

Structure of SiO₂ Films Grown at Low Temperature by Inductively Coupled Plasma Oxidation with Oxygen Gas

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The structure of silicon oxide films grown in inductively coupled plasma (ICP) with oxygen gas at temperatures ranging from 350 to 450 °C was studied. The thickness of the oxide ranged from 10 to 40 nm. A FTIR spectroscopy showed that the Si-O-Si bond angle was smaller than that in the high-temperature thermal oxide. The bond angle decreased as the oxide thickness decreased. An X-ray reflectivity analysis showed that the density of the ICP oxide (2.23 g/cm³) was larger than that of thermal oxide (2.20 g/cm³) grown at 900 °C. The accumulation of compressive stress could be the cause of small bond angles and the high density in the ICP oxide. A very thin surface layer with a lower density was also detected on the as-grown ICP oxide. The ICP oxide showed a high etch rate and low refractive index as the oxide thickness decreased, indicating that these chemical and physical properties were strongly affected by the magnitude of the Si-O-Si bond angle.

Keywords: inductively coupled plasma, low temperature oxidation, SiO₂ structure, Si-O-Si bond angle

1. INTRODUCTION

Oxidation of Si at low temperatures is one of the most important processes in the fabrication of thin film transistors for organic light emitting displays. Polycrystalline-silicon (poly-Si) thin-film transistors require an SiO₂ gate dielectric with a high bulk quality and a high Si/SiO₂ interface quality in order to improve their mobility^[1]. The quality of the bulk SiO₂ and Si/SiO₂ interface formed by thermal oxidation methods is better than that of SiO₂ deposited by chemical vapor deposition methods. However, high-temperature thermal oxidation cannot be applied to a glass substrate where flat-panel display devices are fabricated. It was reported that oxide film grown in high-density plasma has good electrical characteristics^[2,3]. Among high-density plasma systems, the inductively coupled plasma (ICP) system with a planar configuration, which has a simple structure and a low-aspect ratio (height/diameter), is consequently considered to be suitable for utilizing ICP oxidation for the low-temperature poly-Si TFT process.

Oxide growth kinetics by ICP oxidation at low temperatures can be described by the linear-parabolic growth law.^[4] The linear-rate constant of ICP oxidation is negative, unlike

high-temperature thermal oxidation. The reason for this can be understood by assuming that the ICP oxide consists of a surface layer with a larger diffusion coefficient and a bulk layer with a smaller diffusion coefficient. Therefore, the structure of ICP oxide grown at low temperatures might be different from that of thermal oxide grown at high temperatures. Insufficient attention has been focused on the understanding of the structural properties of plasma oxide grown at low temperatures. This paper's focus is on the structural properties of ICP oxides and the existence of a thin low-density surface layer on the top of a high-density bulk SiO₂ film.

2. EXPERIMENTAL

P-type Si wafers with a resistivity of 4 to 12 Ω · cm were oxidized in ICP oxygen plasma at a substrate temperature ranging from 350 °C to 450 °C in a 10 mTorr vacuum. The antenna in the ICP system was made of a 1/4-inch Cu tube, and it was cooled by water. The inner diameter of the antenna was 14.0 cm, and it was a single turn antenna. The RF power and frequency were 2 kW and 13.56 MHz, respectively. The substrate and holder were floated electrically, and no external bias was applied to them. Using a Langmuir probe and optical emission spectroscopy, the density of oxygen ions at 10 mTorr was found to be 3.1 × 10¹⁰ cm⁻³. The electron temperature and plasma potential at 10 mTorr were 5 eV and 22

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V, respectively. For comparison, ICP oxides were annealed at 900 °C for 1 h in N₂ and their structural properties were analyzed.

The peak wave numbers of the transverse optical (TO) mode associated with the asymmetric stretch of Si-O-Si bonds were measured using Fourier transform infrared spectroscopy (FTIR; Bruker, Equinox55) with a resolution of 4 cm⁻¹ and 20 scans. The thickness and refractive index were measured using an ellipsometer (Rudolph Research Auto EL2) at a wavelength of 632.8 nm, and they were calibrated using transmission electron microscopy (TEM). The Si 2p intensities in X-ray photoelectron spectra (XPS) were measured using a VG ESCA2000 with monochromatic Al K_α (1486.6 eV) radiation. The chemical etch rate of the oxide was measured using a p-etch solution (49% HF : 70% HNO₃ : H₂O = 3 : 2 : 100), and the density variation in the oxide layer was calculated using an X-ray reflectivity measurement (Rigaku, ATX).

