

Plasma-enhanced chemical vapor deposition of silicon, germanium, and tin nitride thin films from metalorganic precursors

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Nearly stoichiometric silicon, germanium, and tin nitride thin films were deposited from the corresponding homoleptic dimethylamido complexes $M(NMe_2)_4$ ($M=Si, Ge, Sn$; $Me=CH_3$), and an ammonia plasma at low substrate temperatures ($<400\text{ }^\circ C$). Tin nitride films were also deposited from $Sn(NMe_2)_4$ and ammonia without plasma activation. The films showed little ($<\text{few at. \%}$) or no carbon or oxygen contamination. The barrier properties of the silicon and germanium nitride films were evaluated by using backscattering spectrometry. Homoleptic dimethylamido silicon and germanium compounds are attractive alternatives to silane and germane for use in the plasma-enhanced chemical vapor deposition of nitride thin films. © 1995 American Vacuum Society.

I. INTRODUCTION

Thin films of silicon and germanium nitride can be deposited by chemical vapor deposition (CVD) from a variety of precursor systems. In thermal processes, silicon nitride films have been prepared at high substrate temperatures ($700\text{--}900\text{ }^\circ C$) from silane and ammonia in a hydrogen atmosphere^{1,2} and from dichlorosilane and ammonia at low pressure.^{3,4} The atmospheric pressure CVD (APCVD) of silicon nitride films from tetrakis(dimethylamido)silicon, $Si(NMe_2)_4$, and ammonia precursors at $600\text{--}750\text{ }^\circ C$ has been reported as well.⁵ Remote and direct plasma-enhanced CVD (PECVD) techniques have used silane and either ammonia or nitrogen as the most common precursors to deposit silicon nitride.^{6–10} A disilanyl amine¹¹ and cyclopentadienyl substituted silanes ($Cp SiH_3$ and $Cp_2 SiH_2$) in combination with N_2/NH_3 have also been employed.¹² Finally, electron cyclotron resonance (ECR) plasmas, which have a higher degree of ionization than normal radio frequency (rf) or microwave plasmas, have recently been used to deposit silicon nitride. In the ECR depositions, silane and N_2/NH_3 or $Si(NMe_2)_3H$ and N_2 were used as precursors at substrate temperatures of $50\text{--}250\text{ }^\circ C$ (yielding growth rates of $50\text{--}200\text{ \AA/min}$) and $<150\text{ }^\circ C$ ($<300\text{ \AA/min}$), respectively.^{13–15}

Germanium nitride films have been deposited by thermal chemical vapor deposition from $GeCl_4$ and ammonia at $400\text{--}600\text{ }^\circ C$,^{16,17} from GeH_4 and ammonia at $550\text{ }^\circ C$,¹⁸ and GeH_4 and hydrazine at $440\text{ }^\circ C$.¹⁹ Plasma CVD has also been used to deposit GeN films at substrate temperatures of $250\text{--}400\text{ }^\circ C$ using GeH_4/NH_3 or GeH_4/N_2 .^{20,21}

There has been little mention of tin nitride films in the literature. Remy and Hantzpergue used reactive cathodic sputtering to prepare the first tin nitride films.^{22,23} Crystalline tin nitride films have been recently prepared by reactive sputtering of tin in a nitrogen plasma,²⁴ and by magnetron sput-

tering of a pure tin target in a gas mixture of argon and nitrogen at room temperature.²⁵ The only CVD tin nitride reported to date is the deposition of polycrystalline material by APCVD from $Sn(NMe_2)_4$ and ammonia at substrate temperatures of $200\text{--}400\text{ }^\circ C$.²⁶

The best existing preparations of silicon and germanium nitride thin films rely on the use of difficult-to-handle silane and germane. We were interested in developing alternative precursor systems to the group 14 nitride films that would work with commonly used PECVD equipment. Of the alternative precursor systems tested to date, the dimethylamido compounds, $M(NMe_2)_4$, which were used with ammonia in APCVD depositions of carbon-free silicon and tin nitride, appeared to be the most promising because of their physical and chemical properties.^{5,26,27} The amido compounds are, for example, volatile, readily synthesized in high yields on a large scale, and are only moderately air sensitive.^{5,28,29} In the APCVD depositions the mechanism proposed for nitride formation involved transamination and α -hydrogen elimination reactions.^{5,26} We thought that analogous mechanisms could operate in a PECVD process, where reactive NH_x radicals from plasma-activated ammonia could supplant thermally activated ammonia.

