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Direct Oxidation of Silicon Substrates Using ArF Excimer Laser Photolysis of N_2O at Low Temperatures

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Silicon has been directly oxidized by using oxygen atoms produced from an ArF excimer laser photolysis of N_2O. Uniform SiO_2 films with a thickness of < 130 Å were grown at the substrate temperature range of 30-500 °C and a laser power of about 150 mJ. The dependence of the film thickness on the laser shots, the substrate temperature, and the N_2O pressure was examined.

The trend toward smaller VLSI devices with high packing densities requires the substantial decrease of wafer processing temperature. In this respect, excimer laser-induced processes have attracted considerable interest because of their advantages of lower operating temperature and less radiation damage than plasma processes. The excimer laser-enhanced oxidation of silicon substrates has recently been studied by a few groups.1-4) Orlowski et al.1,2) rapidly (> 100 Å /s) formed a SiO_2 layer on silicon substrates by using a focused XeCl excimer laser in an oxygen environment. Namiki et al.3) studied the oxidation process of Si(111) via an ArF laser decomposition of N_2O under ultra high vacuum employing X-ray photoelectron spectroscopy. Nayar et al.4) irradiated a condensed ArF or KrF laser perpendicularly to Si substrates in an oxygen environment for the application of selective oxidation to direct growth lithography. In the present communication, thin SiO_2 films are grown at low substrate temperatures below 500 °C using an ArF excimer (193 nm) laser and N_2O molecules as an oxygen source.

The schematic illustration of the experimental arrangement is shown in Fig. 1. A stainless-steel reaction chamber with a quartz window was continuously evacuated with a 1420 ℓ/min oil rotary pump. The unfocused

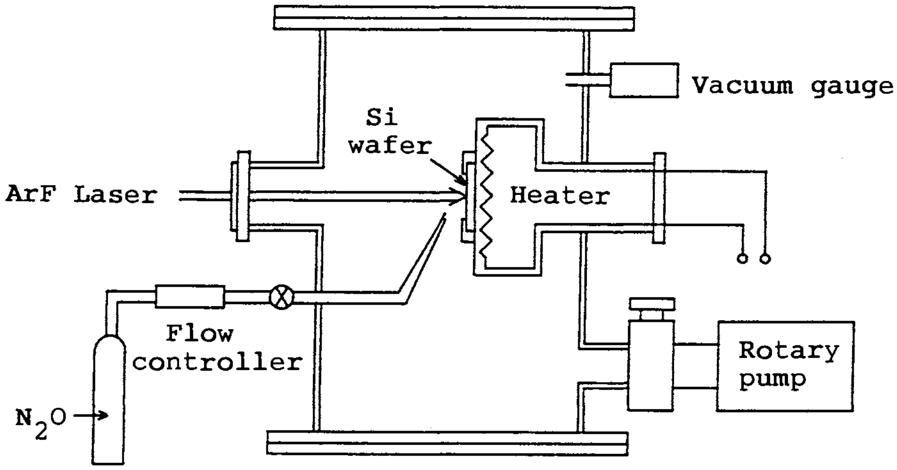

Fig. 1. Excimer laser oxidation system.

ArF laser (Lambda Physik EMG-203MSC) was irradiated perpendicularly to a Si substrate on a heater. The laser was operated at 50 Hz repetition rate with 23 ns pulse width and the maximum power of about 200 mJ. Si substrates were 2-inch p-type (100) orientated Cz crystal. The substrate temperature (T_s) was changed from 30 to 500 °C. The N_2O pressure ranged from 0.05 to 2 Torr (1 Torr=133.3 Pa) with a typical flow rate of 850 ml/min. The film thickness was measured by a Shimadzu AET-100 ellipsometer at a fixed refractive index of 1.462. On the basis of ellipsometric measurements, a uniform stable native oxide with a thickness of 20±2 Å was present on the silicon prior to oxidation. No oxidation occurred under the same experimental conditions without laser irradiation, indicating that thermal oxidation was negligible under the present operating conditions.

Uniform thin SiO_2 films were grown on an irradiated part of the wafer (22 X 10 mm^2) in the substrate temperature range of 30-500 °C. Although a thin SiO_2 film was also formed on the outside of the irradiated part, its thickness was less than a half of the irradiated part. The IR spectra of the laser-grown SiO_2 films consisted of the following three prominent absorption bands: Si-O stretching (1060 cm^{-1}), O-Si-O bending (850 cm^{-1}), and Si-O-Si rocking (450 cm^{-1}). It has been known that there is a linear relationship between the Si-O stretching frequency in SiO_x and the oxygen concentration x, whereas the bandwidth is dominantly determined by the variation of the O-Si-O bond angle.5) Since the peak position of the Si-O band (1060 cm^{-1}) is the same as that in the thermally grown oxide,2) the bulk of the SiO_2 is stoichiometric with no oxygen deficiency. The Si-O stretching band at 1060 cm^{-1} is about twice broader than that in the thermally grown oxide, indicating that a higher degree of structural disorder like large variations in the Si-O-Si bond angle is present in the laser-grown SiO_2.