3. RESULTS AND DISCUSSION

Figure 1 shows FTIR TO-mode vibration spectra of ICP oxides grown at 450 °C. The peak wave numbers of the 20- and 38-nm-thick as-grown oxides were 1064 cm⁻¹ and 1068 cm⁻¹, respectively. The peak wave number of the 20-nm-thick oxide was smaller than that of the 38-nm-thick oxide. The peak wave number of the 38-nm-thick oxide annealed at 900 °C for 1 h in N₂ is 1076 cm⁻¹, which was similar to that of the thermal oxide grown at 800 °C and annealed at 1050 °C^[5]. Note that the peak wave number of the as-grown ICP oxide was lower than that of the annealed oxide and smaller when the oxide thickness was thinner.

The oxygen deficiency may have been the cause of the lower peak wave number in the oxide grown in plasma-enhanced chemical vapor deposition (CVD)^[6]. Figure 2 shows the XPS spectra of the oxides grown by ICP oxida-

tion, thermal oxidation and chemical oxidation. If the oxidation state changed, the peak shifted to a lower binding energy. For example, the peak of the chemical oxide grown in a boiled H₂SO₄ + H₂O₂ solution for 1 h shifted to 103.2 eV because of the change in the oxidation state. However, the peaks in the ICP oxide and in the thermal oxide were located at the same binding energy of 104.1 eV and did not shift after annealing at 900 °C for 1 h, indicating that the oxidation states of Si in the as-grown oxide, annealed oxide and thermal oxide are the same. The oxygen deficiency, therefore, can be excluded for the cause of the lower peak wave number in the as-grown ICP oxide.

From the measured vibration wave number, ν , in the FTIR vibration spectra, the Si-O-Si bond angle, 2θ , can be obtained with the following relations^[7] of

$$\nu = \nu_0 \sin \theta, \quad (1)$$

where $\nu_0 = 1134 \text{ cm}^{-1}$. The measured vibration wave number decreased with the decreasing oxide thickness. Figure 3 shows the Si-O-Si bond angle as a function of the oxide thickness. The bond angle of the high-temperature thermal oxide was 143.8° with a wave number of 1078 cm⁻¹. The average 2θ of the annealed ICP oxides, which was 143.2° with an average peak number of 1075 cm⁻¹, was insensitive to the oxide thickness. Note that the 2θ of the as-grown thick oxide was approximately 141°, which is smaller than the annealed oxide. Also, note that the 2θ decreased as the oxide thickness decreased.

The bond-angle bandwidth, $2\Delta\theta$, has the following relation with the resonance bandwidth, $\Delta\nu$:^[7]

$$\Delta\theta = (\Delta\nu/\nu) \tan \theta. \quad (2)$$

The average $2\Delta\theta$ values of the as-grown and annealed oxides were $27.8^\circ \pm 1.9^\circ$ and $27.9^\circ \pm 1.2^\circ$, respectively. The as-grown oxide had an apparently smaller $2\Delta\theta$ than the

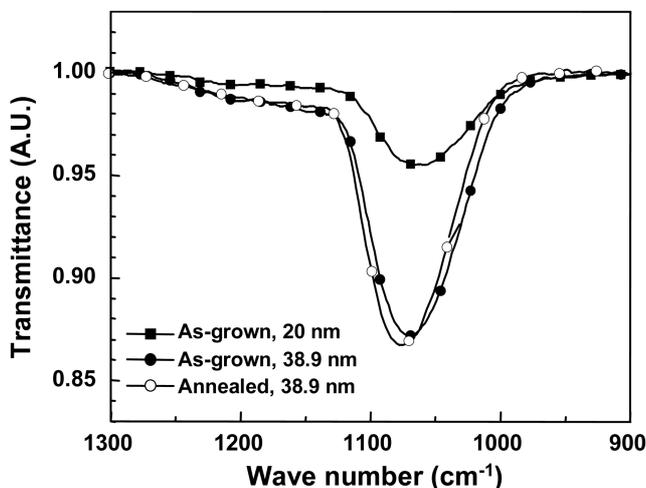


Fig. 1. FTIR spectra of as-grown and annealed ICP oxides.

