MIS junctions, and this possibility is also being studied.

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Silicon nitride films deposited with an electron beam created plasma

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Silicon nitride films have been deposited using an electron beam created plasma in a silane, ammonia, and nitrogen mixture. The films were deposited at substrate temperatures between 50 and 400 °C. Physical, chemical, and electrical properties of these films are reported.

PACS numbers: 81.15.Gh, 68.60. + q, 78.65.Jd, 73.60.Fw

Recently,[1] we have demonstrated electron beam assisted chemical vapor deposition (EBCVD) of SiO_2 films at low substrate temperatures (150–400 °C). The electron beam created plasma is spatially localized and has a unique electron energy distribution.[2] Dissociation of the gaseous reactants occurs primarily in a 0.3-cm-thick by 2.5-cm-wide strip located a few millimeters above the substrate as described previously.[1] A side view of the electron beam created plasma in a silane, nitrogen, and ammonia atmosphere at 0.35 Torr is shown in Fig. 1. This planar dissociation region, defined by the electron beam geometry, provides an extended flux of reactant species and dissociation products which contributes to conformal coverage of irregular features. This occurs because the localized plane source appears infinite in extent compared to characteristic features on the substrate. Moreover, the confined excitation region helps to minimize gas phase generation of particulates and provides efficient use of the gaseous reactants.

Herein we describe the EBCVD of silicon nitride films using NH_3, N_2, and SiH_4 as the reactant gases. The silane source is 5% SiH_4 diluted in N_2. Nitride films have been deposited on aluminum, SiO_2, and polysilicon films as well as on crystalline silicon substrates. The wide range of experimental conditions under which EBCVD silicon nitrides have been deposited includes substrate temperatures, from 50 to 400 °C, electron beam current values from 2 to 40 mA, electron beam energies from 1 to 5 keV, total ambient pressures between 0.1 and 0.4 Torr, and NH_3/SiH_4 mass flow ratios from 1 to 80. The dependence of the deposition rate with electron beam current, gas pressure, and flow rates is

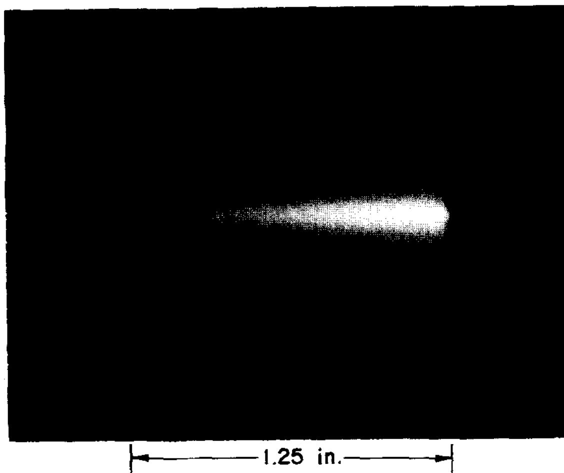

FIG. 1. Side view of the spatially confined electron beam created plasma.

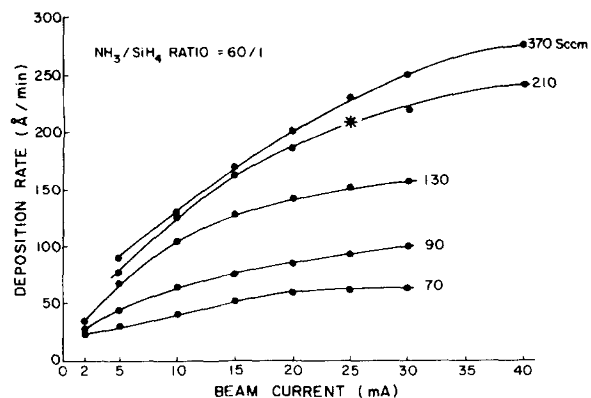

FIG. 2. Deposition rate vs beam current for varying total gas flow ($NH_3 + N_2 + SiH_4$) at a constant pressure of 0.35 Torr, and substrate temperature of 350 °C. The asterisk denotes the typical deposition conditions described in the text.

