



Improvement of electrical properties of silicon oxide thin film with ultraviolet and organic gas assisted annealings

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ABSTRACT

In order to form a silicon oxide thin film at a low temperature, we employed the reaction between spin-coated silicone oil and ozone gas at a low temperature of 250 °C. In the formed silicon oxide films, a large number of Si–OH bonds were observed. To reduce the amount of impurities such as Si–OH bonds, the silicon oxide film underwent ultraviolet (UV) light treatment and alcohol-assisted annealing. The combination of dipping in ethanol and thermal annealing in methanol gas effectively reduced Si–OH bonds. It was hypothesized that the Si–OH bonds were displaced with Si–OCH₃ bonds due to the alcohol treatment. After UV treatment and alcohol annealing, the network Si–O–Si bonds increased, and the cage Si–O–Si bonds decreased. It was predicted that the cage Si–O–Si bonds were broken by UV light and the bonds recombined to form the network Si–O–Si bond. The dielectric property after UV treatment and alcohol annealing was improved owing to the decrease in the cage Si–O–Si and Si–OH bonds.

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1. Introduction

Silicon oxide films are very important in the semiconductor industry because these films can be applied as inter-layer insulators, sacrifice layers, and gate oxide films in ultra-large-scale integration (ULSI) manufacturing. One of the key processes for obtaining a high performance in low-temperature poly-Si (LTPS) thin film transistors (TFTs) on a non-heat-resistant substrate is the low-temperature formation of a high-quality gate dielectric because the TFT performances strongly depend on the Si oxide/Si interface property. A conventional plasma-enhanced chemical vapor deposition (PECVD) process with tetraethylorthosilicate (TEOS; Si(OC₂H₅)₄) gas can be carried out at a sufficiently low temperature. However, the PECVD technique requires an expensive vacuum chamber and plasma system, and we must consider plasma damage, particularly at the Si oxide/Si interface [1]. Moreover, TEOS is toxic to human eyes and throat. Therefore, a safe and inexpensive technology is required to form silicon oxide films.

In order to form gate dielectrics at a low cost, many research groups have studied the spin-on glass (SOG) technique using various liquid materials. However, a temperature higher than 400 °C is necessary to obtain high quality with low impurities [2,3]. Better low-temperature technology is required to form silicon oxide films for fabricating TFTs on low-cost substrate.

In our previous work, we reported a method for forming a silicon oxide thin film by atmospheric-pressure CVD (APCVD) using a dimethyl silicone oil ([SiO(CH₃)₂]_n[Si(CH₃)₃]₂) and ozone (O₃) gas in a low-temperature range below 350 °C. The electrical properties of the metal-oxide-semiconductor (MOS), as evaluated through current-voltage and capacitance-voltage measurements, were close to those of the silicon oxide film formed by the PECVD method using TEOS [4]. Silicone oil is used for lubrication, insulation, and so on, and it is inexpensive and easy to handle owing to its stability. Therefore, it is expected that silicone oil is a useful source material because it is less expensive and safer than TEOS.

When the temperature of ozone gas exceeds 150 °C, it decomposes into O₂ and O [5,6]. In the reaction between silicone oil and ozone, generated O attacks the chains of silicone oil, and a precursor is formed by displacing Si–CH₃ bonds into Si–OH bonds. Then, a silicon oxide film is formed by the dehydration reaction of Si–OH bonds [4,7]. However, the Si–OH bonds and impurities in the film are observed to remain in samples formed at low temperature [8]. These remaining Si–OH bonds are similar to those reported for silicon oxide films formed by other low-temperature deposition methods [9,10]. The inadequate dehydration of Si–OH bonds is the cause of the remaining Si–OH bonds. The Si–OH bonds in the insulator cause the degradation of the electric properties of electric devices.

