Formation of silicon dioxide layers at low temperatures (150–400 °C) by atmospheric pressure plasma oxidation of silicon

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Abstract

The formation of silicon dioxide (SiO₂) layers at low temperatures (150–400 °C) by atmospheric pressure plasma oxidation of Si(001) wafers have been studied using a gas mixture containing He and O₂. A 150 MHz very high frequency (VHF) power supply was used to generate high-density atomic oxygen in the atmospheric pressure plasma. Oxidation rate, structure, and thickness and refractive index profiles of the oxidized layers were investigated by ellipsometry and infrared absorption spectroscopy. Atomic force microscopy was also employed to observe atomic-scale morphologies of the layer surface and wafer Si surface, after chemical removal of the oxidized layers. It was found that stoichiometric SiO₂ layers were obtained at higher oxidation rates than conventional dry O₂ thermal oxidation and radical oxidation processes, even at a very low substrate temperature of 150 °C. Although thickness variations were observed in the plasma region, the refractive index was independent of both substrate temperature and VHF power. In addition, the SiO₂ surface and SiO₂/Si interface roughnesses were comparable to those obtained in conventional dry oxidation at high temperatures.

Keywords: Atmospheric pressure plasma; Plasma oxidation; Silicon oxide; Cylindrical rotary electrode

1. Introduction

The formation of high quality silicon oxides (SiO₂) for gate dielectric layers at temperatures lower than 400 °C is a very important process for fabricating polycrystalline Si thin film transistors (TFTs) on glass or plastic substrates. Plasma-enhanced chemical vapor deposition (PECVD), which is applicable to large area deposition, is widely used at present. The SiO₂ should have a low defect density, as well as a smooth surface. This is essential for achieving high breakdown field strength with low leakage current and high field-effect mobility in a TFT structure. However, plasma damage due to ion bombardment and contamination in the films of undesirable impurities result in the formation of films with poor properties. Although remote plasma-enhanced CVD (RPECVD) [1,2] is considered to be more suitable for making a high-quality film with low damage and low contamination, it is not applicable to large area deposition.

As an alternative method to PECVD and RPECVD, we have used atmospheric pressure plasma oxidation of Si to form SiO₂ layers. During the last years, we have developed an atmospheric pressure plasma CVD (AP-PCVD) technique [3]. In the AP-PCVD process, stable glow plasmas, generated using very high frequency (VHF) electric field at atmospheric pressure, are effectively used to deposit thin films. It is considered that the gas temperature of atmospheric pressure plasmas becomes higher than that of conventional low-pressure plasmas. Additionally, charged particles should have smaller kinetic energy due to the VHF electric field and also due to the high collision frequency with other molecules. Therefore, the reduction of substrate heating temperature and the suppression of ion damage of the film are simultaneously expected by utilizing atmospheric pressure plasma. In contrast to the conventional PECVD technique, it is shown that AP-PCVD is a promising technique for the high-rate and low-temperature growth of high-quality functional thin films [4–10].
The aim of this study is to develop a new technology for the formation of gate oxide layers with good dielectric strength, low interface trap density and low fixed oxide charge density, utilizing the physical and chemical properties of atmospheric pressure plasma. As substrate materials, we can use not only crystalline Si but also amorphous Si (a-Si) films. Oxidation of porous a-Si films would lead to a decrease in the oxide stress and an increase in the diffusion coefficient of the oxidizing species, and thus the formation of high-quality SiO$_2$ layers with high throughput can be expected. In this paper, we present some results of the characterizations of SiO$_2$ layers formed by atmospheric pressure plasma oxidation of Si. In order to study the oxidation process fundamentally, single-crystal Si wafers were oxidized using a gas mixture containing helium (He) and oxygen (O$_2$).

2. Experimental

Fig. 1 schematically shows the experimental setup. The reactor used for the experiments is almost the same as that described in our previous reports [4–6,8–10]. A cylindrical rotary electrode with 200 mm diameter and 150 mm width was placed in the reactor. A substrate was vacuum-chucked on the substrate heating stage made of SiC-coated graphite, which could be heated as high as 1000 °C. Supplying 150 MHz VHF power, atmospheric pressure plasma was generated in the gap between the rotary electrode and a substrate. By rotating electrode, it is also possible to prevent the local heating of electrode surface, so that the accuracy of the gap size is maintained even when a large electric power is supplied. A SiO$_2$ layer was formed in a rectangular region defined by the width of plasma (15 mm), which was determined by the width of substrate, and the plasma length (approximately 40 mm) without substrate scanning.

