Electron beam assisted chemical vapor deposition of SiO_2

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We have demonstrated electron beam assisted chemical vapor deposition of silicon dioxide films on silicon substrates via electron impact dissociation of SiH_4 and N_2O gas. Dissociation of reactant gases occurs primarily in the confined planar region of the electron beam created plasma. Electron beam deposited SiO_2 films have been categorized in terms of their electrical, physical, and chemical properties.

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A new low-temperature (150–500 °C) method to deposit microelectronic thin films using plasma generated direct current electron beams has been investigated. Films of silicon dioxide have been deposited on silicon wafers by electron beam dissociation of nitrous oxide (N_2O) and 5% silane (SiH_4) diluted in nitrogen. SiO_2 films grown with conventional thermal processes and rf plasma assisted chemical vapor deposition (CVD) have well categorized properties and thus provide a vehicle to compare the films deposited with the new electron beam CVD technique.

Deposited silicon dioxide (SiO_2) films are presently used for active area isolation, as an interlayer dielectric between interconnect layers, and phosphorus doped as an encapsulation layer. Both plasma and photon assisted CVD techniques have been used to deposit SiO_2 at lower temperatures, at higher deposition rates and with improved step coverage compared to thermal CVD methods. The above nonthermal CVD techniques produce high quality films at substrate temperatures of 200–500 °C. This allows for reduction of thermal redistribution of dopant profiles, wafer warpage, and defect generation induced by high-temperature processes. These effects become increasingly important as semiconductor device structures are reduced to submicrometer dimensions. Prior to describing electron beam assisted CVD the properties of plasma and photon assisted CVD are briefly reviewed for purposes of comparison.

In radio frequency plasma enhanced CVD the plasma fills the entire interelectrode volume; dissociated reactants are lost by deposition to the chamber walls, and undesired plasma sputtering from walls and fixtures occurs. Laser-assisted CVD offers rapid deposition rates, a spatially localized deposition region and independence of both laser beam power and wavelength from reactor parameters such as gas flow rates and total gas pressures. With proper optics, a planar sheet of photons can be placed 1–2 mm above a substrate surface to initiate chemical reactions between donor gas molecules and minimize undesirable gas phase reactions. Laser-assisted CVD incorporates an expensive and energy inefficient source of photons needed for reactant dissociation. The electron beam assisted CVD (EB-CVD) method introduced herein has a spatially localized excitation volume similar to laser assisted CVD, yet offers the potential for wide area deposits at high rates, and at lower cost.

Figure 1 is a top view of the electron beam produced plasma used to deposit silicon dioxide films. Due to the low scattering angle of kilovolt electrons, the reaction volume is sharply confined to a 25-mm-wide sheet as shown in Fig. 1. The electron beam source is a modified version of glow discharge electron guns originally developed to pump ion lasers. The cathode sheath accelerates the electrons to kilovolt energies with electron beam generation efficiencies up to 80%.

Figure 2 illustrates the reactor geometry of the electron
beam deposition system. The electron beam travels parallel to and a few millimeters above a heated silicon wafer. A molybdenum plate heated by a 500-W tungsten halogen lamp in combination with a thermocouple controller provides variable substrate temperatures from 22 to 500 °C. Oxygen is used as a purge gas for the cathode face to maintain efficient electron emission from the glow discharge electron gun.

Typical silicon dioxide (SiO₂) deposition conditions for the electron beam CVD system are the following: substrate temperatures between 150 and 450 °C, total cell pressure between 0.1 and 1 Torr, N₂ to SiH₄ mass flow ratios between 25 and 100, and electron beam voltages between 1 and 5 kV at current densities of 40–400 mA/cm². Deposited SiO₂ film thicknesses linearly with deposition time. Less than 25 Å of film growth occurred on the heated substrate under the same conditions after exposure times of 30 min with the electron beam off.

Figure 4 shows deposition rate as a function of electron beam current density for three different gas flows with constant N₂O/SiH₄ ratio of 75: (□) N₂O = 200 scm; (△) N₂O = 150 sccm; (○) N₂O = 100 sccm.

Effects of reactant gas flow, electron beam current density, and deposition time on SiO₂ film thickness have been investigated. Figure 3 shows EBCVD SiO₂ film thickness as a function of time for a N₂O/SiH₄ gas flow ratio of 75, substrate temperature of 300 °C, and an electron beam current density of 160 mA/cm². A total gas pressure of 210 mTorr was maintained at all flow rates by throttling the vacuum system. The oxide thickness varies linearly with deposition time. Less than 25 Å of film growth occurred on the heated substrate under the same conditions after exposure times of 30 min with the electron beam off.

