Gate dielectric SiO_2 film deposition on poly Silicon using UV-excited ozone gas without heating substrate.

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Abstract

We have grown SiO_2 film on a polycrystalline Si layer using excited ozone gas, which is produced by ultra-violet light irradiation to ozone gas, without heating substrate. The obtained SiO_2 film shows dielectric properties comparable to the device quality films measured at the MIS capacitor configuration.

1. Introduction

The fabrication of thin film transistors (TFT) or field emission transistors (FET) on polycrystalline silicon (poly-Si) has recently been a topic of intensive studies aimed to realize thinner, more flexible display panels, as processes to form good-quality poly-silicon layers on inexpensive glass or plastic sheet, such as laser annealing, have come into practice. However, the inexpensive glasses or plastics cannot withstand high process temperatures, especially the temperature required for formation of the high quality gate dielectric film. The major method of dielectric film deposition at low temperature has been plasma CVD process. However, plasma CVD temperature is over 350°C, and the obtained film qualities deteriorate with deposition temperature. Therefore, plasma CVD method cannot be adopted for the formation of gate dielectric film of flexible display panels.

For the oxidation of poly-silicon at low temperatures, using ozone gas is effective. Especially, the 100% concentrated ozone gas (~100% O_3) has low activation energy enabling Si oxidation at temperature as low as 410°C[1]. Figure 1 shows the oxidation rate on Si(100) using ~100% O_3. The oxidation rate for the ~100% O_3 at 410°C is almost same as that for the O_2 at 900°C. Moreover, the SiO_2 film by ~100% O_3 has good properties comparable to those of the device quality films. However, below 410°C oxidation rate decreases abruptly due to the lack of the active species, $O(^3P)$, which is produced by the thermal decomposition of O_3 at the sample surface. The oxidation ability of ozone can be further enhanced by photo-excitation using ultra-violet (UV) light to produce atomic oxygen in an excited state, $O(^1D)$ (UV excited-ozone) , which is described as

$O_3 + h\nu(\lambda = 200\sim300nm) \Rightarrow O_2 + O(^1D)$. (1)

$O(^1D)$ can oxidize the Si wafer even at room temperature[2]. In this study, we have performed the Poly-Si oxidation using $O(^1D)$.

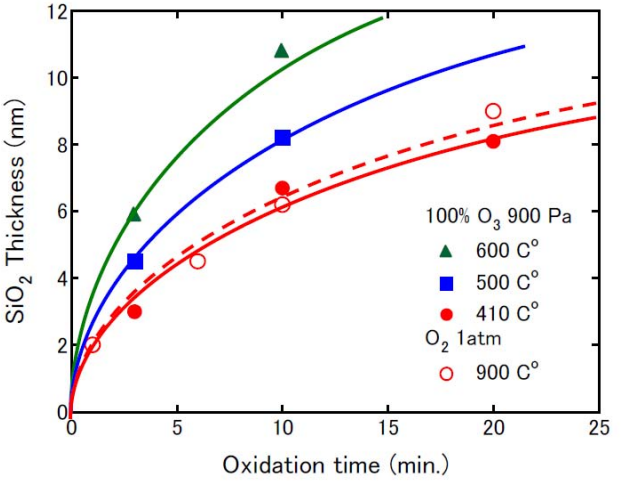

Fig. 1. Thermal oxidation rate of Si(100) by ~100% O_3 gas

2. Experimental

2-1. The system for ~100% O_3 supply

The ~100% ozone gas was supplied using a pure ozone generator (type:MPOG-SM1C1, Meidensha corp., Japan). Figure 2 shows the system for ~100% O_3 supply. The detailed configuration is described in [3]. The ~100% O_3 gas is generated from 100% liquid ozone which is vacuum-distilled from ozone-oxygen mixture generated by commercial ozonator. Therefore, the obtained ~100% O_3 is basically high purity gas, since vapor pressures of impurities generated by the ozonator (*i.e.* NO_2, H_2O) are much smaller than that of O_3 at a temperature range of 90-140K[4]. Using high concentrated O_3 gas at low pressures, the lifetime of the ozone gas can be increased, since the decomposition of an ozone molecule by the reaction between ozone and coexistence gas (O_2) are reduced.