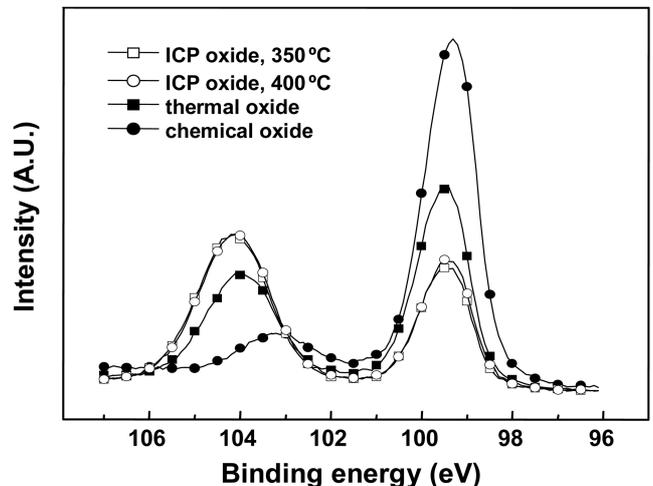


Fig. 2. X-ray photoelectron emission spectra of oxides grown by ICP oxidation, thermal oxidation and chemical oxidation.

annealed oxides even though the data was scattered. However, the $\Delta\theta/\theta$ ratio of the annealed oxide was smaller than that of as-grown oxides, suggesting that the bond angle in the annealed oxide is more reproducible. The calculated $2\Delta\theta$ values are similar to those of oxides prepared by remote plasma CVD^[7].

The decrease of the bond angle in the ICP oxides can be explained while considering the accumulation and relaxation of the compressive strain within the oxide. In the high-temperature thermal oxidation, although the compressively strained oxide (high density) grows at the SiO₂/Si interface due to volume expansion, the oxide relaxes as a result of the viscoelastic flow of the oxide perpendicular to its surface.^[8,9] The slow relaxation of the density and refractive index on the oxide grown at 900 °C is well explained by the viscoelastic flow^[10,11]. In the ICP oxidation, however, no significant viscoelastic flow is expected because its oxidation temperature is relatively low (450 °C). For the thin oxide, the oxidation rate is fast and a compressive strain is built-up in the oxide, resulting in the increase of density and the decrease of the Si-O-Si bond angle. For the thick oxide, the oxidation time is longer as a result of the parabolic growth relation,^[4] and the compressive strain can be more relaxed. Therefore, the as-grown ICP oxide was expected to have a higher density and a smaller Si-O-Si bond angle. In particular, the bond angle is expected to decrease as the oxide thickness decreases because there is less relaxation. In our experiment the thickness of the as-grown oxide was 38.9 nm, and the thickness increased by 4% after annealing at 900 °C for 1 h in N₂. The relaxation of the compressive strain could be indirectly explained by the increase in the oxide thickness.

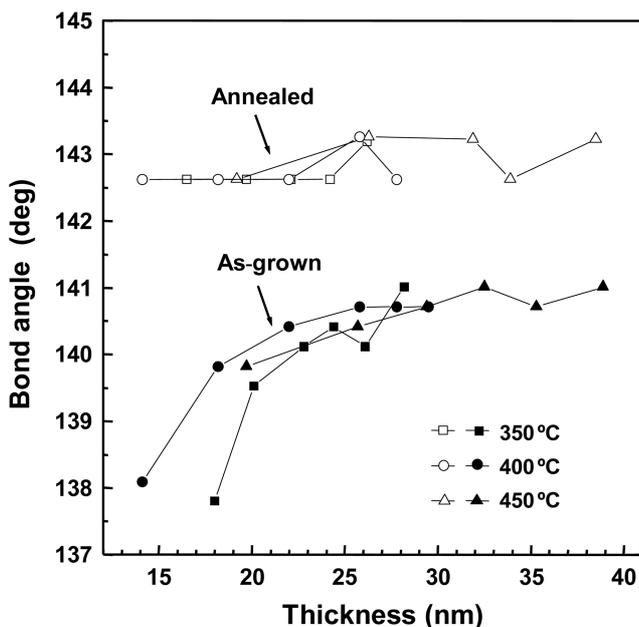


Fig. 3. Si-O-Si bond angle versus oxide thickness of the as-grown and annealed oxides.

