Electron beam assisted CVD of silicon dioxide and silicon nitride films

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Abstract

A glow discharge electron beam has been used to deposit silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) films for microelectronic applications.

Electron beam assisted CVD is a new technique in which the reaction volume is defined mainly by the geometry of the electron beam and offers the possibility of uniform deposition over large areas. The SiO_2 films were deposited in silane-nitrous oxide-nitrogen mixtures, and the Si_3N_4 films were deposited in silane-ammonia-nitrogen mixtures. The films were deposited with a 2-4 kV electron beam parallel to the sample, at 0.1-1 Torr pressures, and at substrate temperatures from 50-400°C. The index of refraction, sthoichiometry, pinhole density, etch rate, conformal step coverage, and hydrogen bonding were measured.

Introduction

A need exists for low temperature dielectric fabrication process which minimizes wafer warpage, dopant redistribution, and defect generation and propagation. This need has been met by commerically available radio frequency generated plasma enhanced chemical vapor deposition (PECVD) systems. All PECVD systems suffer from the process disadvantage that flow rates, pressure, reactor geometry and plasma power are interrelated and difficult to control independently. Moreover, the understanding of PECVD mechanisms is limited and of an empirical nature since these processes are strongly reactor specific.

Recently beam ehanced CVD techniques have been introduced which can achieve device quality films at high deposition rates and low substrate temperatures. The laser CVD (LCVD) technique has been used at Colorado State to deposit SiO_2, Si_3N_4, Al_2O_3, ZnO, Al, Cr, Mo and W films.[1-4] The electron beam CVD (EBCVD) technique has been used to deposit SiO_2[5-7] and Si_3N_4[6-8] films on a variety of substrates.

These beam deposition techniques provide a broader process window than conventional PECVD and thus allow for nearly independent optimization of process variables. Since a planar dissociation region is characteristic of beam assisted CVD, an extended flux of reactant species and dissociation produces is provided. This localized plane source appears infinite in extent compared to substrate features allowing for conformal coverage of irregular surface features.

This confined excitation region helps to minimize gas phase generation of particulates. Scattered energy from the beam generates a diffuse component of energy incident on the surface which can be controlled by varying the beam to substrate distance and cell pressure. In this work we compare plasma enhanced and electron beam assisted chemical vapor deposition of SiO_2 and Si_3N_4 films.

Experimental apparatus

The electron beam assisted CVD (EBCVD) method has a spatially localized excitation volume defined by an aperature allowing for wide area depositions at high rates. The reactor geometry of the electron beam deposition system is shown in Figure 2.[5] A molybdenum plate heated by a 500W tungsten halogen lamp in combination with a thermocouple and temperature controller provides repeatable substrate temperatures from 50°C to 500°C. The electron beam source is a modified version of glow discharge guns originally developed to pump ion lasers.[9] The electron gun cathode is purged with an inert gas to prevent unwanted deposits from forming. The cathode sheath accelerates the electrons to kilovolt energies with electron beam generation efficiencies up to 80%.[9] The electron beam travels parallel to and a few millimeters above a heated substrate. The electron beam created reaction volume is confined due to the low scattering angle of kilovolt electrons[10] to a 3 x 25 mm scheath defined by a rectangular aperature.

The monoenergetic electron beam creates an electron energy distribution with an abrupt upper energy limit as shown in Figure 2. This electron energy distribution for the beam created plasma was calculated for a Hg-He plasma.[9] The deposition rate for EBCVD and PECVD films are related to the product of the dissociation cross section, the electron velocity, the density of reactant species and electrons integrated in energy over the electron energy distribution. The conventional PECVD scheme has a Maxwellian distribution of electrons which is velocity sensitive to process variables.[11] The electron beam created plasma however, allows for a more controllable plasma condition because of the abrupt high energy limit, independent of pressure or gas flow allowing for a wider process window compared to PECVD.

EBCVD and PECVD of SiO_2

Typical conditions for EBCVD and PECVD chemical vapor deposition of SiO_2 are shown in Table I. A higher N_2O/SiH_4 mass flow ratio was used for the EBCVD SiO_2 compared to PECVD SiO_2 to ensure that all of the silane reacts with the oxygen from the N_2O donor. The deposition rate for the EBCVD films increased with increasing total pressure and beam current. Decreasing the N_2O/SiH_4 flow ratio increased the EBCVD deposition rate. Increasing the total flow while maintaining a constant flow ratio, pressure and beam current also increased the EBCVD deposition rate indicating that the reaction is flow limited. SiO_2 films deposited with substrate temperatures of less than 150°C were powdery whereas films deposited at substrate higher temperatures were glass-like in agreement with observations for low temperature laser CVD of SiO_2.[1]

