Low-Temperature Growth of SiO_2 Films by Plasma-Enhanced Atomic Layer Deposition

Jung Wook Lim, Sun Jin Yun, and Jin Ho Lee

ABSTRACT—Silicon dioxide (SiO_2) films prepared by plasma-enhanced atomic-layer deposition were successfully grown at temperatures of 100 to 250 ℃, showing self-limiting characteristics. The growth rate decreases with an increasing deposition temperature. The relative dielectric constants of SiO_2 films are ranged from 4.5 to 7.7 with the decrease of growth temperature. A SiO_2 film grown at 250 ℃ exhibits a much lower leakage current than that grown at 100 ℃ due to its high film density and the fact that it contains deeper electron traps.

Keywords—SiO_2 plasma-enhanced atomic layer deposition (PEALD), C-V, Poole-Frenkel.

I. Introduction

For silicon device fabrication, the reduction of thin films to nanometer dimensions for new technologies requires exquisite control of film thickness, morphology, crystallinity, and conformality [1]. In addition, in the fabrication of a low-temperature poly-silicon (LTPS) thin film transistor (TFT) using a plastic substrate for a flexible device, a process temperature below 200°C should be developed [2]. Low-temperature deposition will also facilitate the use of silicon dioxide (SiO_2) as a protective coating or insulator on polymeric materials. Moreover, SiO_2 can be used in low-refractive-index layers of optical coatings and planar waveguides, which are widely applied in optical communications technology.

To obtain the requirement mentioned above, atomic layer deposition (ALD) can be a suitable deposition method to realize superb uniformity and high quality. In particular, uniformity is a very important issue in the growth of a gate insulator [3]. In recent reports, plasma-enhanced ALD (PEALD) using rf plasma was performed, and superior film quality was obtained in PEALD compared to that in ALD [4]-[8].

In the case of SiO_2 ALD, large reactant exposures are required for the surface reaction [1]. Since the reactivity of the Si precursor is very low, particularly at a temperature below 300°C, the ALD growth of SiO_2 films was performed using catalyzed sequential surface reactions [1], [9]. Hence, it is difficult to achieve a SiO_2 ALD without a catalyst. In our work, we performed a SiO_2 PEALD at temperatures of 100 to 250°C using $Si(N(CH_3)_2)_4$ (tetradimethyl-aminosilicon, or TDMAS) as a precursor of Si, and O_2 and N_2 as reactant gases with rf plasma generation.

II. Experiment

A PEALD (or ALD) apparatus used to grow SiO_2 films has been described in our previous work [7]. In the PEALD apparatus, both the ALD and PEALD processes were feasible; 5, 8, and 12 inch wafers could be loaded; and a very uniform film thickness was obtained. For the PEALD process, plasma was directly turned on between the substrate and upper electrode (3.5 mm gap), and no external bias was applied. As a wafer, a p-type Si(100) wafer was used in our experiments.

The Si precursor was a mixture of $Si(N(CH_3)_2)_4$ and $Si(N(CH_3)_2)_3Cl$ to enhance the reactivity. The vaporization temperature of the Si precursor was 68°C. The oxygen precursors were H_2O in the ALD and O_2/N_2 plasma in the PEALD. The growth temperatures were 100, 150, 200, and 250°C. The working pressure was 3.0 torr and the plasma power was 400 W.

III. Growth Kinetics

In a growth temperature range of 100 to 250°C, a conventional

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ALD of SiO_2 was performed where H_2O vapor was used as a reactant gas. In spite of the steady increase in the amount of precursor supply due to our increasing the vapor temperature, no deposition occurred, which implies that the reactivity and adsorption rate of the Si precursor are too low to be grown on the Si wafer. To enhance the reactivity between the Si precursor and oxygen precursors, O_2 and N_2 gases with rf plasma were used to grow SiO_2 films. In our recent report, the plasma process contributed to making new active sites, enhancing the adsorption rate of the precursors [10]. Rf plasma was turned on during the oxygen precursor injection. Oxygen gas was used as a reactant gas.

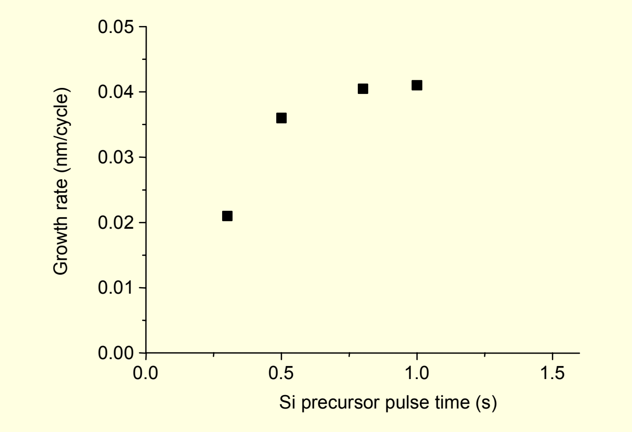

Fig. 1. Growth rate versus Si precursor pulse time of SiO_2 films grown at 150°C. The oxygen precursor pulse time was 1.0 s.

