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Rapid Thermal Formation of Device-quality SiO_2 Film by Using Highly Concentrated Ozone Gas at below 600°C

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1. Introduction

Low-temperature, high-quality SiO_2 film formation with rapid growth rate by thermal oxidation of (poly-) Si has attracted much attention as a tool not only to realize damageless gate dielectric formation in next generation's ULSI but also to replace the current chemical vapor deposition (CVD) processes (e.g., insulating layer on glass for thin film transistor (TFT)) by which SiO_2 with poorer electrical properties than thermal oxide has been obtained.

In this paper, we present a new SiO_2 film formation technique using highly concentrated (100%) ozone (O_3) as an oxidizing species. This new technique has the following advantages. 1) A satisfactory oxidation rate at low temperature is obtained because of O_3's highly efficient generation of oxygen (O) radicals at the Si surface (i.e., $O_3 \rightarrow O_2 + O$).[1] 2) The oxidation rate, which is proportional to the number of supplied O_3 molecules, can be precisely controlled by the oxidation conditions (e.g., O_3 pressure and O_3 flow rate) because of 100% O_3's long life-time in a temperature- (<100°C) and pressure- (<44,000Pa) controlled atmosphere.[2] 3) An electrically superior SiO_2 film is obtained supporting the previously reported results that a O_3-formed SiO_2 film had a homogeneous structure with less Si displacement and a thinner transition layer at the SiO_2/Si interface than thermally grown oxide.[3,4]

2. Experimental

Figure 1 shows a schematic view of 100% O_3 oxidation system. A high-purity ozone-jet generator we developed for semiconductor processes was used as the 100% O_3 gas source.[2] The O_3 flow rate is controlled by the temperature that vaporizes liquid O_3. To prevent a decrease in the concentration of O_3 gas during its flow to a Si surface, we applied a lamp-heated cold-wall process.

An n-type Si(100) sample with a doping concentration of $10^{17}cm^{-3}$ was cleaned by HF dipping and set on an opaque fused quartz susceptor in the oxidation apparatus. The sample was then rapidly heated to the oxidation temperature by a halogen spot lamp after the O_3 gas flow rate was stabilized. The thickness of the grown oxide film was estimated by XPS as well as by ellipsometry. The electrical properties of the O_3 oxides were evaluated by measuring the C-V and the J-E characteristics of the metal-insulator-semiconductor (MIS) structure with Al electrodes of 0.2 mm diameter deposited over the area of the oxide film.

3. Results and discussion

Figure 2 shows the growth rate of SiO_2 film under exposure to 100% O_3 at a fixed flow rate and pressure (20 sccm, 900 Pa). In spite of processing at a relatively low pressure, a 6-nm SiO_2 film could be grown within 3 min. at 600°C. Furthermore, processing was possible at a temperature 500C below that of O_2 oxidation. We also found from the data that the SiO_2 growth rate has a smaller temperature dependence (the activation energy for the parabolic rate constant was 0.32 eV), suggesting the O radicals' high diffusibility into the SiO_2 layer.

Figure 3 shows the dependence of the oxidation rate on the O_3 pressure at the apparatus. The oxidation rate increases with increasing the O_3 pressure, indicating that the number of O radicals diffusing into the SiO_2 layer can be monotonically increased by increasing the number of O_3 molecules around the surface. Thus, O_3 pressure, which can be precisely controlled by the vaporization temperature of liquid O_3 in the generator, can be used as a parameter for controlling the oxidation rate.

Figure 4 shows high-frequency and quasi-static C-V curves for a 5-nm O_3 oxide film grown at 400 °C. The interface trap density (D_{it}) at the midgap and fixed charge density calculated from these curves were 5×10^{10} cm^{-2}/eV and $1\times10^{11}cm^{-2}$, respectively. These values are comparable to those of thermal oxides grown at around 1,000°C,[5] despite being achieved at a 600°C lower temperature with no post oxidation annealing. This is considered due to the O radicals' reactivity that passivates the sub oxide states (Si^{+}, Si^{2+} and Si^{3+}) and non-bonded defects at the SiO_2/Si interface even at 400°C.

