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High-quality SiO_2 film formation by highly concentrated ozone gas at below 600 °C

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Highly concentrated (>93 vol %) ozone (O_3) gas was used to oxidize silicon for obtaining high-quality SiO_2 film at low temperature. Compared to O_2 oxidation, more than 500 °C lower temperature oxidation (i.e., from 830 to 330 °C) has been enabled for achieving the same SiO_2 growth rate. A 6 nm SiO_2 film, for example, could be grown at 600 °C within 3 min at 900 Pa O_3 atmosphere. The temperature dependence of the oxidation rate is relatively low, giving an activation energy for the parabolic rate constant of 0.32 eV. Furthermore, a 400 °C grown SiO_2 film was found to have satisfactory electrical properties with a small interface trap density (5×10^{10} cm^{-2}/eV) and large breakdown field (14 MV/cm). © *2002 American Institute of Physics.*
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The recent trend in downsizing ultralarge-scale integration devices requires a high-quality and highly reliable Si gate oxide (SiO_2) film of a few nanometers in thickness. Through this trend, reduction of thermal budget during SiO_2 film formation has become a key issue for preventing the degradation of the device quality.[1] To achieve a lower-temperature process than conventional thermal oxidation process by O_2 gas in furnaces (e.g., 900 °C), oxidation by new oxidizing sources such as the energetically reactive species generated by plasma[2,3] and the oxygen radicals generated by UV light irradiation[4–6] have been investigated. However, oxidation by these sources has the following problems: (1) Energetically reactive ionic species may impair the grown film; (2) the number of radicals supplied to the Si surface is limited by the microwave power or light intensity of the apparatus; (3) nondestructive transportation of the generated radicals to the Si surface is difficult because of their short life resulting from mutual chemical reactivity ($O+O\rightarrow O_2$). To overcome these problems, oxidation by highly concentrated ozone (O_3) gas under reduced pressure in cold-wall processing is considered to be promising for the following reasons: (1) The O_3 molecules have a long life as long as they are kept in a temperature- (<100 °C) and pressure-(<44 000 Pa) controlled atmosphere,[7] thus enabling the effective transportation of O_3 to the surface; (2) O_3 can also be used as an *in situ* oxygen radical source by way of the O_3 decomposition reaction at the surface (i.e., $O_3\rightarrow O_2+O$),[8] indicating that the number of supplied radicals can be increased by increasing the O_3 pressure at the surface; (3) the O_3-formed SiO_2 film has been confirmed to have a more homogeneous structure with less Si displacement and a thinner transition layer at the SiO_2/Si interface than thermally grown oxide[9,10] which would result in better electrical properties for the thin SiO_2 layer as a gate dielectric film.

In this letter, we first show that, by using highly concentrated O_3 instead of O_2 in cold-wall processing, a processing temperature has been lowered from 830 to 330 °C. We then show that formed oxide film grown at a temperature lower than 600 °C has had satisfactory electrical properties.

A high-purity ozone-jet generator we have developed for semiconductor processes was used as the highly concentrated O_3 source. Details of the operation of this generator have been described elsewhere.[7] To prevent a decrease in the concentration of O_3 gas during its flow to the Si surface, we applied lamp-heated cold-wall processing for oxidation. The results of our previous experiment suggested that, in ideal conditions that limit the heated area (>30 °C) to just around the Si surface, the concentration of O_3 gas arriving at the Si surface was more than 93%.[7]

An n-type Si(100) sample (10×10 mm) with a doping concentration of 10^{17} cm^{-3} was set on an opaque fused quartz susceptor in the oxidation chamber after having been cleaned by the traditional (RCA) method and HF dipping in a class 1000 atmosphere. The sample was then rapidly heated to the oxidation temperature by a halogen spot lamp (Hybec Co.) after the O_3 flow rate had stabilized. The thickness of the grown oxide film was estimated and cross checked by analysis of Si $2p$ peaks with x-ray photoelectron spectroscopy (XPS),[11] ellipsometry at a fixed refractive index of 1.46 and by the oxide capacitance obtained from capacitance–voltage ($C-V$) measurement. The estimated thickness from these three methods showed good agreement within an error of 0.5 nm. The electrical properties of the O_3-formed oxide were evaluated by measuring the $C-V$ and the current density–electric field ($J-E$) of the metal-insulator-semiconductor structure with Al electrodes of 0.2 mm diameter deposited over the area of the oxide film. To remove