Specular reflectivity measurements of intense X-ray beams provided us with information regarding the density profile of a thin film perpendicular to the surface^[12,13]. The X-ray reflectivity of the sample with thin films was approximated using the Born approximation, in which reflectivity is essentially a Fourier transform of the spatial derivative of the sample density in the perpendicular direction averaged over lateral directions^[14,15]. For the X-ray reflectivity measurement, a rotating Cu anode source was used and the $K_{\beta 1}$ radiation ($\lambda = 0.1392$ nm) was selected using a monochromator. The interface was approximated with a Gaussian distribution. The reflectivity of the thermal oxide grown by rapid thermal oxidation at 900 °C was also measured for comparison.

Figure 4 shows the X-ray reflectivity curves as a function of the wave vector normal to the surface of the as-grown ICP oxide at 400 °C, as well as to the surface of the thermal oxide grown by rapid thermal oxidation at 900 °C. The reflectivity curves are not fitted with a single layer simulation. The curves of the ICP oxide and thermal oxide are well fitted with a double layer simulation. For the ICP oxide with a thickness of 11.5 nm, the surface layer (1.2 nm) had a lower density (2.05 g/cm³) and the bulk layer (10.5 nm) had a higher density (2.33 g/cm³). For a thermal oxide with a thickness of 16.2 nm, the surface layer (3.2 nm) had a higher density (2.28 g/cm³) and the bulk layer (13.0 nm) had a lower density (2.20 g/cm³). The fitted parameters are summarized in Table 1. The density of the bulk ICP oxide was expected to be higher than the density of the bulk thermal oxide because ICP oxide grown at low temperatures is more compressively strained. However, a thin surface layer with a low density of 2.05 g/cm³ was detected in the analysis. The

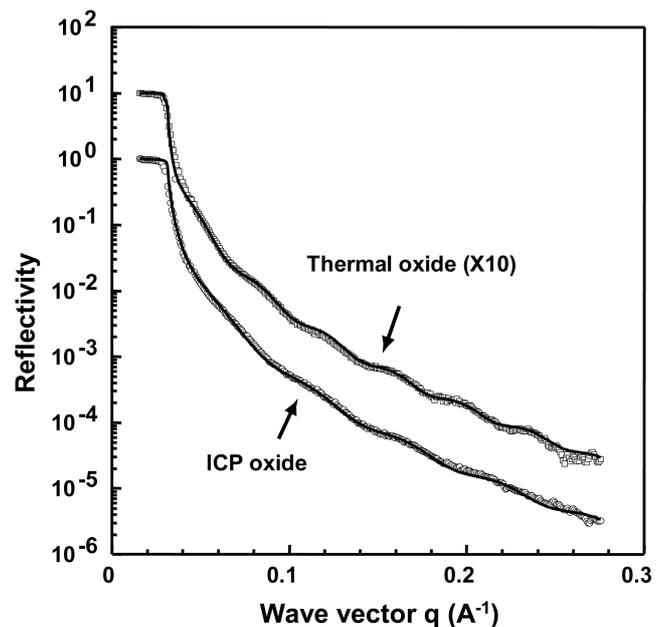
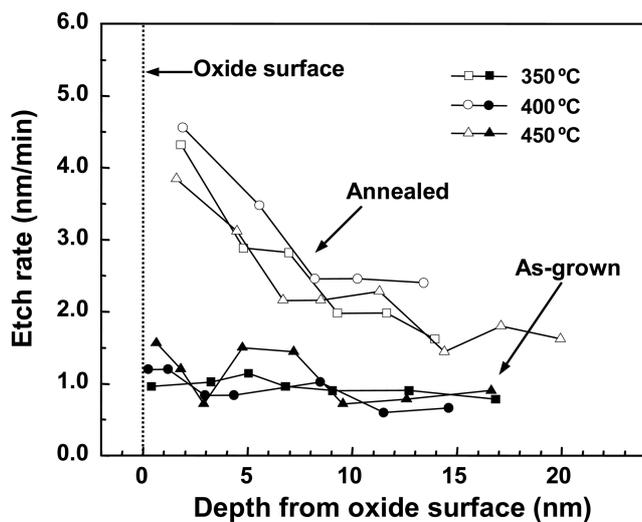