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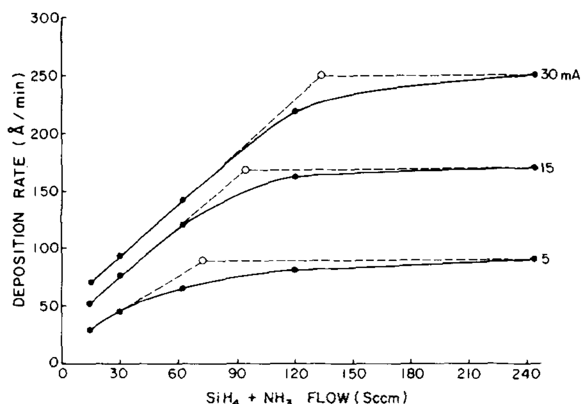

FIG. 3. Deposition rate vs silane plus ammonia flow for electron beam currents of 5, 15, and 30 mA, at a total pressure of 0.35 Torr and a substrate temperature of 350 °C.

summarized in Figs. 2–4. Figure 2 illustrates the effect of varying the total flow rates, while holding the flow ratio of NH_3 to SiH_4 at 60. The total cell pressure was held at 0.35 Torr by a downstream pump throttle valve. The deposition rate increases with both electron beam current and flow rates. However, the deposition rate rapidly saturates at low beam currents (10 mA). The deposition rate at fixed beam current increases with increasing gas flow as shown in Fig. 2. Figure 3 shows the deposition rate as a function of the total gas flow, for different electron beam current. Notice that for a given electron beam current the deposition rate saturates with increasing gas flow. The flow value at which saturation occurs increases with increasing current as shown by the intersection of the broken lines in Fig. 3. This effect is possibly due to depletion of the gas donors. Figure 4 illustrates the effect of varying total gas pressure from 0.2 to 0.4 Torr. The curves indicate that higher gas densities lead to higher deposition rates. Again the deposition rate saturates as the electron beam current increases.

The properties of the EBCVD Si_3N_4 films, summarized in Table I, correspond to the following conditions: substrate temperature of 350 °C, total cell pressure of 0.35 Torr, and NH_3, SiH_4, and N_2 flow rates of 120, 2, and 88 sccm, respectively. The electron beam current is 25 mA and the beam voltage is 4.2 kV. The conditions described above are indicated by an asterisk in Fig. 2.

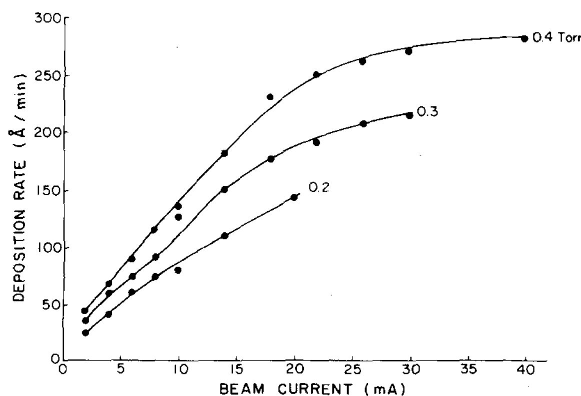

FIG. 4. Deposition rate vs beam current for pressures of 0.2, 0.3, and 0.4 Torr at a constant flow of 97.5 sccm N_2, 150 sccm NH_3, and 2.5 sccm SiH_4, and a substrate temperature of 400 °C.

TABLE I. Properties of electron beam deposited silicon nitride.

Property	Value
Stoichiometry	
Si $43 \pm 2\%$	
N $57 \pm 2\%$	
O $<1\%$	
C $<0.1\%$	
Hydrogen bonding	
Si–H $<0.5\%$	
N–H 12%	
Etch rate	
(5:1 buffered HF) 3–20 Å/s	
Adhesion	
$> 5.5 \times 10^8$ dyne/cm^2	
Pinhole density	
(1000 Å on Si)	5–100 #/cm^2
Refractive index:	1.80–2.0
Breakdown voltage:	4–6 MV/cm
Resistivity at 1 MV/cm:	10^{12}–10^{14} Ω cm
Dielectric constant at 1 MHz:	7.1

Auger measurements taken on the EBCVD Si_3N_4 samples with NH_3/SiH_4 ratios from 1 to 80 are shown in Fig. 5. The films are stoichiometric for NH_3/SiH_4 flow ratios greater than 5. A similar dependence of stoichiometry on flow ratios is observed with conventional plasma enhanced CVD.[3,4] The amounts of oxygen and carbon incorporated in the films were below the detectability limits of sputtered Auger analysis (0.1%). Several spatial locations were evaluated on each sample and the Auger data were taken during sputtering to reduce uncertainties from background oxygen reacting with the sputtered surface. Quantitative information on the Si and N content was achieved by comparing the Si(LMM) and N(KLL) Auger spectra of a Si_3N_4 standard[5] and the EBCVD Si_3N_4 films. Auger measurements on the as-deposited surface show only Si_3N_4 and no elemental silicon, indicating that all of the silane radicals reacted with ammonia forming Si_3N_4 with N–H bonding.