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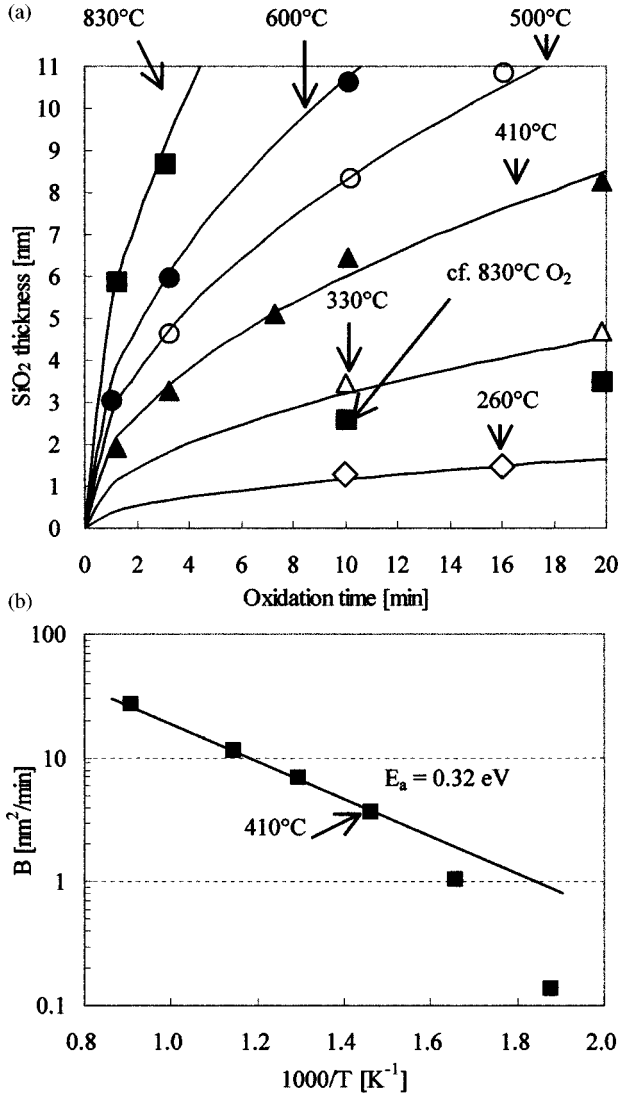

FIG. 1. (a) Oxidation rate of hydrogen-terminated *n*-Si(100). The oxidation pressure and flow rate were 900 Pa and 20 sccm, respectively. The Si temperature was monitored by a chromel–alumel thermocouple. (b) Arrhenius plots of the parabolic rate constant.

defects associated with the electrode deposited process, post-metallization anneal was carried out at 400 °C for 30 min in a 4% H_2/96% N_2 gas atmosphere.

Figure 1(a) shows the growth of the SiO_2 film thickness with time under exposure to highly concentrated O_3 at a fixed flow rate (20 sccm) and pressure (900 Pa) in the temperature range from 260 to 830 °C. In spite of processing at a relatively low pressure, the oxidation rate was very high. For example, a 6 nm SiO_2 film could be grown within 3 min at 600 °C. Furthermore, it was found that, compared to O_2 oxidation under the same conditions (900 Pa, 20 sccm), a temperature more than 500 °C lower, that is, from 830–330 °C, was achieved. This temperature reduction of 500 °C is greater than that achieved by atmospheric O_3 (3%–4%)/O_2 gas, for which a 300 °C reduction has been achieved.[12,13] This suggests that increasing the O_3 concentration to more than 93% was effective for further reducing the temperature of the oxidation process.