Herein we show that relatively pure silicon, germanium, and tin nitride films can be deposited from $M(NMe_2)_4$ compounds and plasma-activated ammonia at low substrate temperatures.^{29,30}

II. EXPERIMENT

The experimental apparatus has been described previously.^{29,30} The plasma was produced by an induction coil connected to a 13.56 MHz rf power supply through an impedance matching network. Plasma powers of 20–25 W were used. System base pressures of less than 3 mTorr were achieved before each deposition. The carrier gas was ultrahigh-purity helium and the ammonia was Matheson

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ULSI purity. The precursor flow rate was adjusted to approximately 6%–10% of the total flow rate by means of a needle valve.

Silicon substrates were cut ($\approx 1 \text{ cm}^2$) from boron-doped (100) silicon wafers (Excil Corporation, CA). The substrates were cleaned by degreasing with dichloroethane for 2 min, followed by immersion in a HF:H₂O (1:10) solution for 2 min, and finally, rinsing in de-ionized water. Quartz substrates were microscope slides (ChemGlass Inc., NJ), which were degreased by rinsing in dichloroethane for 2 min.

Backscattering spectrometry (BS) was carried out by using an NEC Tandetron tandem accelerator.³¹ Data were typically acquired with a beam current of 20 nA until a charge of 4–10 μC (depending on the quality of statistics desired) was accumulated. A He²⁺ incident beam with energies between 3.3 and 3.7 MeV was typically used. In this energy regime there is an enhanced sensitivity for light elements, while the scattering from the heavy elements follows the Rutherford model.³² Elastic recoil detection spectrometry (ERD) was carried out using a beam of 8.2 MeV O⁴⁺. Data for each sample were collected until there was an accumulated charge of 1–5 μC , again depending on the quality of statistics desired. A hydrogen-implanted silicon substrate with a hydrogen concentration of $1 \times 10^{17} \text{ atoms/cm}^2$ was used as calibration standard. The surface morphology of the films was studied by using a Stereo-Scan 250 MK 37 scanning electron microscope with a beam energy range of 20–30 keV. Infrared (IR) spectra were collected for films deposited on silicon substrates using a Mattson Galaxy 5000 series FTIR in the range 500–4000 cm^{-1} . Transmittance spectra for films deposited on quartz substrates were collected on a Hewlett-Packard 8452 A diode array spectrophotometer.

III. RESULTS AND DISCUSSION

A. General growth conditions and film properties

Si(NMe₂)₄, Ge(NMe₂)₄, and Sn(NMe₂)₄, synthesized by following published procedures, were used as the main group precursors.^{5,28,29} The compounds are liquids at room temperature with moderately low boiling points [Si(NMe₂)₄, 74–75 °C/19 mm Hg; Ge(NMe₂)₄, 87–89 °C/15 mm Hg; Sn(NMe₂)₄, 51 °C/0.15 mm Hg].^{27,28}

The germanium and tin nitride depositions were carried out with undiluted ammonia, but the silicon nitride depositions required helium dilution of the NH₃ to avoid unacceptable carbon incorporation (10–20 at. %) in the films. The silicon nitride depositions with undiluted ammonia did, however, give faster growth rates (>400 Å/min). In all cases, helium was passed through the reactor as the substrate was heated to the desired deposition temperature and during cool down after deposition. The precursor flask was maintained at room temperature for the silicon and germanium compounds. The tin complex was gently heated with a heating tape ($\approx 45^\circ\text{C}$) to increase its volatility.

Film growth was observed in all cases on silicon and quartz substrates at temperatures between 100 and 400 °C. In general, the qualitative growth rates of the films increased going down the group; that is, under similar deposition conditions, the tin nitride deposited at the highest rate followed

TABLE I. Compositional data and refractive indexes of silicon nitride films.^a

Temperature (°C)	N/Si ratio ^b	H/Si ratio (at. %) ^c	Refractive index
192	1.2	0.37 (17)	1.5
307	1.4	0.24 (10)	1.8
406	1.5	0.25 (10)	1.8

^aFlow rates: NH₃, 20 sccm; He, 80 sccm, precursor, ~6–7 sccm. Plasma power, 20–25 W.