The physical, chemical, and electrical properties of SiO_2 films are compared in Tables II-IV. The EBCVD films are comparable to PECVD films with respect to adhesion, stress, index of refraction, stoichiometry and hydrogen incorporation. Refractive indices of EBCVD SiO_2 films deposited with N_2O/SiH_4 ratios from 30 to 100 where within ±5% of the thermally grown SiO_2 value of 1.462. Infrared absorption analysis of EBCVD SiO_2 films indicates very little SiH, SiOH, and H_2O bonding. The etch rate for the EBCVD SiO_2 films are greater than the PECVD films because of a higher defect density (high pinhole density) and porosity. No annealing has been performed on the EBCVD films to date, but densification is expected to reduce etch rates as shown previously for other low temperature chemically vapor deposited films.[1,13] Conformal coverage of the EBCVD SiO_2 films was observed over aluminum and polysilicon patterns.[7]

EBCVD and PECVD of Si_3N_4

The deposition of silicon nitride from silane, ammonia and nitrogen mixtures using EBCVD and PECVD is described below. Typical deposition conditions are summarized in Table V. The dependence of the EBCVD deposition rate with electron beam current, gas pressure and flow rates are summarized in Figures 3-5. Figure 3 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 by the 5 curves in Figure 3. Figure 4 shows the deposition rate as a function of the total gas flow, for different electron beam currents. 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 Figure 4. This effect is possibly due to depletion of the gas donors. Figure 5 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 physical, chemical, and electrical properties of EBCVD and PECVD Si_3N_4 are summarized in Tables VI-VIII. The EBCVD and PECVD Si_3N_4 have comparable physical properties as shown in Table VI. Auger measurement taken on the EBCVD Si_3N_4 samples with NH_3/SiH_4 ratios from 1 to 80 are shown in Figure 6. 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.[13,14] The EBCVD Si_3N_4 films are stoichiometric oxygen and carbon free within the limits of Auger (<1%). The SiH bonding from infrared absorbance measurements in EBCVD Si_3N_4 deposited under the deposition conditions listed in Table V is remarkably low compared to PECVD films. The presence of SiH bonding has been observed in silicon rich EBCVD Si_3N_4 films deposited in a N_2 and SiH_4 atmosphere but very little was observed in EBCVD films deposited under a wide range of conditions. The absence of SiH in the stoichiometric EBCVD films is explained by the high NH_3/SiH_4 flow ratio used. Others have observed a similar trend for PECVD Si_3N_4 films.[15,16] The higher etch rate and pinhole density and lower resistivity and breakdown voltage of EBCVD films, suggests EBCVD films are more porous with a higher defect density than PECVD films.

Summary

A novel electron beam assited chemical vapor deposition technique using a unique sheet beam geometry is presented. We have compared the properties of EBCVD and PECVD SiO_2 and Si_3N_4. The unoptimized EBCVD films (deposited outside of a clean room environment) have comparable properties to PECVD films but are inferior in terms of etch rate, pinhole density, and resistivity.

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Table I. Typical SiO_2 deposition conditions.

	Electron Beam	RF Plasma
• Substrate Temperature (°C)	250-400 (350)	380
• Total Pressure (Torr)	0.25	1.1
• Gas Flow $N_2O/SiH_4/N_2$	75/1/75	33/1/0
• Deposition Rate (Å/Min)	500	300
• CVD Parameters	4.7 kV 12 mA	450 kHz

Table II. Physical properties of CVD SiO_2.

	Electron Beam	RF Plasma
• Stoichiometry	SiO_2	$SiO_{1.94}N_{0.06}$
Nitrogen (%)	<1	3
Carbon (%)	<2	0.1
• Hydrogen Bonding		
2270 cm^{-1} SiH (%)	<1	2
3380 cm^{-1} H_2O (%)	<0.001	<0.001
3650 cm^{-1} OH (%)	<0.01	0.002
• Etch Rate in 7:1		
Buffered HF (Å/sec)	30-60	20

Table III. Chemical properties of CVD SiO_2.

	Electron Beam	RF Plasma
• Adhesion (10^8 $Dyne/cm^2$)		
(1000 Å on Si)	>7	>7
• Pinholes ($\#/cm^2$)		
(1000 Å on Si)	100-700	25-100
(2000 Å on Si)	10-100	~1
• Refractive Index (6328 Å)	1.46	1.46
• Stress on Si_2 (10^9 $dyne/cm^2$) Compressive	9.4	3.6

Table IV. Electrical properties of 2000 Å CVD on SiO_2 on <100> silicon.