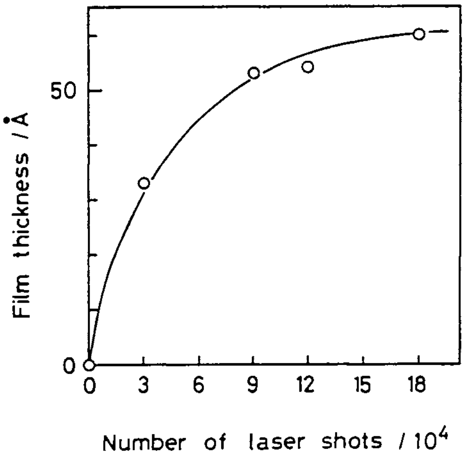

Fig. 2. Oxide growth curve.
T_s=500 °C; N_2O pressure=3 Torr.

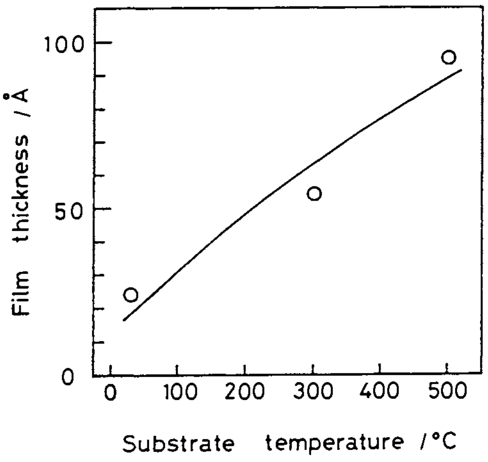

Fig. 3. Dependence of oxide thickness on the substrate temperature.
N_2O pressure=1.5 Torr; 3 h.

Figure 2 shows oxide thickness variation as a function of the number of laser shots delivered to the surface. The oxide thickness rapidly increases up to about 90 000 shots. The pulse width is about 23 ns and thus the total exposure time during 180 000 shots is estimated to be less than 4 ms. From the form of the curve, the oxidation appears to be self-limiting at about 50 Å. Under the optimum conditions (N_2O pressure=0.5 Torr, T_s=500 °C) a uniform SiO_2 film with a thickness of about 130 Å was grown. This value is larger than values of about 25 Å obtained in ArF laser enhanced oxidation using oxygen gas at 1 atm below 650 °C,$^{3)}$ and about 50 Å formed at 500°C under N_2O flow with UV-irradiation.$^{6)}$ Figure 3 shows the dependence of thickness on the substrate temperature. The oxide thickness increases by a factor of about 4 between 30 and 500 °C.

With the ArF laser radiation, a photochemical mechanism contributes to oxidation of silicon besides the local heating effect of wafer. Since the temperature rise by laser irradiation was estimated to be less than 50 °C, the local heating effect would be unimportant under the operating conditions. N_2O molecules effectively dissociate into N_2 and $O(^1D)$ by the ArF (193 nm) laser with a photon energy of 6.4 eV:$^{7)}$

$$N_2O + h\nu \longrightarrow N_2 + O(^1D). \qquad (1)$$

Possible oxidant species are N_2O and $O(^1D)$. For the film growth, these species must arrive at the interface between Si and SiO_2 layers. Since no SiO_2 film was grown without laser irradiation, active O atoms must be more significant. A higher oxidation rate of the irradiated part than its outside can be explained by a higher concentration of active oxygen on the wafer and a cleavage of Si-Si bonds by the ArF laser.$^{8)}$

Figure 4 shows the relationship between the oxide thickness and the N_2O pressure. The growth rate increases rapidly up to 0.5 Torr. However, it decreases above 0.5 Torr. The decrease in the thickness at N_2O pressure above 0.5 Torr is probably due to reduction of $O(^1D)$ concentration through the following secondary reaction,[9]

$$O(^1D) + N_2O \longrightarrow 2NO, \qquad k_{2a} = (7.2\pm1.5) \times 10^{-11}\ cm^3s^{-1}, \qquad (2a)$$

$$\longrightarrow O_2 + N_2, \qquad k_{2b} = (4.4\pm1.0) \times 10^{-11}\ cm^3s^{-1}. \qquad (2b)$$

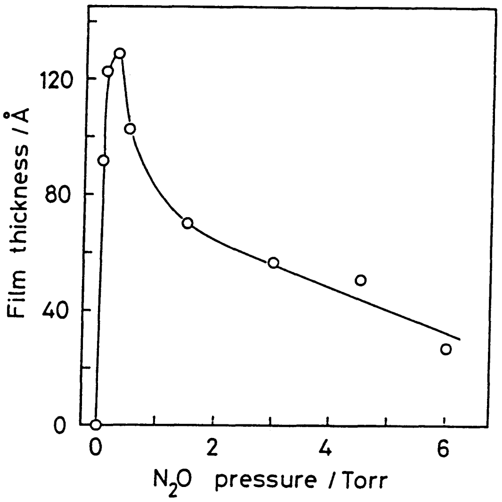

Fig. 4. Dependence of oxide thickness on the N_2O pressure at T_s=500 °C; 1 h.

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