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Laser-induced chemical vapor deposition of SiO_2

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We have demonstrated rapid (3000 Å/min) photochemical deposition of silicon dioxide from gas phase donor molecules. An ArF (193 nm) laser was used to excite and dissociate gas phase SiH_4 and N_2O molecules in contrast to earlier work with incoherent mercury lamps. We have achieved 20 times the deposition rate, limited the dissociation volume to a localized region, and minimized the direct impingement of UV photons on the substrate. Although the SiO_2 deposition rate was insensitive to substrate temperature from 20 to 600 °C, film quality noticeably improved above 200 °C. Metal-oxide-semiconductor capacitors were fabricated and characterized in order to measure SiO_2 electrical properties. Film composition was investigated using Auger and infrared spectroscopy techniques and showed that the SiO_2 is stoichiometric and contains less than 5% nitrogen.

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There is considerable interest in low-temperature techniques for depositing silicon dioxide films because in this way one can reduce dopant redistribution, wafer warpage, and defect generation[1] as well as providing an insulator which requires no high-temperature steps for double level metallization. Deposition at low temperature also permits the use of layered photoresist-SiO_2-photoresist structures for high resolution lithography.[2] Atmospheric chemical vapor deposition (CVD) and low-temperature LPCVD techniques, while reducing process temperatures, are deficient in uniformity, purity, and film stability.[3] Thus there is a need for new methods of film deposition which improve the physical characteristics of interlayer dielectrics such as step coverage, uniformity, and film integrity.

Plasma enhanced CVD techniques have made low-temperature deposition possible with improved physical characteristics, but plasma techniques are not always nondestructive, especially for radiation sensitive metal-oxide-semiconductor (MOS) devices. In plasma assisted CVD the substrate is bombarded with energetic neutral and charged particles, as well as VUV photons, all of which contribute to chemical and physical damage to the substrate, interface, and growing film.[4] Another disadvantage of plasma deposited films is that the plasma potential is always more positive than the walls. This causes ions to be accelerated by sheaths at the walls and thereby enhances impurity sputtering and flaking. Both effects degrade film quality. Finally, plasma process parameters such as rf power, rf frequency, gas flow, electrode spacing, total pressure, and substrate temperature are so interrelated that it is impossible to characterize and control effects due to a single parameter.[5]

Because of these considerations, interest in photochemically deposited insulating films in which the reaction energy is selectively provided by photons has increased considerably. Previous workers have used both mercury photosensitized reactions[2b,6–8] and direct photolytic reactions[8] to deposit SiO_2 at low temperatures. Mercury lamps provided incoherent UV (strong) and VUV[8] (weak) photons to liberate atomic oxygen from molecular donor molecules by photodissociation. When lamps are used, the entire illuminated volume of gas reacts to form products. Unwanted deposition and loss of reactants on reactor walls may be considerable[7] and deposition rates are low. For example, the best mercury sensitized deposition rate that we have found in the literature was just under 200 Å/min. The deposition rate limiting step was attributed to loss of atomic oxygen by recombination on surfaces of the reactor.[7] Our laser induced

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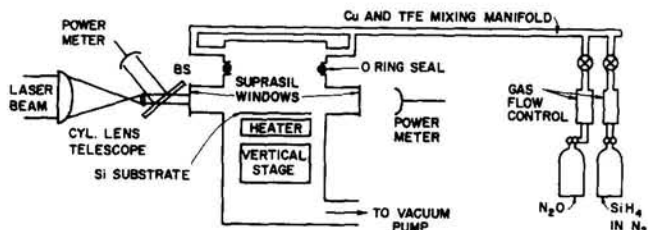

FIG. 1. Experimental arrangement. BS—beamsplitter for power monitor.

scheme eliminates several of the limitations of the mercury sensitized approach.

High deposition rate is of concern in economical production processes and can ultimately determine film purity, given the background pressure of impurities and the desired film thickness. We have investigated rapid (up to 3000 Å/min) deposition of nearly stoichiometric SiO_2 at low temperatures by *direct* photolytic reaction of N_2O and SiH_4 using coherent beams of photons from an ArF laser.