The ~100% ozone gas is reported to have an exploding pressure. The process pressure must be controlled to be lower than the exploding pressure. We can use ~100% O_3 gas at practically high pressure due to the extremely little impurity in ozone gas. Table 1 summarizes the sequence to supply ~100% O_3. The number of ozone liquid vessels determines the maximum flow rate and continuous flow rate.

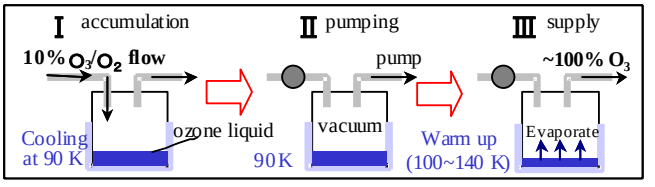

Fig. 2. The generation method of ~100% O_3 gas.

TABLE 1. Meidensha Pure Ozone Generator series.

Type	Bessel No.	Max. Flow (sccm)	Continuous Flow (sccm)
104A1	1	500 (12 min.)	---
HM1A1	3	1000 (25 min.)	100
61014	6(3*2)	2000 (50 min.)	200

2-2. System for Ultra-violet light irradiation

A KrF excimer laser (type:Compex 110, Lamda Physik, Germany) was used to excite the ~100% O_3. The laser wavelength was 248 nm, power density was 200-250 mJ/cm^2 and irradiated area was 10 x 30 mm^2. During the oxidation process, the laser light was irradiated the whole sample surface at a distance of 5 cm from the quarts window in an atomosphere of ~100% O_3. The KrF laser light cannot induce damage to the substrate, since the binding energy between Si-Si (7eV) is larger than UV-light energy (*i.e.* ~5eV).

2-3. Sample preparation

The poly-Si sample was stacked on a Si-wafer (p-type (100)) as shown in Fig. 3. The poly-Si layer was synthesized by CVD at 500°C. The poly-Si thickness is about 200nm and the peak-to-peak roughness of the surface was about 10nm-20nm, and grain size of the poly-Si layer was more than 10 nm according to the scanning microscope observation. These specs of poly-Si layer were similar to those stacked on the glass. The actual samples were prepared by cutting the 8 in. wafer into ~15×15mm^2 chips.

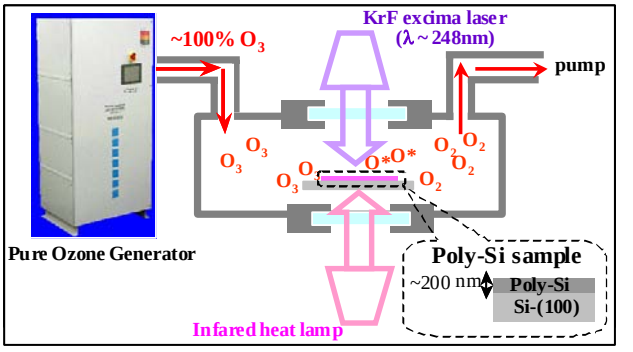

Fig. 3. The schematic experimental configuration and a poly-Si sample.

2-4. Experimental preparation

Figure 3 shows the schematic experimental configuration. Samples were set on an opaque quartz susceptor, which was heated with infrared light from halogen lamp at temperature range of 20-400°C. Without heating, however, the laser light radiation would heat the sample up to 70°C. Chamber wall was made by aluminum and kept at room temperature to prevent the thermal decomposition of ozone gas. The chamber pressure of ~100% ozone gas was 50-250 Pa and flow rate was 50-100 sccm. The optical thickness of the SiO_2 film was determined with a spectroscopic ellipsometer (type: GES-5, Sopra Corp., France). For an electrical measurement of the SiO_2 film, an MIS capacitor was fabricated (see Fig. 5). The electrode area was about 0.028mm^2 and thickness of evaporated Al electrodes was about 80 nm. The transmission electron microscopy (TEM) image was taken with a high-resolution transmission electron microscope (type:H-9000UHR, Hitachi corp., Japan) operated at 300 kV.