^bThe error in the determination of the N/Si ratio is estimated to be ± 0.1 .

^cA density of 3.44 g/cm³, the bulk value, was assumed for silicon nitride (Ref. 53). The error in the H/Si ratio is estimated to be ± 0.06 .

by germanium and silicon nitride, respectively. This is consistent with an initial associative step in the deposition mechanism because the size of the group 14 atoms increases going down the period from silicon to tin, making the respective amido compounds less hindered, but other factors may be involved as well.

The deposited films varied in thickness along the substrate area with the thickest part growing near the metalorganic inlet and decreasing in thickness along the substrate diagonal away from the inlet. All of the films had the highly colored rainbow-like interference patterns usually observed for coatings with high refractive indexes. The films were smooth and adhered well to the substrates as judged by the standard tape test.³³

The silicon and germanium nitride films were unaffected by concentrated HCl and aqua regia as judged by visual inspection, but they readily dissolved in 48% hydrofluoric acid. The tin nitride films dissolved readily in concentrated HCl, aqua regia and 48% HF. This is in contrast to tin nitride films produced from Sn(NMe₂)₄ and NH₃ by APCVD, which did not dissolve readily in these reagents.²⁶

In control experiments, films deposited at 300 °C from the M(NMe₂)₄ compounds in the absence of ammonia had large amounts of carbon contamination (10–20 at. %) as estimated by backscattering spectrometry (BS) measurements.^{5,26} Also, Si(NMe₂)₄ or Ge(NMe₂)₄ and NH₃ gave no depositions in the absence of a plasma at substrate temperatures of 200–400 °C.⁵ Tin nitride films were deposited, however, from Sn(NMe₂)₄ and ammonia at substrate temperatures of 100–200 °C without a plasma.

X-ray diffraction was used to examine the crystallinity of selected samples of silicon (deposition temperature 307 °C, on silicon), germanium (302 °C, on silicon), and tin nitride films (148 °C, plasma deposited on silicon; 154 °C, thermally deposited on silicon). In all cases there were no peaks, suggesting that the films were amorphous.

B. Silicon nitride films

Table I lists compositional data and refractive indexes for silicon nitride films deposited at various temperatures using Si(NMe₂)₄ and plasma activated NH₃. In all cases the flow rates of ammonia and helium were 20 and 80 sccm, respectively, and the precursor flow rate was approximately 6–7 sccm.

Growth rates were determined from film thicknesses obtained by BS measurements. Growth rates in the range of

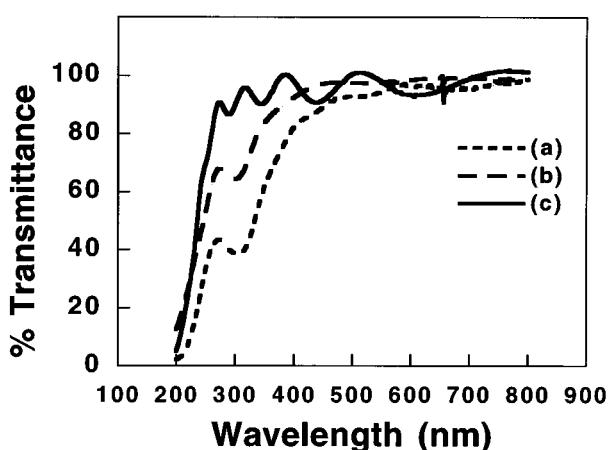


FIG. 1. Transmission spectra of silicon nitride films deposited from $\text{Si}(\text{NMe}_2)_4$ and plasma-activated NH_3 at (a) 188, (b) 304, and (c) 401 $^{\circ}\text{C}$ on quartz.

75–120 $\text{\AA}/\text{min}$ were obtained at substrate temperatures of 192–406 $^{\circ}\text{C}$. The rather small dependence of the growth rate on substrate temperature suggests that the rate limiting step has a low activation energy. Growth rates for plasma-deposited silicon nitride typically range from 10 to 300 $\text{\AA}/\text{min}$,^{6,11,13,15} although rates of approximately 1500 $\text{\AA}/\text{min}$ have been achieved in higher-power ($\approx 180 \text{ W}$) PECVD reactors.³⁵

Compositional analyses of the films were primarily carried out by using BS.³¹ According to the BS data, the silicon nitride films were close to stoichiometric, with N/Si ratios varying between 1.2 to 1.5. This is to be compared to a N/Si ratio of 1.33 for perfectly stoichiometric films. There appears to be a trend towards a nitrogen excess as the deposition temperature increases but firm conclusions are not warranted because of the experimental error in the ratios. BS spectra showed little or no carbon contamination (<few at. %). Oxygen was not observed in the spectra, again suggesting <few at. % contamination.