The N–H (3340, 1170 cm^{-1}) bond density for the Si_3N_4 films was obtained by using IR transmission spectroscopy (integrated baseline tangent method).[6] A k value of 8.2×10^{16} cm^{-1}, at 3340 cm^{-1} as suggested by Adams[6] for PECVD Si_3N_4 films, was used. The N–H bond density, assuming a film density of 2.7 gm/cm^3, was calculated to be 12%. There was no detectable Si–H bonding ($<0.5\%$) in the films over a wide range of deposition conditions. The current versus voltage and capacitance versus voltage properties of the

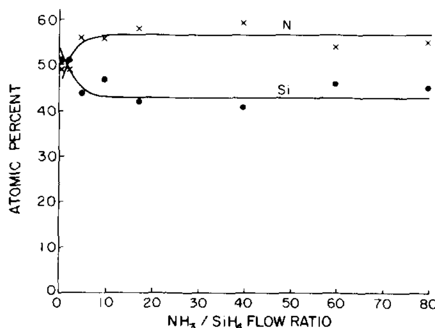

FIG. 5. Atomic percent of Si and N vs NH_3 to SiH_4 flow ratio with a total pressure of 0.3 Torr and a substrate temperature of 350 °C.

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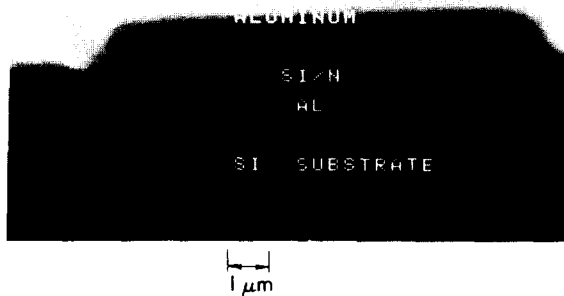

FIG. 6. SEM micrograph of EBCVD Si_3N_4 covered by Al and conformally covering a 0.8-μm-high step. Deposition conditions include substrate temperature 350 °C, total pressure of 0.35 Torr, NH_3, SiH_4, and N_2 gas flows of 120, 2, and 88 sccm, respectively.

EBCVD Si_3N_4 films were measured on $Al/Si_3N_4/Si/Al$ structures. From current versus voltage analysis, the current conduction mechanism for the Si_3N_4 films followed the Frenkel–Poole dependence. This behavior is typical of silicon nitride films and characteristic of field-enhanced charge emission from trapping centers.[4,7]

We have also studied the step coverage properties of the EBCVD technique.[8] No film cracking has been observed in all scanning electron microscope (SEM) micrographs taken of the Si_3N_4 films, however, a slight cusping at the base of the step has been observed. Figure 6 illustrates a 0.9-μm-thick EBCVD Si_3N_4 film deposited as an interlayer dielectric between a 0.8-μm-thick patterned aluminum step and a 0.7-μm-thick aluminum film. The aluminum was sputter deposited and patterned using conventional photolithographic processing. A selective aluminum etch was then used to distinguish the Si_3N_4/Al interfaces.

In summary, we have deposited stoichiometric, device quality silicon nitride films using a glow discharge electron gun.

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High-rate deposition of amorphous hydrogenated silicon from a SiH_4 plasma

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An extremely high deposition rate of amorphous hydrogenated silicon has been achieved by employing a new rf discharge technique. The deposition rate has been increased to more than 50 Å/s at a substrate temperature of 200 °C without accompanying any appreciable deterioration in the electronic and structural properties as compared to those of specimens prepared at a conventional deposition rate (~1 Å/s). Thermal stability of the high-rate samples is improved with respect to that of low-rate specimens.

PACS numbers: 81.15. – z, 68.55. + b, 73.60.Fw, 68.60. + q

Recent developments in technological applications of discharge-produced amorphous hydrogenated silicon (*a*-Si:H) to photoreceptors and low-cost solar cells raise a strong demand for realizing high-rate deposition. The deposition rate from a SiH_4 plasma is increased by increasing the rf power density and the concentration of a SiH_4 feed gas as well.[1] However, the growth rate has been limited typically in the range of 1–5 Å/s because an increase in the deposition rate results in silicon flake formation in the gas phase and in deterioration of film properties.[2] The optimum growth of high quality *a*-Si:H appears to take place through the heterogeneous reactions of adsorbed chemical species on the substrate surface.[3] Therefore, to achieve high-rate deposition it is necessary to enhance the concentration of reactive species near the substrate surface and to suppress the gas phase polymerization reactions which lead to silicon flake formation.

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