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Plasma enhanced chemical vapor deposition of silicon nitride films from a metal-organic precursor

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Silicon nitride films are grown by plasma enhanced chemical vapor deposition from tetrakis(dimethylamido)silicon, $Si(NMe_2)_4$, and ammonia precursors at substrate temperatures of 200–400 °C. Backscattering spectrometry shows that the films are close to stoichiometric. Depth profiling by Auger electron spectroscopy shows uniform composition and no oxygen or carbon contamination in the bulk. The films are featureless by scanning electron microscopy under 100,000× magnification.

Silicon nitride thin films are used in microelectronic device fabrication as an interlevel dielectric, as a mask for ion implantation, oxidation, or diffusion, and for device passivation.[1] They have been prepared at high substrate temperatures (700–900 °C) by pyrolytic deposition in a hydrogen atmosphere from silane and ammonia precursors[2,3] and by low pressure chemical vapor deposition from dichlorosilane and ammonia precursors.[4,5] Silicon nitride films have also been deposited by remote and direct plasma enhanced chemical vapor deposition (PECVD) techniques from silane and either ammonia or nitrogen,[6–8] and recently from a disilanyl amine and ammonia.[9] The PECVD processes allow lower temperatures of deposition (150–400 °C) than the thermal processes, an advantage when using thermally sensitive substrates such as those found in microelectronics applications.

Recently, the preparation of silicon nitride films by atmospheric pressure chemical vapor deposition from tetrakis(dimethylamido)silicon, $Si(NMe_2)_4$, and ammonia precursors has been reported.[10] Also, $Si(NMe_2)_4$ and NH_3 or N_2 have reportedly been used in a LPCVD multiwafer system (with or without plasma excitation) to deposit films, but stoichiometry and film properties were not given.[11] $Si(NMe_2)_4$ has attractive features that make it a promising CVD reagent. It is, for example, a volatile liquid (bp 180 °C at 760 mm Hg, 74.5 °C at 19 mm Hg) that can be readily prepared in large quantities from inexpensive reagents and purified by distillation.[10] Importantly, it is only moderately air sensitive and therefore much safer to handle than silane, the conventional silicon CVD precursor. We show in this report that $Si(NMe_2)_4$ can be used in a plasma enhanced chemical vapor deposition process to deposit nearly stoichiometric silicon nitride films at low substrate temperatures without carbon or oxygen contamination.

Depositions were carried out using a low pressure cold wall tubular reactor with a 3.5 cm inside diameter (Fig. 1). The plasma was excited with a coil connected to a 13.56 MHz power supply through an impedance matching network. A mixture of helium and ammonia was passed through the plasma. The plasma-activated gases were mixed with the metal-organic precursor downstream of the coil just before the substrate. This configuration resembles the remote plasma CVD reactor reported previously.[12] The substrate was bonded to an aluminum holder, and the holder was positioned

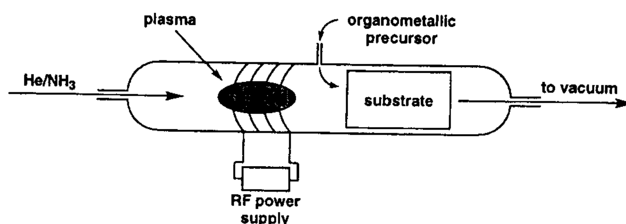

FIG. 1. Schematic of the experimental apparatus.

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such that the substrate leading edge was a few mm from the organometallic outlet. The substrate temperature was monitored by a thermocouple inserted into a thermowell drilled near the surface of the holder. A diffuse plasma glow encompassed the region of the precursor inlet as well as the substrate. The helium and ammonia flow rates were regulated by mass flow controllers. A flask containing $Si(NMe_2)_4$ was connected to the reactor through a needle valve which was used to adjust the precursor flow rate. The latter was calculated from the known reactor volume and the pressure rise in the system measured with the needle valve open and the reactor isolated from the pump. Before each deposition, base pressures of <1 mTorr were achieved, and the leak rate was confirmed to be less than 5×10^{-3} sccm. Typical operating pressures were from 0.15 to 0.30 Torr and the plasma power was in the range 20–25 W.