Literature reports suggest that stoichiometric films have been difficult to prepare by using other PECVD precursors. For example, silicon nitride films deposited from a $\text{SiH}_4/\text{NH}_3/\text{N}_2$ plasma were found to have N/Si ratios varying between 0.92 and 1.47 for different ammonia partial pressures, and SiN_x films deposited from SiH_4/N_2 , had an excess of silicon with the highest N/Si ratio achieved being 1.22.^{6,36}

Hydrogen concentrations, evaluated by ERD (Table I), decreased with increasing substrate temperature, a phenomenon also observed in silicon nitride films prepared by other plasma CVD techniques.^{10,37,38}

IR spectra showed bands arising from the Si–N stretch around 880 cm^{-1} , the N–H stretching and bending motions around 3300 and 1170 cm^{-1} , respectively, and the Si–H stretch at around 2180 cm^{-1} . The observed frequencies agree well with the literature values.^{37,39,40}

Transmittance spectra of the silicon nitride films deposited on quartz at various temperatures are shown in Fig. 1. The films, all approximately 1800–2000 \AA thick, are highly transparent with optical transmittances of 90%–95% at 632 nm, the region of the visible spectrum important for mask–

wafer alignment in a lithography process.⁴¹ The reported optical transmittance of low-pressure CVD SiN_x membranes around 2 μm thick is about 85%–95%.^{14,41}

The optical band gap of the silicon nitride films was calculated from the absorbance measurements by plotting d^2E^2 vs E , where d is the optical density or absorbance and E is the photon energy.^{42–44} The band gaps ranged from 5.2 to 5.5 eV, increasing with increasing deposition temperature. This is probably due to the increased nitrogen content, as suggested from calculations by Martin-Moreno *et al.*⁴⁵ There are only a few reports of band-gap measurements for silicon nitride films in the literature with the reported values varying from 2.8 to 4.0 eV.^{41,45} The optical band gap of stoichiometric Si_3N_4 films is reported to be around 5 eV.⁴⁶

The refractive indexes (Table I) varied from 1.5 to 1.8. Refractive indexes for nearly stoichiometric silicon nitride films deposited by PECVD are reported to be between 1.9 and 2.0 with lower values indicating nitrogen-rich films.^{6,12,35} The deviation of our results from the literature values is probably due to the variable nitrogen and hydrogen concentrations, which cause deviations in the film densities.

Silicon nitride is used extensively as a final passivation and coating layer for integrated circuit applications because of its excellent diffusion barrier properties.^{36,39} The effectiveness of our silicon nitride films as a diffusion barrier in $\text{Au}/\text{SiN}_x/\text{Si}$ metallization scheme was evaluated using BS.⁴⁷ The experiment consisted of comparing BS spectra of gold-coated silicon nitride films before and after annealing. Figure 2(a) shows the BS spectrum of a silicon nitride film about 600 \AA thick with a 500- \AA -thick gold overlayer before annealing. The sample was then annealed at 510 $^{\circ}\text{C}$ under a 100 sccm flow of helium for 1 h and its BS spectrum was again recorded [Fig. 2(b)]. The spectrum reveals only a slight broadening of the gold peak at the base of the peak, indicating only a small amount of gold interdiffusion into the silicon substrate after the high-temperature treatment. A scanning electron microscope (SEM) image of the gold-coated SiN_x films after annealing showed numerous globular structures which may be beads of gold–silicon eutectic that reportedly form at $\approx 377 \text{ }^{\circ}\text{C}$.⁴⁷

C. Germanium nitride films

Compositional data and refractive indexes of germanium nitride films deposited at three temperatures using $\text{Ge}(\text{NMe}_2)_4$ and plasma-activated ammonia are presented in Table II.