Figure 4 shows deposition rate as a function of electron beam current density for three N₂O/SiH₄ mass flows with a fixed N₂O/SiH₄ mass flow ratio of 75, a substrate temperature of 300 °C, and a total chamber pressure of 250 mTorr. The increase in deposition rate with increased N₂O flow with a fixed N₂O/SiH₄ flow and chamber pressure indicates that the dissociation process is flow limited. The deposition rate appears constant over an order of magnitude change in electron beam current density but falls off at higher values. In an electron beam glow discharge, higher discharge voltages are necessary to achieve higher electron beam current densities. A 250 mTorr total pressure the electron energy increases from 1 to 3 kV as beam current density varies from 50 to 400 mA/cm². The small decrease in SiO₂ deposition rate with increasing current is judged to occur because SiH₄ and N₂O reactants become more transparent to beam electrons due to the decrease in the electron collision cross sections at higher energies.

The physical and electrical properties were measured for the SiO₂ films deposited with electron beam CVD on n-type single crystal silicon wafers with (100) orientation and substrate resistivity of 5–10 Ω-cm. SiO₂ films deposited on 100-mm silicon wafers at substrate temperatures from 150 to 450 °C had adherence values in excess of 10⁷ dynes/cm². Refractive indices of SiO₂ films deposited with N₂O/SiH₄ ratios from 30 to 100 were within ± 5% of the stoichiometric value of 1.462. Wet chemical etch rates for EBCVD films of 36–60 Å/s are comparable with etch rates reported for laser deposited SiO₂ films. Films produced by laser and electron deposition techniques have three to six times faster etch rates than thermally grown SiO₂ films. 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 CVD films.⁶,¹¹

The electrical characteristics of metal-insulator-semiconductor (MIS) test structures for different EBCVD substrate temperatures are shown in Table I. The data in Table I were obtained from three runs at 250, 350, and 450 °C substrate temperature with measurements at several locations on the wafer. The deposition conditions for these runs are 3.4 kV, 150 mA electron beam voltage, and current at 1.75 mTorr SiH₄, 160 mTorr N₂O, 25 mTorr O₂, and 63 mTorr of N₂ to give a total chamber pressure of 250 mTorr. The total deposition time was 25 min, with a N₂O/SiH₄ mass flow ratio of 75. The substrate was (100) n-type single crystal silicon, with a sputtered Al back contact annealed at 425 °C in forming gas prior to SiO₂ EBCVD. The resistively evaporated Al front contacts to the SiO₂ defined the area of the MIS capacitor (—0.02 cm²). The thickness of the oxide, T₀x, and the index of refraction n₀x were measured with an ellipsometer. The substrate doping was calculated from Cₓmin (1 MHz) and Cₓ.¹³ The fixed interface charge density Nₓ was calculated from the equation...
TABLE I. Electrical properties of EBCVD films.

<table>
<thead>
<tr>
<th>Substrate temp (°C)</th>
<th>MIS sample location</th>
<th>$N_{ox}$ ($\text{cm}^{-2}$) $\times 10^{14}$</th>
<th>$T_{ox}$ (Å)</th>
<th>$C_{FB}$ (F/cm$^2$) $\times 10^{-8}$</th>
<th>$V_{FB}$ (V)</th>
<th>$N_{traps}$ (#/cm$^2$) $\times 10^{10}$</th>
<th>Pinhole density (#/cm$^2$)</th>
<th>$V_{p}$ (MV/cm)</th>
<th>$\epsilon_{ox}$</th>
<th>$n_{ox}$</th>
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$N_{p} = (C_{ox}/q)\phi_{MS} - V_{FB}$,

where $C_{ox}$ is the oxide capacitance density, $V_{FB}$ is the voltage at the flatband capacitance ($C_{FB}$), and $\phi_{MS}$ is the metal-semiconductor work function difference.\(^{14}\) The values measured for the dielectric constant, $\epsilon_{ox}$ ($\sim 3.5$) shown in Table I are lower than values obtained from thermal SiO$_2$ films ($\sim 3.8$).

Current versus voltage ($I$-$V$) measurements were performed on the EBCVD SiO$_2$ MIS capacitors in accumulation. The pinhole density was measured with an electrophoretic tester. Catastrophic breakdown occurred at $> 5$ MV/cm, with self-healing breakdown events occurring in the 2–5-MV/cm range, presumably due to pinholes. The values listed in Table I for $V_p$ were taken at the first breakdown event. Infrared transmission spectra of 0.6-μm-thick EBCVD films deposited at 300 °C show characteristic SiO$_2$ peaks with no measurable absorbance due to SiOH, H$_2$O, or SiH groups at 3650, 3300, or 2270 cm$^{-1}$ respectively,\(^{15}\) which is consistent with the low etch rates of the deposited films.

Summarizing an electron beam assisted CVD technique using a unique sheet beam geometry is demonstrated for the first time. Preliminary SiO$_2$ deposition conditions and deposited films have been characterized. Other thin films such as amorphous or polycrystalline silicon, silicides, as well as metallic films may also be deposited with the electron beam induced chemical vapor deposition (CVD) technique introduced here. Electron beam assisted CVD offers the possibility of uniform deposition over large areas using a confined plasma region that is located several millimeters above the substrate surface.

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\(^{2}\) Brad Mattson, Solid State Technol. 23, 60 (1980).