The growth rate increases and levels off at 0.8 s of precursor pulse time, and a 0.041 nm/cycle was obtained as shown in Fig. 1. For the plasma pulse time, saturation of the growth rate occurs after a very short time. In a ZrO_2 PEALD, a similar phenomenon was observed and the growth rate versus plasma time was described [5]. From these results, the self-limiting characteristics of surface reactions is demonstrated by the saturation of the growth rate, satisfying ± 2.5% of thickness uniformity in a 5 inch wafer for all samples.

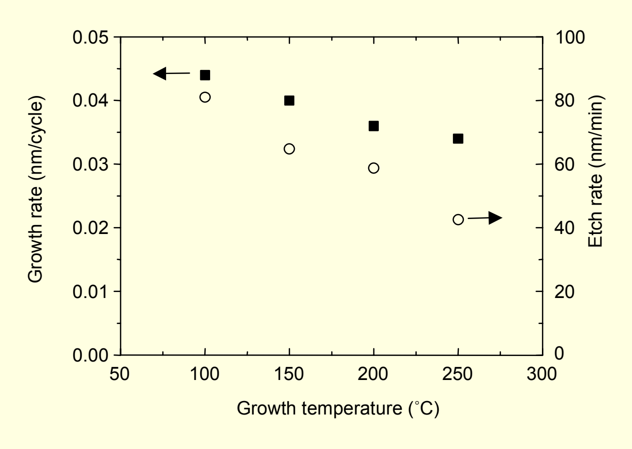

Fig. 2. Growth and etch rates as a function of deposition temperature. The Si precursor pulse time was fixed at 1.0

Figure 2 shows the growth rate as a function of deposition temperature from 100 to 250°C. The growth rate decreases with an increasing deposition temperature. In the PEALD method, this behavior of a gradual decrease of growth rate has been reported in the growth of dielectric films such as Al_2O_3 and TiO_2 [7], [10]. The reason for this tendency is unknown. To evaluate film density, etch rates of all samples were investigated using an HF solution. As growth temperature increases, the etch rate steadily decreases. Hence, SiO_2 grown at 250°C is more dense than the other samples.

The C and N content of SiO_2 films was 3.3 to 4.6 at% and 3.3 to 4.2 at%, respectively, while Cl was not detectable (<0.5 at%) when measured by Auger Electron Spectroscopy (AES) analysis. In the case of using only O_2 plasma, similar N content was observed; thus almost all of the N content must be originated from the Si precursor. In our previous reports, N_2 plasma contributes little nitrogen incorporation [7], [10]. The impurity content and oxygen-to-silicon atomic ratio (O/Si) are listed in Table 1.

Table 1. Impurity content and oxygen-to-silicon atomic ratio (O/Si) of SiO_2 films grown at various temperatures.

	100°C	150°C	200°C	250°C
C (at%)	3.3	3.8	4.4	4.6
N (at%)	3.9	4.0	4.2	3.3
O/Si	2.15	2.19	2.14	2.09

IV. Electrical Properties

In order to examine the current-voltage (I-V) characteristics, aluminum dots (400 μm diameter) were formed on SiO_2/ITO films using e-beam evaporation. MOS structures were also fabricated to examine the capacitance-voltage (C-V) characteristics. The thickness of SiO_2 films ranges from 50 to 65 nm.

From the maximum capacitance at 1 MHz in the C-V curves, the values of the relative dielectric constants of SiO_2 films can be estimated and plotted. Also, with high and low frequency C-V curves of the MOS capacitor, the values of density of interface states (D_{it}) can be obtained as expressed in Fig. 3. As the deposition temperature increases, the dielectric constant and D_{it} decrease and then slightly increase at 250°C. The higher value of the dielectric constant at lower temperature may be due to the imperfection of the films. Moreover, the film with a low D_{it} of about 1×10^{11} $cm^{-2}eV^{-1}$ was obtained at the deposition temperatures of 200 and 250°C, which can be applicable to the gate insulator in an LTPS TFT for a flexible device.

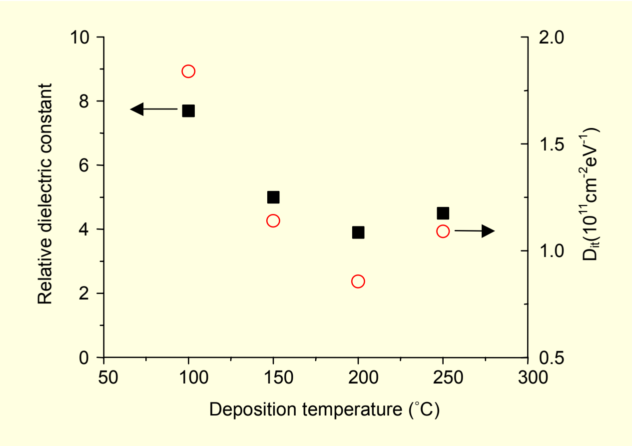

Fig. 3. Relative dielectric constant and density of interface states (D_{it}) as a function of deposition temperature.