As shown in Fig. 1 a Lumonics 860T Excimer Laser operated on the 193-nm ArF line provided a rectangular beam which was focused by a cylindrical lens telescope. This optical setup provided a sheet of photons parallel to and a controlled distance above the substrate surface (typically 0.3 mm). This photodissociation scheme created a reaction volume very close to the substrate with a minimal number of UV photons interacting with the substrate, most via scattering. The pulsed ArF laser, run at 100-Hz repetition rate, provided 40-W/cm^2 average power to the reaction volume which had a cross-sectional area of 1.5×12 mm. In this planar configuration, approximately one-half of the photoexcited reactants diffuse less than 1 mm from the reaction volume directly to the substrate, the remainder being lost to the walls and the vacuum system. The photon flux and geometrical factors account for the laser induced deposition rates being 20 times faster than previous schemes using incoherent photons from mercury lamps.[6-8]

Gaseous silicon and oxygen donors were 5% silane (SiH_4) in nitrogen and N_2O, respectively. Silane, with an absorption cross section[9] of 1.2×10^{-21} cm^2, is normally transparent to wavelengths in the 193-nm region.[8] However, direct deposition of silicon following photodissociation of SiH_4 by ArF laser irradiation with a power threshold <10 MW/cm^2 has been demonstrated.[10] In our experimental geometry, the focused ArF laser provides 10-ns pulses with a peak power of 40 MW/cm^2. By turning off the N_2O flow, we have deposited amorphous silicon to verify dissociation of silane. N_2O (Scientific Gas Products USP grade, without further purification) was used since it is far more stable than O_2 in the presence of silane over a wide range of pressures, temperatures, and flow ratios. The quantum yield for dissociation of N_2O is 1.0 in the wavelength region 138–210 nm,[11] and its photochemistry has been well categorized for single-photon excitation.[12,13] The photofragment kinetics of N_2O following irradiation by an ArF laser has also been studied.[14] The primary product is reactive excited atomic oxygen, $N_2O + h\nu$ (193 nm) $\rightarrow N_2 + O(^1D)$. The kinetics in our system will be controlled by competition between quenching and recombination of atomic oxygen, oxidation of silicon hydrides, creation of reactive nitric oxide species, and substrate reactions. The importance of substrate reactions is enhanced in our scheme because of the close proximity (0.3 mm) of the excitation volume to the substrate, while at the same time the walls of the vacuum chamber are far (10 cm) from the excitation volume. Since Auger analysis and infrared (IR) spectrophotometry showed low nitrogen incorporation in our films, we judge that only the oxygen species [O_2^* and $O(^1D,^3P)$] are important in SiO_2 film growth kinetics.

Figure 1 shows the experimental arrangement of the cell containing a temperature controlled silicon substrate (variable from room temperature to 600 °C) and a pair of suprasil windows to allow passage of 193-nm radiation into the vacuum chamber and parallel to the surface of the 3-in. (⟨100⟩, 10 Ω cm, n type) silicon wafer. Reactant gases were mixed in the manifold and flowed through the cell which was maintained at 8 Torr by a vacuum pump. Flow rates were held at 70 sccm 5% SiH_4 in N_2 and 800 sccm N_2O. Input and output windows were purged with N_2 to prevent opaque deposits from forming. At substrate temperatures below 200 °C deposited oxide films were milky in appearance and easily scratched. All films formed above 200 °C were transparent and uniform. Films produced at $\geqslant 250$ °C were extremely scratch resistant and adherent, being unaffected by all variations of the "scotch tape test" and mechanical scribing.

No study of the effect of total pressure or N_2O/SiH_4 ratio on index of refraction or growth rate of SiO_2 films will be reported here. We were striving for stoichiometric films so we used an oxidant-rich ($N_2O/SiH_4 > 90$) environment, as suggested in Ref. 7. Our operating pressure of 8 Torr is considerably higher than the 0.3–2 Torr used in nearly all but atmospheric CVD systems. It was dictated by the slow pump speed and by the required flow rate of nitrogen for window purges. Stripes of oxide 15 mm wide were grown on the wafers which were uniform in thickness within 100 Å front to back. This is because the reactant gases are optically thin at these pressures and laser intensity is essentially constant along the beam path.