In the present study, we formed silicon oxide thin films using the reaction of spin-coated silicone oil and ozone gas at a low temperature of 250 °C. In order to reduce the amount of impurities such as Si–OH bonds, the silicon oxide film was treated with ultraviolet (UV) light and alcohol-assisted annealing.

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2. Experimental

Dimethyl-silicone-oil (MOMENTIVE, TSF451-10) was coated onto chemically cleaned *p*-type Si (100) substrates by a spin coater at 5000 rpm for 20 s. The viscosity at 25 °C and the mean molecular mass of the silicone oil were 10 mm²/s and 1300, respectively. The sample size was 2 cm × 2 cm. After spin coating the silicone oil, the sample was set on a hot plate at 250 °C and exposed to 15% ozone gas for 15 min. The thickness of the silicon oxide film formed under this condition was 130 nm.

The sample was annealed at low temperature to improve its quality. First, the sample was treated with UV light (wavelength; 254 nm, power density; 54.38 mW/cm²) at 250 °C for 120 min. After that, the sample was dipped in ethanol at room temperature for 15 min and then annealed on a hot plate at 250 °C in methanol gas for 30 min, as shown in Fig. 1.

The molecular structure of the silicon oxide film was measured by Fourier transform infrared spectroscopy (FT-IR).

The metal-oxide semiconductor (MOS) structure was fabricated by depositing aluminum electrodes (diameter of top electrode: 100 μm). The current density–electric field (*J*–*E*) and capacitance–voltage (*C*–*V*) characteristics were measured.

3. Results and discussions

Fig. 2 shows the FT-IR spectra of silicon oxide thin films with (a) no annealing (as formed), (b) dipping in ethanol and thermal annealing in methanol gas, and (c) thermal annealing with UV, dipping in ethanol, and thermal annealing in methanol gas.

The peaks at around 810 and 1070 cm⁻¹ were identified as absorptions due to a bending (TO₂) mode and an asymmetric stretching (TO₃) mode of the Si–O–Si bond, respectively [11–13]. In the spectrum of the unannealed sample (a), large peaks from the Si–OH bonds were observed at around 960 and 3400 cm⁻¹. After dipping in ethanol and annealing in methanol gas (b), the peak from the Si–OH bond was considerably reduced and could hardly be observed. The combination of dipping in ethanol and thermal annealing in methanol gas removed Si–OH bonds effectively. After thermal annealing with UV and alcohol-assisted annealing (c), the peak from Si–OH bonds increased in comparison with the sample (b), and the peak at around 1110–1250 cm⁻¹ decreased.

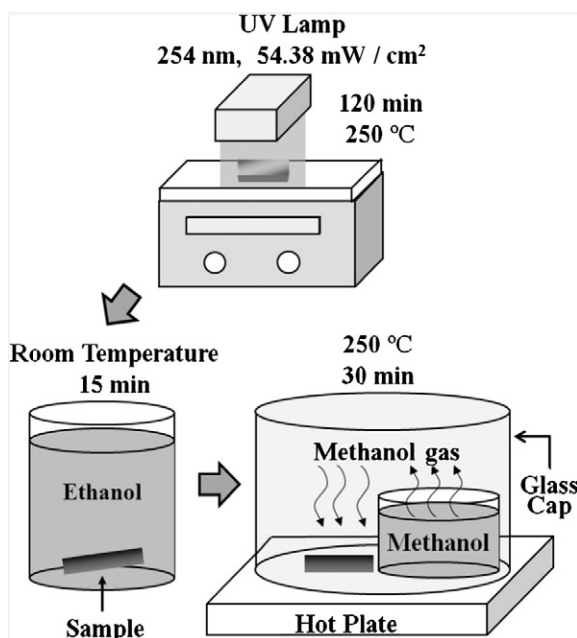


Fig. 1. Schematic diagram of equipment for UV treatment and alcohol treatment.