The growth rate varied between 110 and 310 $\text{\AA}/\text{min}$ for deposition temperatures in the range of 190–385 $^{\circ}\text{C}$. For comparison, germanium nitride films deposited by low-pressure CVD from GeCl_4 and ammonia have growth rates of 5–50 $\text{\AA}/\text{min}$.¹⁶ Germanium nitride films deposited from plasma-activated GeH_4 and N_2/NH_3 have growth rates of ≈ 10 –25 $\text{\AA}/\text{min}$.^{20,21}

The stoichiometries of the GeN_x films deposited on silicon were determined by backscattering spectrometry. The films were nearly stoichiometric (Table II), and carbon and oxygen contamination was typically <3 and <1 at. %, respectively. Germanium nitride films deposited from plasma-activated GeH_4 and N_2/NH_3 were reported to have a N/Ge

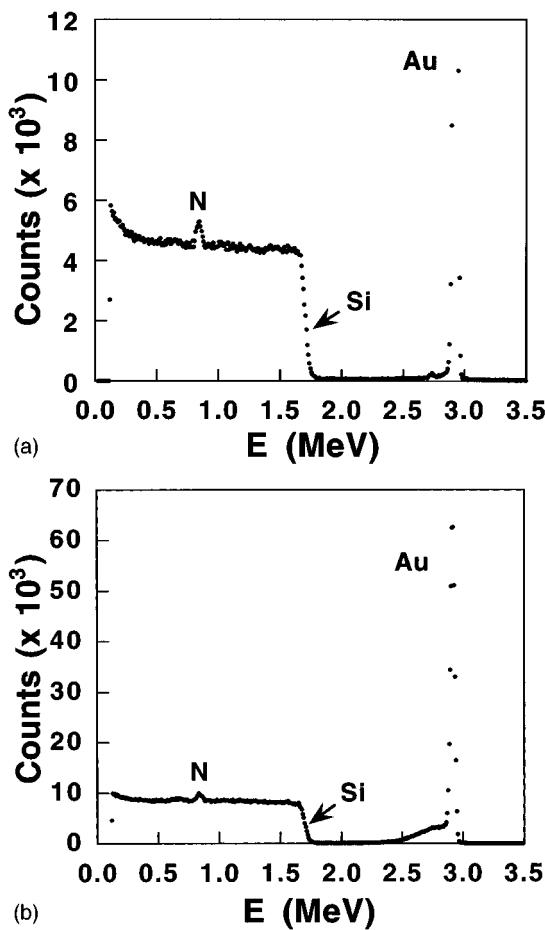


FIG. 2. (a) BS spectrum of a silicon nitride film ($\approx 600 \text{ \AA}$ thick) deposited at 279°C on silicon that was subsequently coated with gold ($\approx 500 \text{ \AA}$ thick). BS beam: 3.3 MeV He^{2+} . (b) BS spectrum of the gold-coated silicon nitride film shown in (a) after annealing in a flow of He (100 sccm) at 510°C for 1 h. BS beam: 3.3 MeV He^{2+} .

ratio of 0.5 and films deposited by reactive sputtering of germanium in a hydrazine plasma had N/Ge ratios of 0.18–0.2.^{21,48}

Calculated hydrogen contents, taken from ERD spectra, are also listed in Table II. A slight decrease in hydrogen content is observed on increasing the substrate temperature from 302 to 385°C . There appear to be no other reports in the literature on the determination of the hydrogen content in germanium nitride films.

TABLE II. Compositional data and refractive indexes of germanium nitride films.^a

Temperature (°C)	N/Ge ratio ^b	H/Ge ratio (at. %) ^c	Refractive index
190	1.2	0.28 (13)	2.1
302	1.3	0.29 (13)	2.2
385	1.3	0.23 (10)	2.1

^aNH₃, 70 sccm; precursor, $\sim 5\text{--}6$ sccm. Plasma power, 20–25 W.

^bThe error in the determination of the N/Ge ratio is estimated to be ± 0.1 .

^cA density of 5.24 g/cm^3 , the bulk value, was assumed for germanium nitride (Ref. 53). The error in the H/Ge ratio is estimated to be ± 0.06 .