Measured physical and electrical properties of photolytic SiO_2 films as a function of substrate temperature during deposition are shown in Table I. Included for comparison are a LPCVD film (860 °C; $SiCl_2H_2$ and N_2O) and a thermal oxide (1000 °C; trichloroethylene and O_2) film both of which underwent capacitor fabrication and testing with the photolytic oxides.

Measurements of surface states (N_{ss}), flatband voltage (V_{FB}), and breakdown voltage (V_B) were obtained both from polysilicon gate MOS capacitors (2×10^{-4} cm^2 area) and from evaporated Al gate capacitors (0.03-cm^2 area). Polysilicon capacitor fabrication consists of additional high-temperature steps including a densification at 950 °C in N_2 for 60 min, whereas aluminum capacitors only undergo a 425 °C anneal for 30 min (10% H_2, 90% N_2).

Etch rate and index of refraction measurements were made on both as-deposited and densified films. Etch rates of undensified films decrease with increasing deposition tem-

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TABLE I. Properties of photodeposited SiO_2 films.

Temp. °C[a]	Oxide depth (Å) P-Si	Oxide depth (Å) Al	N_{ss} (10^{11} cm^{-2}) P-Si	N_{ss} (10^{11} cm^{-2}) Al	V_{FB} (V) P-Si	V_{FB} (V) Al	as-depos. etch rate (Å/s)[b]	Densified etch rate (Å/s)[b]	Refractive index	Breakdown voltage V_B(MV/cm)	Pinhole density (cm^{-2})
500	2009	1440	8.2	1.3	− 8.0	− 0.3	48	16	1.452	8.8	c
450	1670	1460	8.6	1.5	− 8.3	− 0.4	57	11	1.464	9.0	c
400	1930	1630	7.4	2.6	− 8.3	− 1.3	67	20	1.447	7.9	c
350	1700	...	10	...	− 9.8	...	83	14	1.457	8.9	⩽1
300	1800	1300	12	4.5	− 11.8	− 2.1	92	...	1.473	9.4	4–6
250	1940	...	9.5	...	− 10.4	...	102	...	1.476	5.2	~16
Thermal oxide	978	...	0.3	...	− 1.3	...	14	...	1.452	8	
LPCVD	1800	...	1.9	...	.01	...	41	...	1.440	8.2	

[a]Substrate temperature during photolytic oxide deposition.
[b]5 to 1 buffered HF.
[c]None observed.

perature. Etch rate reduction occurs upon densification, becoming comparable to thermal oxide.

Pinhole density measurements were made after a 30-min (10% H_2, 90% N_2, 425 °C) anneal. Pinhole densities for films deposited at ⩾350 °C were less than 1 cm^{-2} as measured on a Ga Sonics Pinhole Density Monitor.

Breakdown voltages were measured on a Tektronix Model 117 curve tracer using two techniques: (1) 20 V per second increase until breakdown and (2) 2 V/s increase with 1.0-min dwell every 10 V. Separate scans were made usig ac and dc applied voltages. In all cases breakdown voltages for a given wafer agreed within 10%.

Refractive index and thickness measurements were made with an ellipsometer. Thickness measurements were verified on a Dektak profilometer and with a Nanospec film depth computer. These measurements were taken before and after densification except for the 250 and 300 °C deposits. Variation in refractive index due to densification was ⩽1%, and thickness reductions of 10–15% were seen in agreement with previous work.[7] Index of refraction for the photolytic oxides closely agrees with the thermal oxide.

The N_{ss} values for photolytic oxides were 10 to 100 times larger than for LPCVD and thermal oxides. These differences may be due to the fact that the photolytic oxides were grown on wafers handled in an uncontrolled laboratory environment, while the LPCVD and thermal oxides were grown in a clean room environment. Sputter-profiled Auger and secondary ion mass spectroscopy (SIMS) showed evidence of hydrocarbon throughout the films, probably due to oil backstreaming from the fore pump in our laser photodeposition setup.

Deposition rate of SiO_2 films was observed to be independent of substrate temperature between 20 and 600 °C and directly proportional to gas pressure and laser intensity. During profile measurements of oxide thickness, low-temperature SiO_2 films (< 200 °C) were damaged by the stylus as they were mechanically soft.