	Electron Beam	RF Plasma
• Breakdown Voltage (MV/cm)	2-3	10
• Resistivity at 5 MV/cm (Ω-cm)	10^{14}-10^{16}	10^{16}
• Flatband Voltage (V)	0.5-3	<0.2
• Dielectric Constant at 1 MHz Thermal Oxide (3.9)	3.5	4.6

Table V. Tyipcal Si_3N_4 deposition conditions.

	Electron Beam	RF Plasma
• Substrate Temperature	250-400°C (400°C)	380°C
• Total Pressure (Torr)	0.35	2
• Gas Flow $NH_3/SiH_4/N_2$	60/1/44	7/1/0
• Deposition Rate (Å/min)	200	350
• CVD Parameters	2.4 kV 25 mA	450 kHz

Table VI. Physical properties of CVD Si_3N_4.

	Electron Beam	RF Plasma
• Adhesion (10^8 dyne/cm^2)		
(1000 Å on Si)	>5.5	>6
• Pinholes (#/cm^2) (50 V bias)		
(1000 Å on Si)	5-100	2-3
(2000 Å on Si)	--	<1
• Refractive Index (6328 Å)	1.85	2

Table VII. Chemical properties of CVD Si_3N_4.

	Electron Beam	RF Plasma
• Stoichiometry	Si_3N_4	Si_3N_4
Oxygen (%) Carbon (%)	<0.1 <0.1	<1 <1
• Hydrogen Bonding by FTIR		
Si-H (%) N-H (%)	<0.1 8-10	12-16 2-7
• Etch Rate (Å/sec; 5:1 BOE)	3-20	1.7

Table VIII. Electrical properties of CVD Si_3N_4.

	Electron Beam	RF Plasma
• Breakdown Voltage (MV/cm)	3	4
• Resistivity at 1 MV/CM (Ω-cm)	10^{12}-10^{14}	10^{15}-10^{16}
• Dieletric Constant at 1 MHz	7.1	7

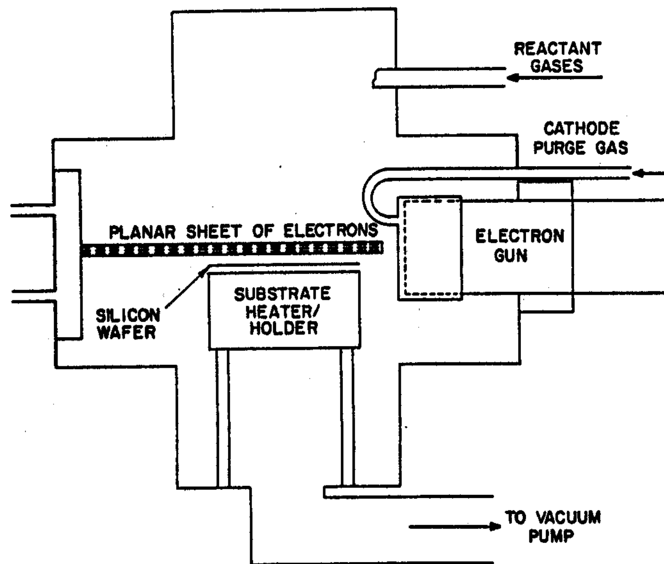

Figure 1. Electron beam CVD system.

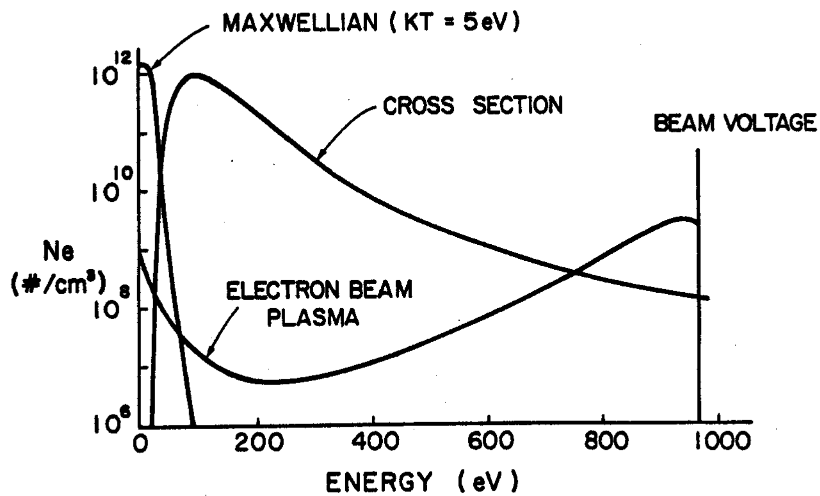

Figure 2. Comparison of electron beam created plasma (EBCVD) with Maxwellian electron energy distribution (PECVD) and typical dissociation cross section.