Depositions were carried out on silicon and quartz at substrate temperatures of 200–400 °C. The films were characterized by ellipsometry, Auger electron spectroscopy (AES), backscattering spectrometry (BS), and elastic recoil spectrometry (ERS).[13] The films were featureless by scanning electron microscopy at 100,000× magnification, and were amorphous by x-ray diffraction. All of the films showed good adhesion to the substrates (Scotch tape test).[14] The films did not dissolve in concentrated HCl or aqua regia, but they readily dissolved in 48% hydrofluoric acid. Film thicknesses, as determined by BS, were up to 3000 Å, and growth rates, which increased as the deposition temperature was increased, ranged from 75–120 Å/min (Table I). These growth rates are typical of remote PECVD systems.[15,16] Higher growth rates can be obtained in direct PECVD.[17]

Silicon nitride films deposited by PECVD normally display significant departures from compound stoichiometry, having an excess of nitrogen or silicon depending on the deposition parameters.[18,19] In the present case, BS data (e.g., Fig. 2) indicate that the films are nearly stoichiometric. There appears to be a trend toward a nitrogen excess as the deposition temperature

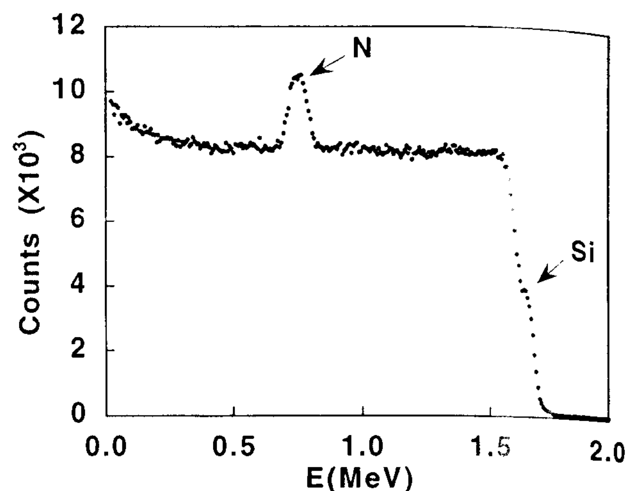

FIG. 2. Backscattering spectrum for a silicon nitride film deposited on silicon at 192 °C (3.55 MeV He^{2+} beam).

increases, but firm conclusions are not warranted because of the experimental error in the N/Si ratios. Oxygen and carbon peaks are not observed in the BS spectra of our best films, suggesting < few at.% contamination, nor are oxygen and carbon observed by AES depth profiling (argon ion sputtering) of a film deposited on silicon. The AES spectrum does show there is a thin layer of oxygen and carbon on the film surface arising from its routine handling in air. Interestingly, when pure plasma-activated ammonia was used rather than a plasma-activated He/NH_3 mixture, generally higher growth rates (≈50% higher) were observed at the same total flow, but there was also a large amount of carbon contamination (10–20 at.%) in the films.

The hydrogen content of the films, determined by ERS, was less than 20 at.%. Infrared spectra showed both N–H (≈3336 cm^{-1}) and Si–H (≈2181 cm^{-1}) bands. Films deposited by direct PECVD commonly have 20–40 at.% of incorporated hydrogen.[20-22] The refractive indexes of the films (Table I) were in the range 1.52 to 1.84. 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.[6,22] It is not clear why the refractive indexes of our films deviate from the values reported for the stoichiometric material, but low film densities may be responsible.

In control experiments, film depositions carried out using only $Si(NMe_2)_4$ and plasma activation gave films contaminated with carbon (10–20 at.%). $Si(NMe_2)_4$ and NH_3 did not deposit films at substrate temperatures of 200–400 °C without the plasma.

In a simplistic view, the film depositions probably proceed similarly to the $M(NR_2)_n/NH_3$ thermal processes[23]: that is, via transamination-like reactions involving NH_x radicals produced in the plasma, and

TABLE I. Growth rates, stoichiometries, and refractive indexes as a function of temperature for silicon nitride deposited on silicon [flow rates: He = 80 sccm, NH_3 = 20 sccm, $Si(NMe_2)_4$ = 6–7 sccm].

Temperature (°C)	Growth rate (Å/min)	N/Si ratio[a]	H content[b] (at.%)	Refractive index
192	76	1.2	17	1.52
307	87	1.4	10	1.84
406	118	1.5	10	1.77

[a]The error in these numbers is approximately ±0.1.
[b]The error in these numbers is approximately 10 at.%. To convert from H atom concentrations we assumed a density of 3.44 g cm^{-3}. The standard for ERS was amorphous silicon implanted with hydrogen ion to a dose of 1×10^{17} ions/cm^2 at an energy of 12.5 keV.

subsequent α–H elimination reactions. Judging by the observation of little or no carbon contamination in the films, the transamination and α–H elimination reactions must efficiently rid the silicon precursor of the carbon-containing dialkyl amido ligands. The rather weak dependence of growth rate on substrate temperature (Table I) suggests that the rate limiting step has a low activation energy.

In conclusion, we have shown that $Si(NMe_2)_4$ and ammonia are promising PECVD precursors for the low temperature deposition of silicon nitride films. Importantly, $Si(NMe_2)_4$ is safer to handle than SiH_4, making our method an attractive alternative to the conventional silane route. Because main group amides share a common chemistry, it is possible to plasma deposit other main group nitride films using analogous $M(NR_2)_n/NH_3$ precursor systems.[24,25]

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