The electrode rotation has a considerable viscous drag effect at atmospheric pressure. This means that the process gas in the reactor can be readily and homogeneously introduced into the small gap between the electrode and a substrate, and thus the flow rate of the process gas is precisely controlled by the electrode rotation speed. This is very important when depositing a uniform thin film at a high rate [4,9]. In the case of forming SiO$_2$ layers by oxidizing Si, however, it is reasonable to mention that the diffusion of oxidizing species through SiO$_2$ network is the limiting step to increase the SiO$_2$ thickness. Thus, a high-speed rotation of electrode is not necessary. In this study, the electrode rotation speed was fixed at 60 rpm.

Czochralski (CZ) p-type Si(0 0 1) wafers with a resistivity of 10–20 Ω cm were used as substrates. The wafers were cut into a size of $15 \times 90$ mm$^2$ corresponding to the heating stage size, and were cleaned by the room temperature wet cleaning process [11]. Before experiment, the reactor was evacuated to a pressure less than 10$^{-6}$ Torr and then filled with the process gas mixtures containing He and O$_2$ to 760 Torr. He and O$_2$ used in this study were purified by gas purifiers to impurity levels less than 1 ppb. The substrate temperature ($T_{sub}$) was monitored using a thermocouple embedded in the heating stage and was varied in the range from 150 to 400 °C as a parameter. The O$_2$ concentration was maintained constant at 5%. During oxidation, a sufficiently large VHF power (600–1200 W) was supplied to ensure the sufficient decomposition of O$_2$ molecules in the plasma. The smallest gap between the rotary electrode and a substrate was fixed at 0.6 mm.

The thickness of SiO$_2$ layers and their refractive index were determined by ellipsometry (Rudolph, Auto EL III) using a wavelength of 632.8 nm. The layer structure was investigated by infrared (IR) absorption spectroscopy with a Fourier transform IR spectrometer (Shimadzu, FTIR-8600PC) in the wavenumber range of 400–4000 cm$^{-1}$. The surfaces of the SiO$_2$ layers and the Si substrates after oxide removal were probed by atomic force microscopy (Seiko Instruments, SPI3800N). A 5% HF aqueous solution was used for SiO$_2$ dissolution.

3. Results and discussion

First, oxidation rate was examined. The experiments were performed without substrate scanning, and the central portions of the oxidized areas were evaluated by ellipsometry. Fig. 2 shows the oxidation time dependence of oxidized layer thickness as a function of $T_{sub}$. The VHF

![Fig. 1. Schematic illustration of the experimental setup. (a) Front view and (b) side view.](image)

![Fig. 2. Oxidation time dependence of the thickness of oxidized layers formed with a sufficiently large VHF power of 600 W as a function of $T_{sub}$.](image)
power is fixed at 600 W. For all the samples plotted in Fig. 2, the refractive index was almost constant at around 1.46, which is the stoichiometric value of silicon dioxide. The initial oxidation rates derived from the layer thickness after 1 min oxidation at \( T_{\text{sub}} = 150, 300 \) and 400 \(^\circ\)C are 6.2, 6.9 and 14.1 nm min\(^{-1}\), and the thicknesses of oxidized layers reach the maximum values of 34.7, 38.7 and 64.4 nm after 30 min oxidation, respectively. It is reported that the thickness of SiO\(_2\) layer after 30 min oxidation is as large as 30 nm in a conventional dry oxidation process at 1000 \(^\circ\)C [12] and 10–20 nm in radical oxidation processes using low-pressure plasmas [12,13]. Thus, in the present study, the higher oxidation rates than those in dry and radical oxidation processes are obtained.

From Fig. 2, the oxidation kinetics is considered to be diffusion-limited. Fig. 3 shows the Arrhenius plot of parabolic rate constant deduced from Fig. 2 under the assumption that the oxidation kinetics is diffusion-limited. The activation energy for the diffusion of oxidizing species through the SiO\(_2\) network is approximately 0.097 eV, whose value is extremely smaller than that in the conventional thermal oxidation process [14]. Such low activation energy implies that a \( T_{\text{sub}}\)-independent process partly contributes to the diffusion of oxidizing species. Similar results are reported in radical oxidation processes using low-pressure plasmas [12,13]. It is considered that the principal oxidizing species are not oxygen molecules but atomic oxygen of which diffusion coefficient in SiO\(_2\) layer is assumed to be much higher than that of oxygen molecule. It is worth noting that atmospheric pressure plasma can generate atomic oxygen so efficiently that high-rate and low-temperature oxidation of Si is readily realized.