3. Results and discussion

3-1. Oxidation rate by UV-irradiated ~100% O_3

Figure 4 shows SiO_2 film growth rate on Si(100). Oxidation temperatures are blow 300°C. Within a few minutes from the start, the oxidation rate is large and almost temperature independent. This high activation is explained by the large energy release of the excited state of the $O(^1D)$ from the excited state to the grand state (~2eV), as well as by the thermal excitation at Si/SiO_2 interface by UV-irradiation. After a few minutes, the oxidation rate abruptly decreases and shows a temperature dependence. It may be due to the $O(^1D)$ diffusion-limited process for the SiO_2 growth ,since the activation energy of the $O(^1D)$ is almost same as that of thermal O_3 oxidation.

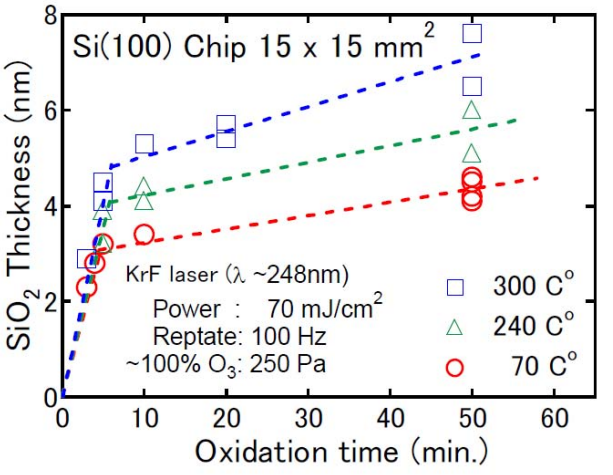

Fig. 4. The oxidation rate of the $O(^1D)$ on Si(100). KrF laser conditions are fixed.

3-2. Electrical properties of the $O(^1D)$ oxidation SiO_2 film on the poly-Si.

Figure 5 shows *J-E* characteristics of the SiO_2 film grown on poly-Si using $O(^1D)$ oxidation at room temperature at MIS capacitor configuration. Below a field density of 6 MV/cm the leakage current density remains as low as 10^{-8} A/cm^2, which was the lower limit of our measurement range. Above 6 MV/cm, the leakage current density follows ideal leakage property calculated from F-N mechanism. At a higher electrostatic field, breakdown occurred at nearly 13 MV/cm. The behavior of the leakage current presented here well reproduces the result of the O_2 oxidized film.

3-3. TEM image of the $O(^1D)$-oxidized SiO_2 film on poly-Si

Figure 6 shows the cross sectional the transmission electron microscopy (TEM) image of the SiO_2 film grown on poly-Si using $O(^1D)$ oxidation at room temperature. The SiO_2 thickness is quite homogeneous at about 6.0 nm with a variation of less than 0.1 nm. This result suggests that the oxidation rate by $O(^1D)$ is independent of Si crystal orientation, since poly-Si surface has grain boundaries of various crystallographic orientations.

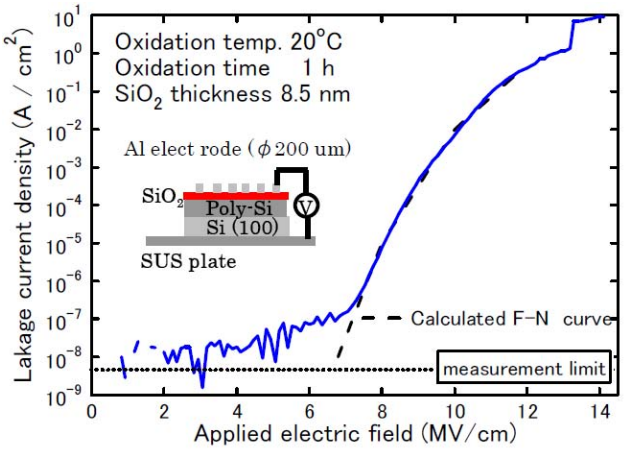

Fig. 5. *J-E* characteristic of the SiO_2 film on the poly-Si grown at room temperature in the MIS capacitor configuration.