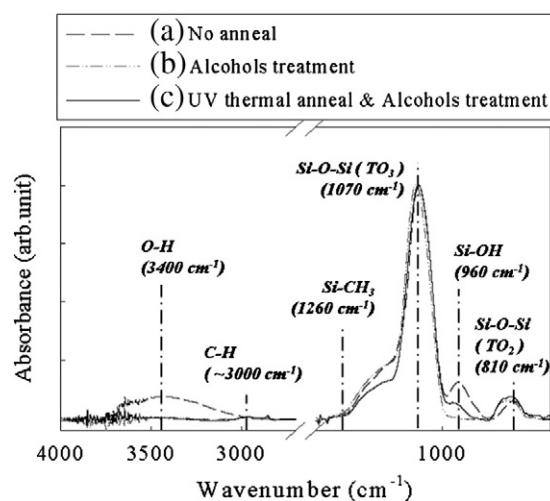


Fig. 2. FT-IR spectra of silicon oxide thin films with (a) no annealing (as formed), (b) dipping in ethanol and thermal annealing in methanol gas, and (c) thermal annealing with UV, dipping in ethanol, and thermal annealing in methanol gas.

We analyzed the FT-IR spectrum in detail. Fig. 3 shows the results of peak separation in the spectrum range of 750–875 cm⁻¹. In the case of samples (b) and (c), a peak around 840 cm⁻¹ was generated in the spectrum. The peak at around 805–850 cm⁻¹ indicated the existence of Si–CH₃ and Si–OCH₃ bonds [14]. However, another peak from Si–CH₃ bonds at around 1260 cm⁻¹ was hardly observed, as shown in Fig. 2. It is considered that the Si–OCH₃ bonds were generated by the alcohol treatment. It has been reported that the displacement of Si–OH bonds occurred by the chemical reaction between Si–OH bonds and alcohol [15]. It is hypothesized that the Si–OH bonds were displaced by the Si–OCH₃ bonds due to the alcohol-assisted treatment. As a result, the Si–OH bonds decreased, and the Si–OCH₃ bonds were generated.

Fig. 4 shows the results of peak separation in the spectrum range of 850–1300 cm⁻¹. The peaks at 1200 and 1070 cm⁻¹ were identified as the absorptions due to a TO₄ mode and TO₃ mode of the network Si–O–Si bonds (bond angle ≈ 144°), respectively. The peaks at 1120 and 1020 cm⁻¹ were identified as the absorptions due to cage Si–O–Si bonds (bond angle ≈ 150°) and a sub-oxide (bond angle < 144°), respectively. The sub-oxide has a linear structure of Si–O–Si bonds. The cage Si–O–Si structure is the mixed structure of network and sub-oxide bonds [16,17]. The silicon oxide film formed by thermal oxide has a network Si–O–Si bonds. The film quality of silicon oxide increases with increasing the ratio of network Si–O–Si bonds.

Table 1 shows the peak height of the FT-IR spectrum of each separated bond in the silicon oxide thin films with (a) no annealing (as formed) and (c) thermal annealing with UV and dipping in ethanol and thermal annealing in methanol gas. At first, we formed sample (a) and measured the FT-IR spectrum. Next, we performed the UV treatment and alcohol-assisted annealing, and measured the FT-IR spectrum. After the UV and alcohol annealing, the network Si–O–Si bonds increased, and the cage Si–O–Si bonds decreased. It has been reported that the Si–O–Si structure is improved by UV thermal annealing [16,18]. In those reports, it was predicted that the cage Si–O–Si bonds were broken by UV light, and the bonds recombined to form network Si–O–Si bonds. The increase in Si–O–C bonds can be explained by the generation of Si–OCH₃ bonds as described above.

As shown in Fig. 2, the peak from Si–OH bonds in sample (c) was higher than that in sample (b). This means that the UV irradiation interrupted the removal of Si–OH bonds. Because of the UV irradiation, the structure was improved to the three-dimensional network Si–O–Si structure, and the density of the film increased. It is predicted that the chemical reaction to remove the Si–OH bonds is prevented by the

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