Next, the structure of the oxidized layers was characterized by IR absorption spectroscopy. Fig. 4 shows IR absorption spectra of the oxidized layers after 30 min oxidation with 600 W at 150, 300 and 400 \(^\circ\)C. In all the spectra in Fig. 4, characteristic absorption bands due to the stretching and deformation of Si–O–Si are observed at wavenumbers of 1070 and 810 cm\(^{-1}\), respectively [15]. The band at 440 cm\(^{-1}\) due to the Si–O–Si rocking vibration was also observed (not shown in Fig. 4). If the oxide is porous or substoichiometric and/or N and H impurities are incorporated, it is reported that the position of the 1070 cm\(^{-1}\) peak moves towards the lower wavenumber side [16]. Thus, it is considered that the oxidized layers are high-quality pure SiO\(_2\) with a dense network.

To know whether it is possible to form a homogeneous SiO\(_2\) layer over a large-sized substrate, the entire areas of the oxidized layers were investigated. Fig. 5 shows the thickness (a) and refractive index (b) profiles of the oxidized layers after 5 min of oxidation at 400 \(^\circ\)C as a function of VHF power.

![Graph showing Arrhenius plot of parabolic rate constant](image)

**Fig. 3.** Arrhenius plot of parabolic rate constant deduced from Fig. 2, where the solid line shows an exponential fit to the data.
amount of process gas fed to the plasma region is not the electrode rotation but the diffusion from the atmosphere. This consideration is supported by the fact that the SiO\textsubscript{2} thicknesses are larger near the plasma edges than those at the central portions, as shown in Fig. 5(a). The thickness variation may also be caused by the plasma density variation across the plasma length because of the varying gap between the substrate and the cylindrical electrode.

From the results mentioned above, it should be noted that when oxidized with substrate scanning at a constant speed, homogeneous SiO\textsubscript{2} layers with uniform thickness will be obtained in the area having the width of plasma and the substrate scanning distance, even if there are some temperature deviations on a large-sized substrate.

Finally, the surface and interface roughnesses of the above described SiO\textsubscript{2} layers were observed by AFM. Fig. 6 shows the AFM images and corresponding roughnesses of the sample after 5 min oxidation with 600 W at $T_{\text{sub}} = 400 \, ^\circ\text{C}$, before and after etching the SiO\textsubscript{2} layer. The SiO\textsubscript{2} thickness is 26.3 nm. As shown in Fig. 6(a), the root mean square (rms) roughness ($R$) value of the SiO\textsubscript{2} surface is a little larger than that of the surface of CZ–Si wafers ($<0.1 \, \text{nm}$). It is also revealed that the roughness of the wafer Si surface, after chemical removal of the SiO\textsubscript{2} layer, is larger than that of the SiO\textsubscript{2} surface. However, the roughness values shown in Fig. 6 are comparable to those for ultra-thin SiO\textsubscript{2} layers formed by conventional dry O\textsubscript{2} thermal oxidation of Si [17–19], indicating that the SiO\textsubscript{2} layer obtained in this study has a sufficiently smooth surface and an interface in spite of the high oxidation rate and the relatively large thickness. It is considered that the roughness is related to the oxidation rate. Indeed, the SiO\textsubscript{2} surfaces and SiO\textsubscript{2}/Si interfaces were smoother at the lower $T_{\text{sub}}$, although the dependence of rms roughness on $T_{\text{sub}}$ is not described in the literature. Toward the application of the SiO\textsubscript{2} layers to the industrial uses, the electrical properties, such as dielectric strength, leakage current, and the densities of interface trap and bulk charge, must be evaluated in the future study.

4. Conclusions

Atmospheric pressure plasma oxidation was studied as an alternative method for fabricating gate oxide layers for TFTs. Stoichiometric SiO\textsubscript{2} layers were obtained at very high oxidation rates, even when the substrate temperature is as low as 150 °C. Since a cylindrical electrode was used in this study, thickness variations were observed across the plasma length. However, the refractive index was independent of both substrate temperature and VHF power, and was almost constant in the plasma region. Moreover, surface and interface roughnesses were similar to those obtained in conventional dry oxidation at high temperatures. Therefore, it can be expected that homogeneous SiO\textsubscript{2} layers with uniform thickness is obtained if oxidation is performed with substrate scanning at a constant speed. Future study will focus on the investigations on the electrical properties of the high-rate oxidized SiO\textsubscript{2} layers, and also on the oxidation of amorphous Si thin films.

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