Fig. 4. X-ray reflectivity curves of the as-grown ICP oxide and thermal oxide as a function of the wave vector normal to the surface.

Table 1. Fitted parameters of the X-ray reflectivity curves in Fig. 4. The thermal oxide was grown by a rapid thermal oxidation at 900 °C and the ICP oxide was grown at 400 °C.

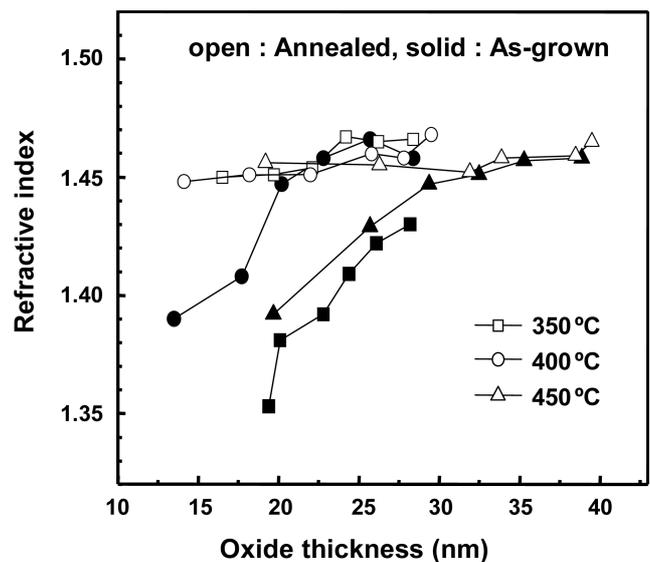
Oxide type	Oxide layer	Thickness (nm)	Density (g/cm ³)	Roughness (nm)
Thermal oxide	Surface layer	3.2	2.28	0.50
	Bulk layer	13.0	2.20	1.00
	Si/SiO ₂ interface			0.50
ICP oxide	Surface layer	1.2	2.05	0.35
	Bulk layer	10.5	2.23	0.50
	Si/SiO ₂ interface			0.35

**Fig. 5.** Etch rate of the as-grown and annealed ICP oxide as a function of the depth from the original surface.

possible cause of this low density, which is as yet undetermined, will be discussed in the last paragraph of this section.

The bending of Si-O-Si bonds by the compressive strain during oxidation may affect the chemical and physical properties of the oxides. Pai *et al.* reported that the etch rate of oxide by a p-etch solution is sensitive to density and Si-O bond distortion^[6]. The p-etch solution was employed for the measurement of the etch rate of the ICP oxide. The starting thickness of the oxide was in the range of 35 to 45 nm. The etch rate was calculated by measuring the remaining oxide thickness after etching the oxide for a fixed time and repeating the experiment until the oxide thickness could not be measured.

Figure 5 shows the etch rate as a function of the depth from the original surfaces of the as-grown oxide and the annealed ICP oxide. The overall trend is very similar to that of the change in the Si-O-Si bond angle, although conversely so. Even though the bulk densities of the as-grown oxide and annealed oxide were expected to be similar, as noted in the previous paragraph, the etch rate of the bulk oxides was quite different. The etch rate deep inside the as-grown oxide was about 1.7 nm/min, while that of the annealed oxide at 900 °C for 1 h in N₂ was about 0.8 nm. This result indicates

**Fig. 6.** Refractive index of as-grown and annealed ICP oxides as a function of the oxide thickness

that the Si-O-Si bond angle, instead of density, dominates the chemical property of the ICP oxide. In other words, the Si-O-Si bond's bending caused by the compressive stress strongly enhances the etch rate. The etch rate is increased as the thickness of the as-grown oxide decreases due to the smaller Si-O-Si bond angle. Since the smaller bond is caused by the increase in compressive stress, compressive stress seems to play a major role in determining the fast etch rate in the thin ICP oxide.