Since the reactant gas mixture used was 89% N_2O, 10% N_2, and < 1% SiH_4, nitrogen incorporation in the SiO_2 films was a concern. By using IR spectrophotometry a shift of less than 20 cm^{-1} of the 1080-cm^{-1} Si-O absorption peak toward the 850-cm^{-1} Si-N peak was measured. This corresponds to less than 5% Si_3N_4 content in the SiO_2 films.[15] In addition, sputtering Auger analysis was used to analyze incorporation of nitrogen in the films and showed 2–4% nitrogen content. Hence there is low nitrogen incorporation in the films, the bonding of which is unknown. Index of refraction values in Table I also show that the films are neither silicon rich nor nitride rich.

In conclusion, we have used UV photons from an excimer laser to deposit nearly stoichiometric SiO_2 films at low temperatures and at high deposition rates (3000 Å/min). Although nitrogen and N_2O are the major gas constituents, all SiO_2 films examined have low nitrogen incorporation. Pinhole densities and breakdown voltage are comparable to thermally grown native oxides. The laser photodeposition scheme used in this work creates a thin sheet of photofragments in a localized region just above the substrate surface. This allows for greater deposition rates as well as minimizing the creation of undesired photoproducts in regions which do not contribute to film growth on the substrate itself. In addition laser beam power, wavelength, and spatial location may be independently varied without affecting *any* other parameters of the deposition system such as substrate temperature, gas flow ratios, and total gas pressure. This is a considerable advantage over plasma deposited films for achieving a specified deposition rate in terms of repeatable conditions.

This process shows promise for low-temperature encapsulation and as an interlayer dielectric in multilevel metallization applications. Deposition rates are high (3000 Å/min) and film integrity is good.

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Effect of oxide precipitates on minority-carrier lifetime in Czochralski-grown silicon

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The effect of oxide precipitate in Czochralski-grown silicon crystals on minority-carrier lifetime was investigated. The oxide precipitates generated by heterogeneous nucleation in as-grown crystals were found to decrease the lifetime. On the other hand. the oxide precipitates generated by homogeneous nucleation decreased the lifetime when their length was greater than 100 Å. The minority-carrier lifetime was nearly proportional to the reciprocal of the oxide precipitate length.

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About 10^{18} at./cm^3 of oxygen atoms are contained in Czochralski-grown (CZ) silicon crystals. These oxygen atoms precipitate when cooled during crystal growth or annealed after crystal growth. These oxide precipitates act as nuclei of secondary defects, such as stacking faults or dislocation loops, which are generated during the device fabrication.[1] It is well known that stacking faults and dislocation loops degrade the device characteristics, but there are few reports on the effect of oxide precipitates on electrical properties.[2] Because most of electrical methods for defect characterization [such as capacitance-voltage (C-V) method, capacitance-time (C-t) method, etc.] need device fabrication, it is impossible to avoid the generation of secondary defects. Therefore, it is difficult to characterize only oxide precipitates by these methods.

Using noncontact photoconductive decay method, minority-carrier lifetime can be measured without device fabrication.[3] Therefore, the electrical property of oxide precipitates can be investigated by this method without any effects of secondary defects. In the present work, effects of oxide precipitates, which are in as-grown crystal or generated by relatively low-temperature annealing, on minority-carrier lifetime are clarified by noncontact photoconductive decay method.

Two kinds of oxide precipitates are contained in as-grown CZ silicon crystal. One of them is about 10 Å in size and is generated by homogeneous nucleation in the process of cooling during crystal growth. This is referred to as "as-grown microprecipitate." Their density is estimated to be 10^8–10^{11}/cm^3, which increases with increasing oxygen concentration in the crystal. Another one is about 1000 Å in size and is generated by heterogeneous nucleation resulting from some fluctuations during crystal growth. This is referred to as "as-grown large precipitate." Their density is estimated to be 10^3–10^6/cm^3.

Homogeneous nucleation of oxide precipitates is generated not only by cooling during crystal growth but also by annealing. Oxide precipitates, whose sizes are greater than the critical radius at an annealing temperature, grow by annealing. Annealing temperature dependence of nucleation rate and annealing time dependence of oxide precipitate size were previously reported.[4,5] Their results which are related

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