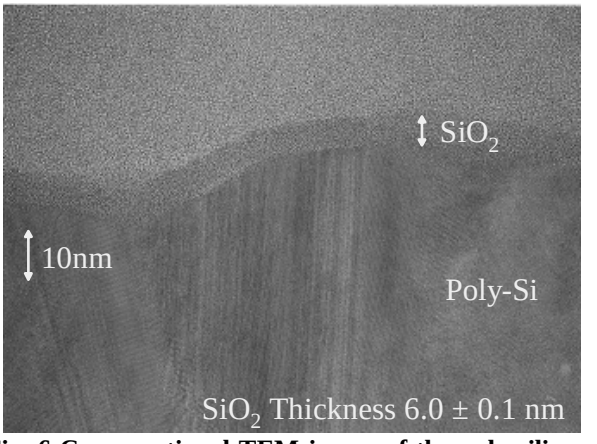

Fig. 6 Cross-sectional TEM image of the poly-silicon sample with the $O(^1D)$ oxidized SiO_2 film. The oxidation temperature and time were 20°C and 30 min, respectively.

In the case of the conventional O_2 oxidation, the oxidation rate is known to have strong Si crystal orientation dependence. For example, the oxidation

rate on Si(111) wafer is 1.5-1.7 times larger than that on Si(100) wafer at 900°C. Therefore, the O_2 cannot oxidize the poly-Si homogeneously. As a reference, we prepare the SiO_2 film on our poly-Si sample using O_2 at 820°C for 15 min. The SiO_2 film thickness was confirmed to be nonuniform between 11.8-15.9 nm (not shown).

In the case of the thermal O_3 oxidation, there is no difference in the resulting SiO_2 growth rate on Si(100) and Si(111)[5]. The mechanism of Si oxidation by $O(^1D)$ is probably similar to that by thermal O_3.

3-4. Technique for uniform oxidation of 8-inch wafer

Figure. 7 illustrates two types of large substrate oxidation by the $O(^1D)$. One is expanded KrF laser area with scanning substrate along vertical direction to irradiation (Fig. 8(a)). The other is using UV-lamp, which can irradiate large a sample area (Fig.8 (b)). It is not necessary to cut the emission of 310 nm or longer from the irradiation light, as long as it has the emission between 210 to 300 nm. The visible light cannot decompose the O_3 and does not induce damage in the Si-substrate, since Si-Si binding energy is far larger than light energy. In the both cases, ~100% O_3 flows along substrate surface. We could oxidize on the 8-inch size Si wafer homogeneously using (a)[6] and (b)[7]. In the both cases, the distribution of the SiO_2 thickness was within 4 nm.

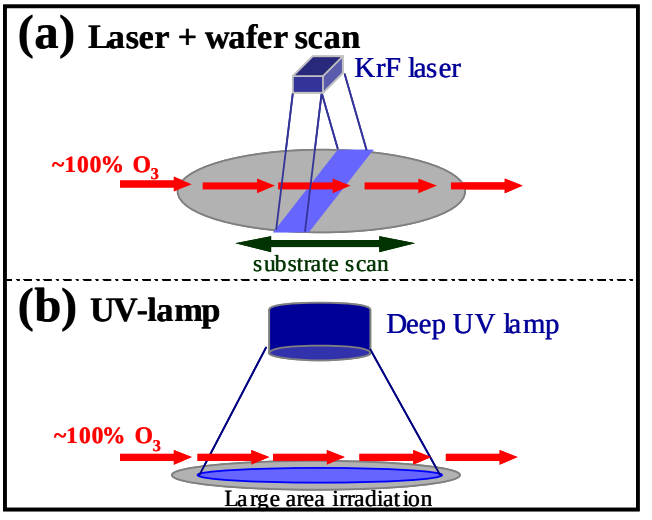

Fig. 7. The schematic experimental configurations for the large size substrate $O(^1D)$ oxidation.(a) liner emission type of light + wafer scan (b) circular-emission type light.

4. Summary

We have demonstrated Si and poly-Si oxidation at low temperatures using the excited ozone $O(^1D)$ produced by UV-light irradiation to high purity ozone. The obtained SiO_2 film on the poly-Si at room temperature has good *J-E* properties comparable to device quality film in MIS capacitor configuration. The SiO_2 thickness is homogeneous along poly-Si layer observed by TEM image. This result indicates that $O(^1D)$ oxidation rate is independent of Si crystal orientations.

We conclude that excited ozone is one of the most efficient reactive species for device quality SiO_2 film formation on poly-Si without heating substrate.

5. References

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