The data also show that, within an SiO_2 film thickness range from 3 to 11 nm, the SiO_2 growth rate seems to follow a parabolic kinetics ($d^2=Bt$, where d is the grown SiO_2 film thickness, t the oxidation time and B the parabolic rate constant) as was also reported in the case of plasma and UV light oxidation in an ultrathin region (<15 nm).[2–4] This would suggest that the oxidation process was controlled by the diffusion of the oxidizing species (probably O atom). Assuming that the rate constant has Arrhenius temperature dependence (i.e., $B=C\exp(-E_a/kT)$, where C is a constant, E_a the activation energy, k Boltzmann's constant, and T the absolute temperature), the value for E_a was calculated to be 0.32 eV from the Arrhenius plot shown in Fig. 1(b). This value is about 1/4 of that for dry O_2 oxidation (1.34 eV),[14] indicating that the O atom dissociated from O_3 diffused into the Si network much more easily. However, the B values of 330 and 260 °C oxidation are smaller than $E_a=0.32$ eV line depicted in Fig. 1(b). We have considered that this was caused by a reduced number of diffusing species (i.e., O atom) due to the lowered decomposition reaction of O_3 at the Si surface whose temperature was lower than 400 °C. The results of a directional mass analysis also support this consideration.[15]

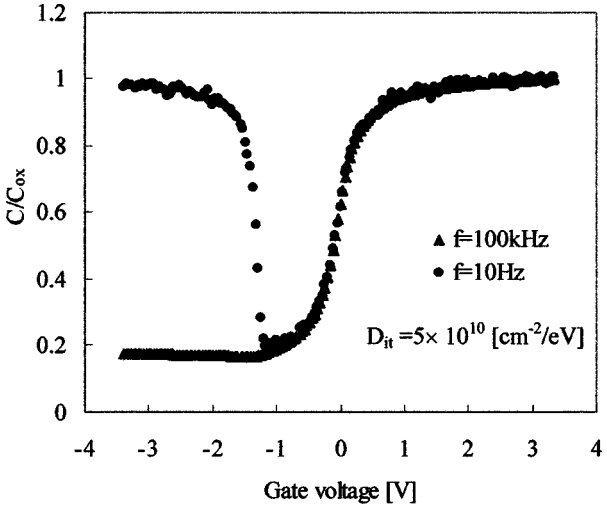

FIG. 2. High frequency and quasistatic $C-V$ curves of metal-oxide-semiconductor (MOS) capacitors with an SiO_2 film thickness of 5 nm. The oxidation temperature was 400 °C.

Figure 2 shows high frequency and quasistatic $C-V$ curves for a 5 nm O_3 oxide film grown at 400 °C. The interface trap density (D_{it}) can be estimated from these curves by using the following equation:[16]

$$D_{it}=q^{-1}A^{-1}[(C_q^{-1}-C_{ox}^{-1})^{-1}-(C_h^{-1}-C_{ox}^{-1})^{-1}], \quad (1)$$

where q is the electrical charge, A the Al gate area (=0.0314 mm^2), and C_h, C_q and C_{ox} are the high-frequency, quasistatic and oxide capacitance, respectively. The calculated value for D_{it} at the midgap was 5×10^{10} cm^{-2}/eV. This value is comparable to those of thermal oxides grown at around 1000 °C,[17] despite being achieved at a 600 °C lower temperature process. This is believed to have been due to the oxygen radicals' reactivity. In other words, the radical dissociated from O_3 was chemically so reactive and free to migrate that it could passivate the sub oxide states (Si^+, Si^{2+} and Si^{3+}) and nonbonded defects at the SiO_2/Si interface, in spite of an Si temperature as low as 400 °C. This notion is