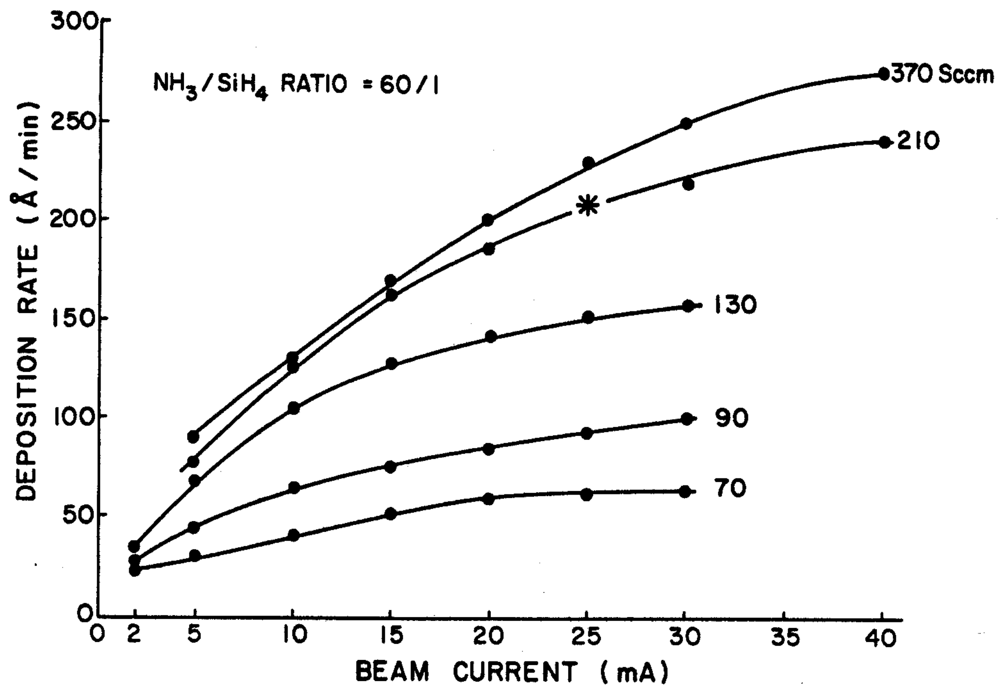

Figure 3. Deposition rate versus beam current for varying total gas flow (NH_3+N_2+SiH_4) at a constant pressure of 0.35 Torr, and substrate temperature of 350°C. The asterisk deontes the typical deposition conditions described in Table V.

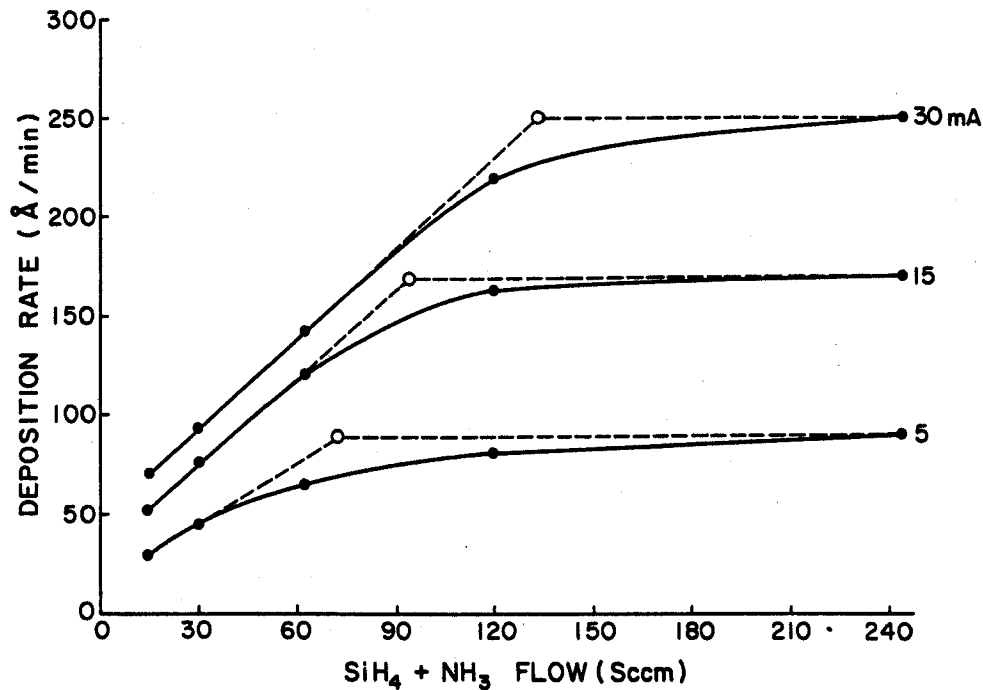

Figure 4. Deposition rate versus silane plus ammonia flow for electron beam currents of 5, 15, and 30 mA, at a total pressure of 0.35 Torr and a substrate temperature of 350°C.