Figure 5 shows typical J-E characteristics of 100% O_3 oxides grown between 400°C and 600°C measured with the Al gate positively biased. The catastrophic breakdown field strength exceeded 14 MV/cm, which is higher than that of thermally grown 7 to 10 nm thick oxides.[6] Furthermore, we found that, with an electrical field of between 6 and 14 MV/cm, the current through an oxide was described by the Fowler-Nordheim (F-N) mechanism with an ideal barrier height at the SiO_2/Si interface. The slope of the plot of $\ln(J/E^2)$ vs. $1/E$ (i.e., an F-N plot) shown in **Fig. 6** gives the barrier height to be 3.2eV irrespective of the growth temperature and oxide thickness (here, m_{ox}=0.42m is applied). This lower tunneling current due to the ideal barrier height and the higher breakdown electrical field would be originating from 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.

4. Conclusions

In summary, by applying reduced-pressure, cold-wall processing using 100% O_3 gas as an oxidizing species, we were able to lower the process temperature by more than 500°C compared to conventional O_2 oxidation. The oxidation rate was found to be controllable by O_3 pressure. Furthermore, 100% O_3 oxide films grown at temperatures as low as 400°C were found to have suitable electrical properties for up-to-date gate oxide use. This 100% O_3 oxidation technique would be especially useful in processes requiring a low temperature such as SiO_2-on-glass fabrication.

References

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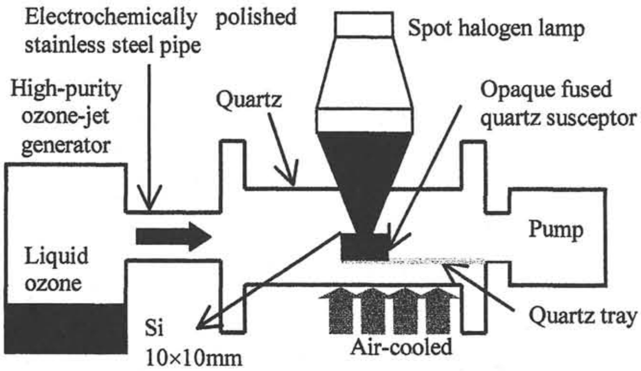

Fig. 1 Schematic view of the 100% O_3 oxidation system.

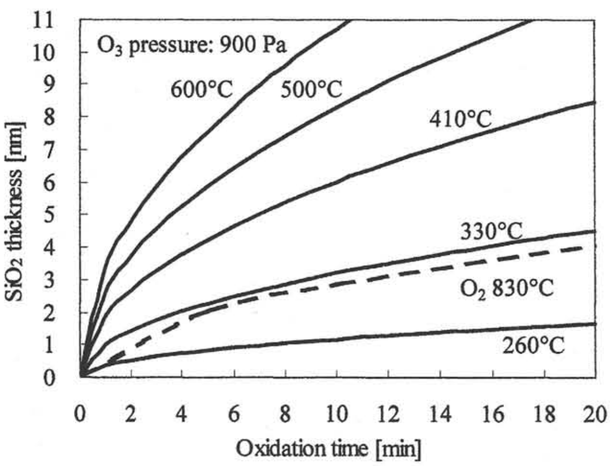

Fig. 2 Oxidation rate of hydrogen-terminated n-Si(100).