TABLE III. Compositional data and refractive indexes for plasma-deposited and thermally deposited tin nitride films.^a

Temperature (°C)	N/Sn ratio ^c	H/Sn ratio (at. %) ^d	Refractive index
112 ^a	1.4	0.16 (7)	2.0
148 ^a	1.3	0.18 (8)	1.5
200 ^a	1.3	0.34(15)	1.9
106 ^b	1.3	0.25(11)	2.1
154 ^b	1.3	0.36(16)	2.1
201 ^b	1.6	0.15 (7)	2.2

^aFlow rate: NH₃, 30 sccm; precursor, $\sim 2\text{--}3$ sccm. Plasma power, 20–25 W.

^bFlow rate: NH₃, 30 sccm. No plasma was used.

^cThe error in the determination of the N/Sn ratio is estimated to be ± 0.1 .

^dA density of 3.53 g/cm^3 , was assumed for tin nitride (Ref. 54). The error in the H/Sn ratio is estimated to be ± 0.06 .

IR spectra for the germanium nitride films had two prominent bands at 723 and $\approx 3300 \text{ cm}^{-1}$. Bands at 3300 and 714 cm^{-1} in $\alpha\text{-Ge}_3\text{N}_4$ were previously assigned to N–H and Ge–N stretching motions, respectively.^{17,21} We also observed a weak intensity band at 1159 cm^{-1} that may arise from N–H bending motions (cf., the N–H bend in SiN_x films, which is reported to occur at $\approx 1180 \text{ cm}^{-1}$).³⁷

Germanium nitride films deposited on quartz (approximately $2500\text{--}2800 \text{ \AA}$ thick) had transmittances of $70\text{--}85\%$ at 632 nm , which increased with increasing deposition temperature. Band gaps of the films varied from 4.4 to 4.8 eV. There appears to be only one other reported band gap measurement for Ge_3N_4 films (4.0 eV).²³ The refractive indexes of the films were close to 2.1 (Table II), the value reported for bulk and thin-film germanium nitride.^{16,17,23}

The barrier properties of the GeN_x films in a Au/ GeN_x /Si metallization scheme were investigated by BS.⁴⁷ A 900-Å-thick germanium nitride layer on silicon with a 500-Å-thick gold overlayer was subjected to thermal treatment at 411°C for 20 min under a 100 sccm flow of helium. Backscattering spectra were collected before and after annealing. The spectra showed that there was some interdiffusion of the gold overlayer into the germanium nitride, but not into the silicon substrate. SEM micrographs of the annealed samples showed nodular structures that may be beads of Ge–Au eutectic, which form at temperatures below $<400^\circ\text{C}$.⁴⁷

D. Tin nitride films

Tables III lists compositional data and refractive indexes for tin nitride films deposited using $\text{Sn}(\text{NMe}_2)_4$ and ammonia with and without the use of plasma excitation. All the films were deposited using undiluted ammonia flowing at a rate of 30 sccm. To obtain films that would adhere to the substrates, it was necessary to maintain low substrate temperatures (100–200 °C).

The growth rates of the plasma-deposited tin nitride films ranged from 750 to 1625 \AA/min for substrate temperatures from 112 to 200°C . In general, a lower growth rate was obtained without plasma activation, under otherwise identical conditions. This suggests that the plasma-activated ammonia is more reactive to the tin precursor than nonactivated ammonia, thereby leading to higher deposition rates. In some

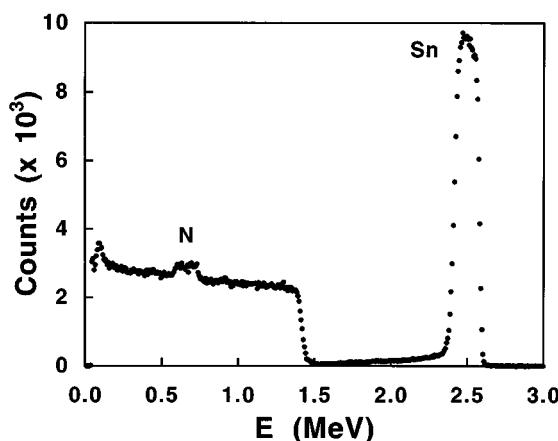


Fig. 3. BS spectrum for a plasma-deposited tin nitride film on silicon. Deposition temperature: 200 °C. BS beam: 3.3 MeV He²⁺.

instances, a growth rate of over 5000 Å/min was observed at 200 °C due to uncontrolled rapid injection of the precursor. Interestingly, these very high growth rate films had properties comparable to the rest of the films. Tin nitride films deposited from Sn(NMe₂)₄ and NH₃ by the APCVD technique at 200–400 °C had growth rates of ≈1000 Å/min.²⁶

The N/Sn ratios determined by BS (e.g., Fig. 3) are close to the stoichiometric value of 1.33 for both the plasma- and nonplasma-deposited tin nitride films. Surface oxide was usually observed in the BS spectra of the tin nitride films for both the plasma-deposited and thermally deposited materials. The thickness of the oxide layer was estimated to be between 25 and 30 Å. The oxide layer was formed during the routine handling of the films in air.

