

P-1-8

Nanoscale-order Homogeneous Structure of SiO₂ Film on Poly-silicon Grown at Room Temperature using UV Light Excited Ozone.

Naoto Kameda^{1,2}, Tetsuya Nishiguchi^{1,2}, Yoshiki Morikawa¹, Mitsuru Kekura¹,
Hidehiko Nonaka², and Shingo Ichumura².

¹Meidensha Corporation, Core Technology Research Laboratories
515, Kaminakamizo, Numazu, Shizuoka 410-8588, Japan
Phone: +81-55-929-5481 E-mail: n-kameda@aist.go.jp

²National Institute of Advanced Industrial Science and Technology (AIST).
1-1-1 Umezono, Tsukuba, Ibaraki 305-8565, Japan

1. Abstract

We have grown SiO₂ films on polycrystalline Si using excited ozone produced by ultra-violet light irradiation to ozone. An over-5 nm thick SiO₂ film was grown in 30 min even at room temperature. The TEM image indicates that the spatial distribution of the SiO₂ film thickness is 6.0 ± 0.1 nm over an area of 100 nm square at the surface of poly-Si, where the grain sizes of poly-Si are less than 10 nm. This result suggests that the oxidation rate of silicon by excited ozone is independent of Si crystal orientation. The SiO₂ film by the excited ozone is expected to be utilized for the buffer layer with good interface properties.

2. Introduction

The fabrication of thin film transistors (TFTs) or field effect transistors (FETs) on poly-crystalline silicon (poly-Si) has recently been the topic of intensive studies aiming 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, which may well be over 900°C[1].

The ozone gas is well known as one of the most reactive species for the oxidation of Si at low temperature. We have studied the Si oxidation at low temperatures using undiluted ozone (~100% O₃) supplied from a pure ozone generator. Using the pure ozone can reduce the activation energy for the Si oxidation resulting in a reaction temperature as low as 410°C [2]. For oxidation of Si at a still lower temperature, the reactivity of ozone can be further enhanced by photo-excitation using ultra-violet (UV) light, which hits the Hartley bands (200 to 300 nm) of ozone to produce atomic oxygen in an excited state, O(¹D)[3, 4]. We have shown by using a KrF excimer laser or a deep UV lamp that UV-light excited ozone can oxidize the Si wafer even at room temperature [5,6]. The O(¹D) can also oxidize the poly-Si at room temperature, and the SiO₂ film on the poly-Si has good dielectric properties as well as that on the Si-wafer. That is the *J-E* curve (leakage current density vs. field strength) measured at the

metal-insulator-semiconductor (MIS) capacitor configuration was scaled by the theoretical Fowler-Nordheim (F-N) curve over 6 MV/cm, and the electrical breakdown occurred at an electrostatic field above 12 MV/cm[7].

However, the oxidation of poly-Si with grain boundaries of various crystallographic orientations may result in formation of a non-uniform oxide film, as it is well known that the oxidation rate for the conventional O₂ method strongly depends on the orientation of the Si crystal: For example, the oxidation rate of the Si(111) wafer was reported to be 1.5~1.7 times larger than that of Si(100) at 900°C [8].

In this paper, we report the TEM images of the SiO₂ film on poly-Si grown at room temperature using the O(¹D) generated by UV-light excited ozone to determine the spatial fluctuation of SiO₂ film thickness.

3. Experiment

The poly-Si sample was stacked on the 8" Si(100)-wafer. The thickness of the poly-Si layer was about 200 nm. The actual samples were prepared by cutting the wafer into 15 x 15 mm² chips. A KrF excimer laser (Compex110, Lambda Physik, Germany) was used to excite the pure ozone (~100% O₃). The laser wavelength was 248 nm (energy of 5.0 eV) with the pulsed power of 234 mJ in an area of 10 x 30 mm². During the oxidation process, the laser light was irradiated the whole sample surface through a distance of 5 cm from the quartz window in low pressure ~100% O₃. Pulse repetition rate was 100 Hz. The KrF laser light would not directly break the chemical bonds in the substrate, since the binding energy between Si-Si (~7 eV) is larger than UV-light energy (*i.e.* KrF laser: ~5 eV). However, it may excite the Si-Si bonding state, but its duration is within the relaxation time of the excitation, *i.e.* a few microseconds, as the laser pulse width is only ca. 10 ns. Therefore, we conclude that the UV light irradiation to Si itself does not have influence on the Si oxidation. The ~100% O₃ was supplied using a pure ozone generator (Type: MPOG-SM1C1, Meidensha corp., Japan). The principles of the production method of the 100% ozone and the details of the pure ozone generator are described elsewhere [9-12]. The detail of the experimental setup is also described in a previous paper [5]. No heater for the sample was employed in the experiment, but the laser light irradiation was confirmed to heat the sample up to 70°C.