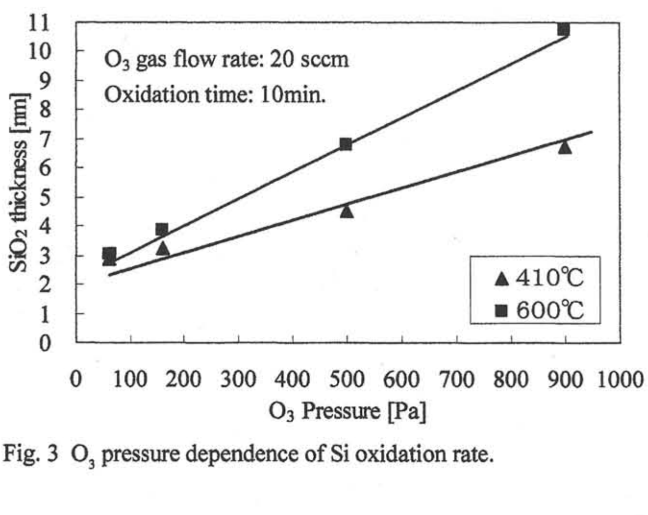

Fig. 3 O_3 pressure dependence of Si oxidation rate.

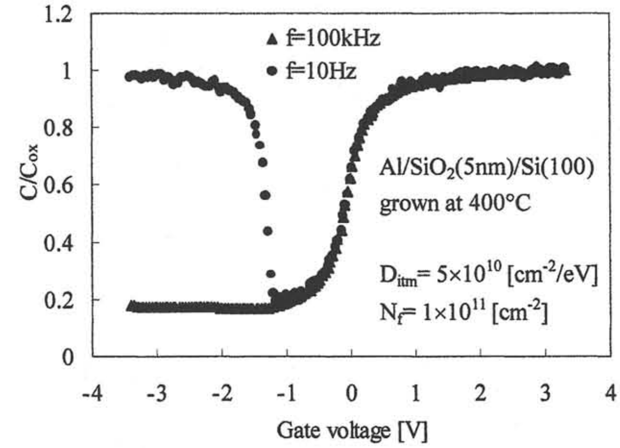

Fig. 4 High-frequency and quasi-static C-V curves of O_3 oxides.

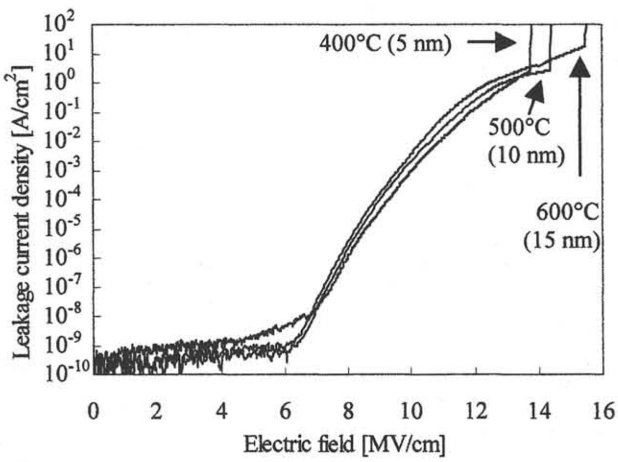

Fig. 5 Typical J-E characteristics of 100% O_3 oxides.

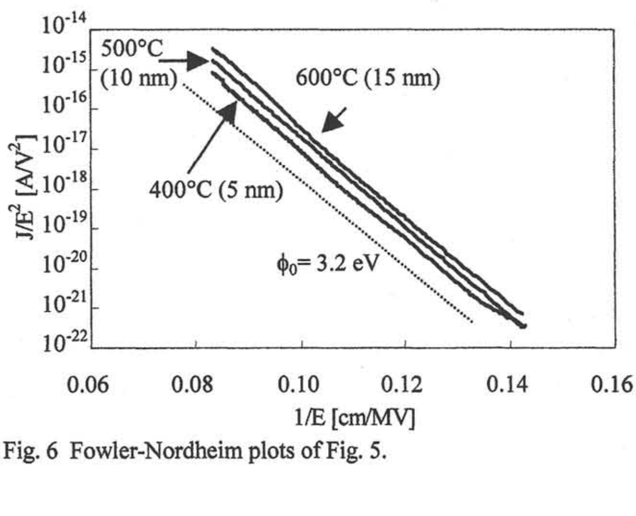

Fig. 6 Fowler-Nordheim plots of Fig. 5.