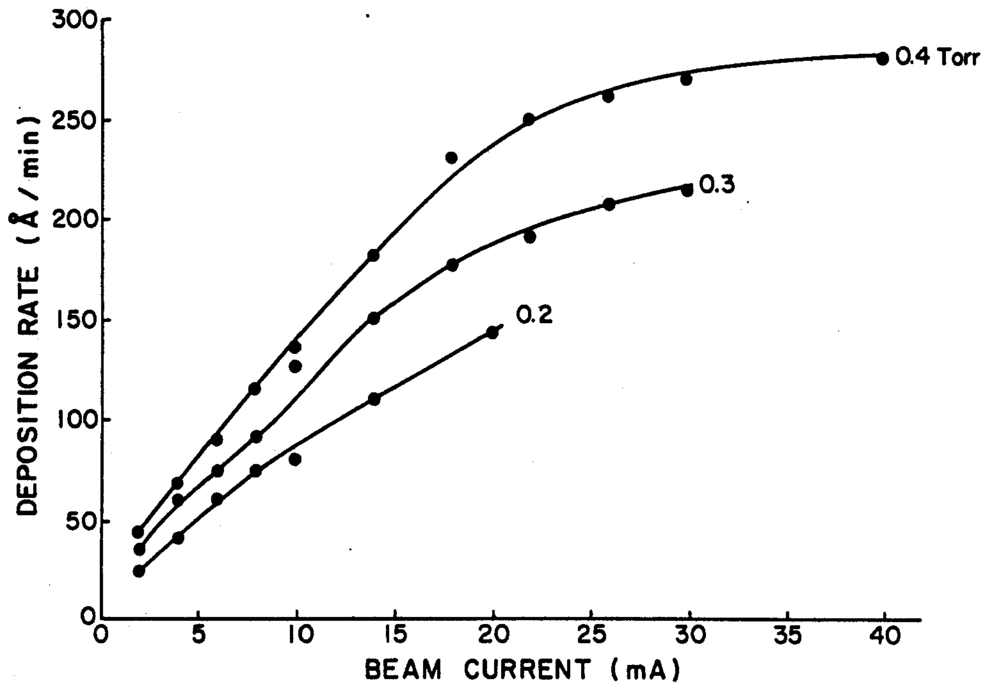

Figure 5. Deposition rate versus beam current for pressures of 0.2, 0.3 and 0.4 Torr at a constant flow of 97.5 sccm N_2, 150 sccm NH_3, and 2.5 sccm SiH_4, and a substrate temperature of 400°C.

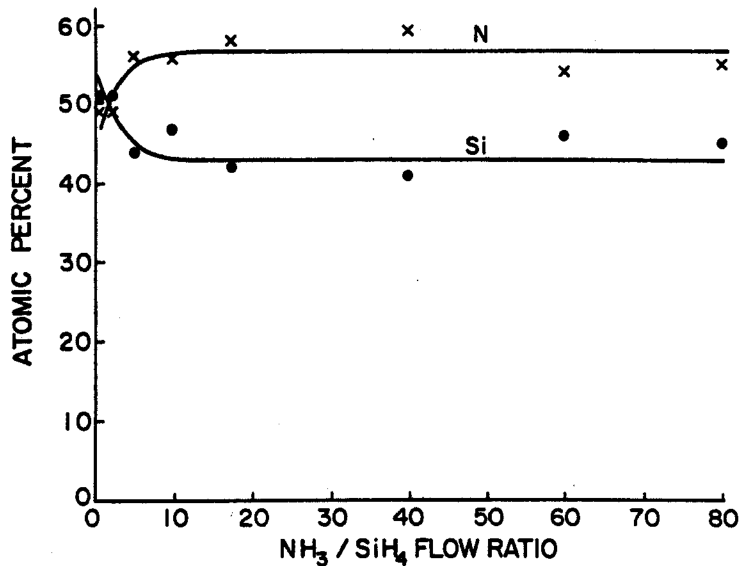

Figure 6. Atomic percent of Si and N versus NH_3 to SiH_4 flow ratio with a total pressure of 0.3 Torr and a substrate temperature of 350°C.

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