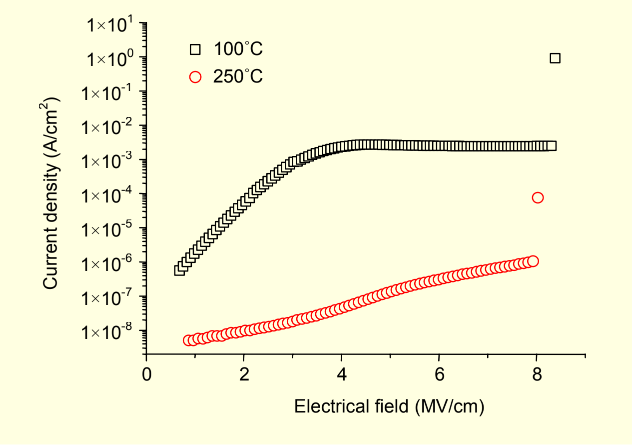

Fig. 4. Current density versus electrical field for PEALD SiO_2 samples grown at 100 and 250°C.

As shown in Fig. 4, the leakage current of SiO_2 grown at 250°C is much lower than that at 100°C. A breakdown field of as high as 8.0 MV/cm is achieved in SiO_2 grown at 250°C, which is a value comparable to the SiO_2 films grown by inductively-coupled plasma oxidation at 350°C [11]. Since the impurity level of the sample at 250°C is similar to that at 100°C, the lower leakage current can be explained by the higher film density of a sample grown at 250°C. Another possible reason for a lower leakage current can be explained by the difference of distribution of the impurities with deep and shallow electron traps between samples grown at 100 and 250°C. To confirm this, the current leakage mechanism was investigated.

With Schottky and Poole-Frenkel emission equations, a relative dielectric constant can be obtained from the plot of ln (J) versus $E^{1/2}$ and ln (J/E) versus $E^{1/2}$, where J is the current density and E is the electrical field [12]. Since the thickness of samples is more than 50 nm, the tunnel current can be ignored.

Figure 5 shows the relative dielectric constants calculated by the Schottky and Poole-Frenkel emission equations for samples grown at 100 and 250°C.

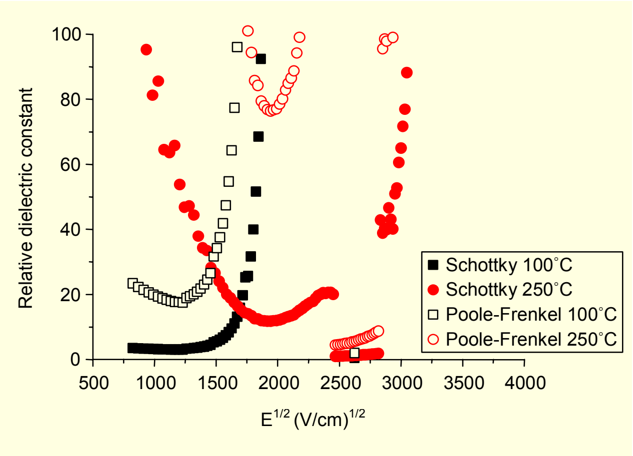

Fig. 5. Relative dielectric constant as a function of the square root of the electrical field indicating that Schottky and Poole-Frenkel current leakage mechanisms dominantly occur in different regions for samples grown at 100 and 250˚C.

By comparing the calculated values of the relative dielectric constants in Fig. 5 with those measured by the C-V curve in Fig. 3, it can be found that Schottky and Poole-Frenkel emissions coexist at a low electric field region for samples grown at 100°C (< 2.2 MV/cm) since the dielectric constant obtained by C-V curve is about 8, whereas that by Schottky curve is 4 and that by Poole-Frenkel curve is 20. For samples grown at 250°C, Schottky emission is dominant from 3.0 to 4.8 MV/cm and Poole-Frenkel emission from 5.8 to 7.8 MV/cm. Since Poole-Frenkel emission results from the field-enhanced excitation of trapped electrons into the conduction band, a sample grown at 100°C contains shallower electron traps than a sample at 250°C. The shallow trap allows electrons to escape and contribute to conduction of the current. Therefore, shallower electron traps in a SiO_2 film grown at 100°C generate a higher leakage current at a low field region than in a film grown at 250°C.

V. Conclusion

SiO_2 films were successfully grown at low temperature below 250°C by PEALD, showing a self-limiting characteristic. The growth rate decreases with an increasing deposition temperature. Films grown at 250°C exhibit a lower dielectric constant and leakage current than that at 100°C, which can be applicable to the gate insulator in LTPS TFT for flexible devices. For enhancing the growth rate and reducing the impurity level, further investigation is required.

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