According to ERD analysis, the hydrogen content of the tin nitride films ranged from 7 to 16 at %. These numbers are comparable to those found for tin nitride films deposited from Sn(NMe₂)₄ and NH₃ by the APCVD technique, which had 15–18 at % of hydrogen.²⁶

IR spectra for the plasma-assisted and thermally deposited tin nitride films showed the characteristic Sn–N stretch at 684 cm⁻¹.²² In addition, a N–H stretch was observed at 3300 cm⁻¹.³⁷ A weak band appearing at 941 cm⁻¹ may be due to surface Sn–O.^{50,51}

The transmittance of plasma-deposited tin nitride films, approximately 2000–3000 Å thick, was in the range of 50%–82% at 632 nm. The thermally deposited films (1100–1500 Å thick) showed transmittances of 78%–85% at the same wavelength. The band gap derived from the spectra varied from 2.9 to 4.1 eV for the plasma-deposited tin nitride films and from 3.8 to 4.9 eV for the thermally deposited films. For both the plasma-deposited and thermally deposited tin nitride films, the band gap became larger with increasing deposition temperatures. The band gap of tin nitride films deposited by APCVD from Sn(NMe₂)₄ and NH₃ ranged from 1.95 to 2.25 eV,²⁶ while tin nitride films deposited by reactive pulvulation had a band gap of 3.55 eV.²³

The refractive indexes of the plasma-deposited films varied from 1.5 to 2.0 and those deposited without the plasma were 2.1 to 2.2 (Table III). Refractive indexes of APCVD tin nitride films were reported to vary between 2.8 and 3.3.²⁶

IV. CONCLUSION

We have prepared silicon, germanium, and tin nitride films at low substrate temperatures using the corresponding group 14 amido complexes and plasma-activated ammonia as precursors. In addition, the composition and properties of tin nitride films deposited without plasma excitation were investigated. The silicon and germanium nitride films prepared in our PECVD process are nearly stoichiometric with <few at. % carbon or oxygen contamination. This is in contrast to silicon nitride films prepared by other plasma CVD techniques using SiH₄/N₂, SiH₄/NH₃, or SiH₄/N₂/NH₃ precursor systems where nonstoichiometric films are generally produced.^{6,9,36} Germanium nitride films produced by PECVD from GeH₄/N₂ or GeH₄/NH₃/N₂ are also reported to be nonstoichiometric, having a N/Ge ratio of 0.5.²¹ The growth rates for our silicon nitride films are comparable to those produced by other PECVD techniques using SiH₄/NH₃ or SiH₄/N₂ as precursors,^{6,11,13} though they are lower than the rates achieved for films produced by ECR plasma deposition from SiH₄/N₂.³⁵ However, the power density in ECR reactors is higher than we used. The growth rates of our germanium nitride films, on the other hand, are at least five times higher than the highest growth rate reported for germanium nitride films prepared by CVD techniques.^{16,20,21} The deposition rates of the nitrides increased as we moved down the column to heavier congeners.

Transmittance measurements indicate that our plasma-deposited silicon and germanium nitride films have high transmittances in the visible region, an essential requirement for accurate mask–wafer alignment in a lithography processes.⁴¹ The silicon and germanium nitride films displayed moderate-to-good barrier properties in diffusion experiments for a Au/M₃N₄/Si metallization scheme.

In a simplistic view, our film depositions probably proceed similarly to the M(NR₂)_n/NH₃ thermal processes, that is, by transamination-like reactions involving NH_x species produced in the plasma and subsequent α-hydrogen elimination reactions.^{29,30,52} Judging by the observation of little or no carbon contamination in the films, the transamination and α-hydrogen elimination reactions must efficiently rid the metalorganic precursor of the carbon-containing dialkyl amido ligands.

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