to 55 °C and the feed lines were maintained at 120 °C.

The films show good adhesion (Scotch tape test) and are chemically resistant except to KOH or HF. The refractive indexes of the films (λ 632.8 nm) are $1.458 \pm .003$, which agree with the typical value of 1.46 reported for SiO₂ [10]. X-ray diffraction for a SiO₂ film deposited at 350 °C indicates the film is amorphous. Scanning electron microscopy show that the film is smooth with no obvious cracks or other features.

Tin oxide films are deposited on silicon, glass and quartz substrates from Sn(NMe₂)₄ and oxygen at substrate temperatures of 250–450 °C. No deposition is observed at 350 °C in the absence of oxygen. The O/Sn ratio is 2.00 ± 0.10 by RBS. Auger depth profiling show the film deposited at 350 °C has uniform composition. The carbon content in the films is less than 0.8 atom % based on NRA and the nitrogen content is less than 0.3 atom % from XPS survey scans. No hydrogen was detected in three films examined by ERS.

The growth rates of the SnO₂ films are up to 10,000 Å/min. At a substrate temperature of 375 °C the growth rates do not vary significantly with oxygen flow rate and at a low oxygen flow rate (250 sccm/1000 sccm total flow) the rates do not appear to vary with temperature. For depositions with substrate temperatures greater than 375 °C and high oxygen flow rates (400 sccm/1000 sccm total flow), however, the growth rates decrease with increasing temperature. The inverse relationship between the growth rate and temperature at high oxygen flow rates may be due to significant reaction of the precursor and oxygen before reaching the substrate, which decreases the observed deposition rate.

X-Ray diffraction indicates a SnO₂ film deposited at 250 °C is amorphous, while films deposited at 350 °C are crystalline cassiterite with some (101) orientation (see Figure 1). The grain size is estimated from the diffraction study to be approximately 100 Å. Scanning electron microscopy of SnO₂ films deposited at 350 °C reveal nodular grains while the film deposited at 250 °C is smooth and featureless. The films demonstrate good chemical stability to common acids (except HF) and adhere well to the substrates with no delamination observed over a period of months.

The SnO₂ films show good transmittance in the visible range. A 1400 Å SnO₂ film on quartz, for example, is 70-75% transmittant between 400 and 700 nm. The optical band gap was calculated from the absorbance data by plotting $(AE)^2$ vs. E, where A is the absorbance of the film and E is the photon energy. A sample plot is shown in Figure 2 for a 6600 Å SnO₂ film deposited on quartz at 400 °C where the calculated band gap is 3.95 eV. This value is within the range of values reported for SnO₂ films (3.6-4.1 eV) [11]. The films are conductive, with resistivities ranging from 10^{-2} – 10^{-3} Ω cm. The resistivities of the films did not appear to vary significantly with deposition temperature.

Figure 1. X-Ray diffraction data for a 400 Å SnO_2 film deposited at 350 °C on silicon.

Figure 2. Plot to determine the band gap for a tin oxide film deposited on quartz at 400 °C. (A) is the absorbance, (E) is the photon energy.

DISCUSSION

The homoleptic amido precursors $M(\text{NMe}_2)_4$ ($M = \text{Si}, \text{Sn}$) react with oxygen at low temperatures to give oxide films with little or no carbon or nitrogen contamination. The mechanism of the reaction probably involves insertion of dioxygen into the reactive M-N bonds of the precursors followed by decomposition of the unstable peroxo intermediates. The fact that we see little or no carbon or nitrogen indicates that all of the amido ligands are cleanly removed from the precursors.

CONCLUSION

Homoleptic main group amido complexes appear to be viable precursors for the low temperature deposition of oxide thin films. The films adhere well to the substrates and demonstrate promising electrical and optical properties. The reactions to give the oxides are proposed to occur via oxygen insertion into the M-N bonds of the amido precursors.

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