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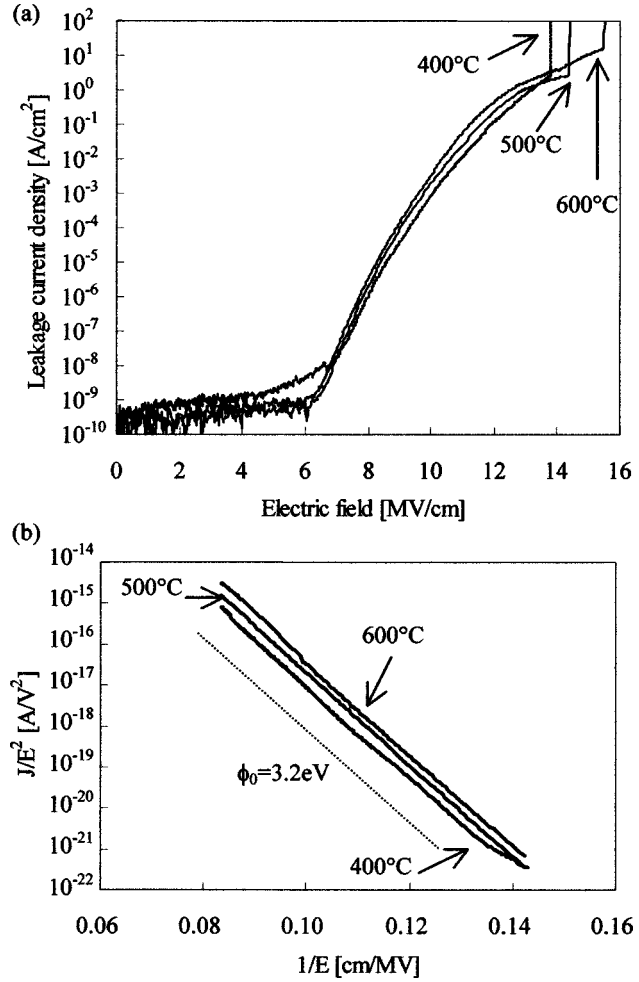

FIG. 3. (a) Current density vs electrical field characteristics for MOS capacitors with an oxide film thickness of 5 nm (400 °C), 11 nm (500 °C) and 15 nm (600 °C). (b) Fowler–Nordhelm plots for 5–15 nm O_3-grown SiO_2 films.

supported by previous XPS measurements showing that even 70 °C grown O_3 oxide had fewer suboxide states than thermal oxides grown at 400 °C.[18]

The $J-E$ characteristics of ~100% O_3 oxides grown between 400 and 600 °C were also measured with the Al gate positively biased. Figure 3(a) shows typical $J-E$ characteristics with an oxide thickness between 5 and 15 nm. The leakage current with an electrical field of 5 MV/cm and the catastrophic breakdown field strength were, respectively, about 10^{-9} A/cm^2 and 14 MV/cm, regardless of the oxidation temperature. This breakdown strength is higher than that of thermally grown oxides of the same thickness.[19] Furthermore, it has been found that, with an electrical field of between 6 and 14 MV/cm, the current through an oxide can be described by the ideal Fowler–Nordheim (FN) mechanism that is expressed as follows:

$$J = AE^2 \exp(-B/E), \tag{2}$$

$$B = 6.83\times 10^7 \left(\frac{m_{ox}}{m}\right)^{1/2} \phi_0^{3/2} (\mathrm{V/cm}),$$

where J is the current density, A a constant, E the electric field, m the free electron mass, m_{ox} the electron mass in the oxide, and ϕ_0 the barrier height in units of eV.[20] The slope of a plot of $\ln(J/E^2)$ vs $1/E$ (i.e., an FN plot) gives the barrier height between Si and SiO_2. Applying the conventionally used electron mass in the oxide ($m_{ox}=0.42\,m$),[21] the ϕ_0 value can be calculated to be 3.2 eV, irrespective of the grown temperature and oxide thickness, as shown in Fig. 3(b). This value is slightly higher than that for thermally grown oxides which varied from 2.7 to 3.1 eV depending on the oxidation temperature.[17] The lower tunneling current due to the higher (ideal) barrier height at the SiO_2/Si interface and the higher breakdown electrical field (~14 MV/cm) can be explained by the formation of a homogeneous SiO_2 structure from the SiO_2 surface to the SiO_2/Si interface with a low density of defects. This is also suggested by medium-energy ion scattering spectroscopy signals from ~30% O_3-formed oxide film[8] and by its HF etching rate.[9]

In summary, by using highly concentrated O_3 gas as an oxidizing species in cold-wall processing, the process temperature has been lowered considerably. The dependence of the oxidation rate on the oxidation temperature was found to be relatively small which would reflect the ease by which the oxygen radical could diffuse into the thicker layer. Furthermore, O_3-formed oxide films grown at below 600 °C were found to have suitable electrical properties for up-to-date gate oxide use. This O_3 oxidation technique would be especially applicable to processes requiring a low temperature such as the oxidation of poly-Si on glass for thin-film transistor applications.

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