4. Results and Discussions

For transmission electron microscopy (TEM), the sample was fabricated by mechanical planarization and ion thinning, and the TEM image was taken with a high-resolution transmission electron microscope (H-9000UHR, Hitachi Corp., Japan) operated at 300 kV.

Figure 1 shows the TEM image of the SiO₂ film on the poly-Si using O(¹D) (a) or O₂ (b). Although there are many grains at the poly-Si surface, the SiO₂ thickness after 30 min O(¹D) oxidation at 20 °C is quite homogeneous at about 6 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. On the other hand, the SiO₂ film after 15 min O₂ oxidation at 820°C has been observed to have some thickness variations, as shown in Fig. 1 (b). The SiO₂ thickness ranges from 5.3nm to 7.5nm. This SiO₂ thickness variation must be due to the Si crystal orientation dependence of the oxidation rate by O₂.

In the conventional O₂ oxidation, the oxygen molecules diffuse through the SiO₂ film to the interface where these molecules undergo dissociative adsorption to Si bond sites, generating oxygen atoms to be incorporated in the SiO₂ network [1]. Therefore, the reaction probability between the Si bonds and the O₂ molecules is strongly affected by the density of Si bond sites. Thus the oxidation rate for the O₂ oxidation should have a strong Si-crystal-orientation dependence. In the case of the O₃ oxidation, however, it is the atomic oxygen O(³P) generated from the thermal decomposition of an O₃ molecule that contributes to the formation of SiO₂ [13-16]. That is, the O(³P) diffuses through the SiO₂ film and directly goes into the back bonds of Si atoms to form the Si-O-Si network. Therefore, in this case the number of Si bond sites at the Si interface does not affect the oxidation rate, and the O(³P) can oxidize Si surfaces with various crystal orientations at an equal rate. Actually, it has been reported that for O(³P) oxidation of Si(100) and Si(111) films, there is no difference in the resulting SiO₂ thickness[17]. Very probably the mechanism of Si oxidation by O(¹D) is similar to that by O(³P).

5. Conclusions

We observed TEM of the SiO₂ film grown on the poly-Si using the excited ozone, *i.e.* O(¹D), produced by UV-light irradiation to high purity ozone, as well as the one using O₂ gas as the conventional oxidation method. The SiO₂ film thickness for the O(¹D) oxidation has small spatial variation, while the SiO₂ film thickness for the O₂ oxidation has much larger variation. These results are well explained by the Si orientation dependence of the oxidation rate using the simple oxidation models.

Acknowledgements

We thank Dr Hiroshi Itoh, for the sample oxidation using O₂ gas.

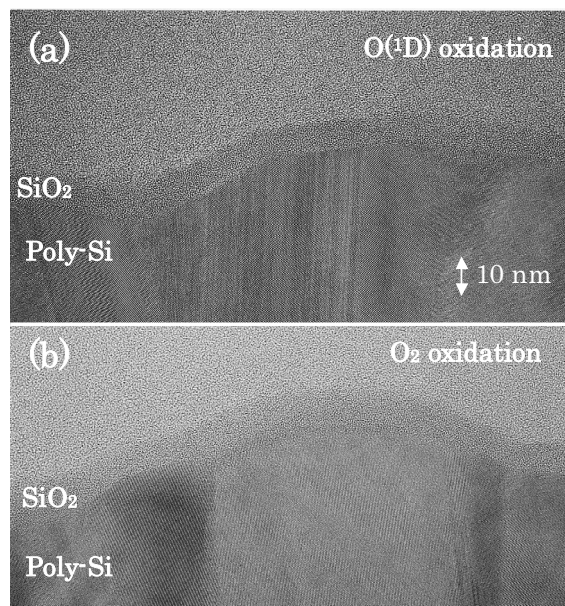


Fig. 1 Cross-sectional TEM image of the poly-silicon sample with the O(¹D) SiO₂ film(a) or the O₂ SiO₂ film(b). The O(¹D) oxidation temperature and time were 20 °C and 30 min, respectively. The O₂ oxidation temperature and time were 820°C and 15 min, respectively.

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