Figure 6 shows the refractive index of the ICP oxides as a function of oxide thickness. Both the thick as-grown oxides and all the annealed oxides had a refractive index of about 1.460, which is the refractive index of fully relaxed thermal SiO₂^[10]. On the other hand, the refractive index of the thin as-grown oxide decreased as the thickness of the as-grown ICP oxide decreased. The trend of the refractive-index change is similar to that of the Si-O-Si bond-angle change.

The factors that affect the refractive index are the polarizability of the atoms in the film and the density of the film. In insulating materials the refractive index is the square root of the dielectric constant, which is an indication of the degree

of polarizability. Since the refractive index trend is similar to the change in the bond angle, the polarizability that depends on the structure seems to play a major role in determining the refractive index.

The SiO₂ structure with a smaller Si-O-Si bond angle in the as-grown oxides was more difficult to vibrate or polarize by the electric field of light because the oxide layer was compressively strained. However, the same refractive index for the thick as-grown oxide and the annealed oxide showed that the higher density in the as-grown oxide also played a role in determining the refractive index. In Fig. 6, the refractive index of the as-grown oxide decreased with the decreasing oxide thickness because of the smaller polarizability. However, the value shifted to a higher value because of the larger density of the as-grown oxides.

In our experiment, we found that chemical properties such as the etch rate and physical properties such as the refractive index are critically dependent on the Si-O-Si bond angle caused by compressive stress. Finding a surface oxide layer that had a lower density on the ICP bulk oxide was another important result in our analysis. The clue to the existence of the surface layer was reported during an oxidation kinetics study where the surface layer had a very high diffusion coefficient of oxygen^[4]. The cause of the formation of the surface oxide layer in the ICP oxidation is unknown. Surface damage by plasma during the oxidation process may be a factor^[16]. However, no shift in the TO-mode vibration wave number was observed when the ICP oxidation was performed with an Si wafer covered with a chemical oxide approximately 1 or 2 nm thick^[4]. In this case, no such surface layer effect was monitored in the oxidation kinetics study^[4]. The plasma damage effect, therefore, can be excluded.

We reported that hydrogen was incorporated into the poly-Si film even though the plasma was generated with O₂ gas^[3]. The hydrogen may have induced the formation of the surface layer in the ICP oxide. Hydrogensilsesquioxanes (HSQ, HSiO_{1.5}) are siloxane-based polymers in which oxygen and hydrogen are directly attached to silicon atoms. HSQ has been extensively studied for use in integrated-circuit applications because of its low dielectric constant. The theoretical density of fully dense HSQ is comparable to the density of a-SiO₂ (2.2 g/cm³). Nevertheless, SQ shows a lower density due to the open volume at the center of the cage-like molecular structure^[17], with a porosity in the range of 28% to 43%^[18]. With curing above 500 °C, hydrogen evolves and properties similar to a-SiO₂ are produced^[18]. The presence of hydrogen in the plasma during oxidation may make the formation of a lower density HSQ possible at the initial stage of oxidation.

4. CONCLUSIONS

The SiO₂ films oxidized in ICP plasma at a temperature

range of 350 °C to 450 °C showed the following properties: The thickness of the oxide under study ranged from 10 to 40 nm. The Si-O-Si bond angle was smaller in the ICP oxide than in the high-temperature thermal oxide. The bond angle decreased as the oxide thickness decreased. The X-ray reflectivity analysis was best fitted with a bilayer assumption and the density of the ICP oxide (2.23 g/cm³) was larger than that of the thermal oxide (2.20 g/cm³). An accumulation of compressive stress may have caused the smaller bond angle and the higher density in the ICP oxide. A very thin surface layer with a low density was detected on the as-grown ICP oxide; the density and thickness of the surface layer grown at 400 °C were 2.05 g/cm³ and 1.2 nm, respectively. The ICP oxide showed a high etch rate and a low refractive index as the oxide thickness decreased, suggesting that these chemical and physical properties were strongly affected by the magnitude of the Si-O-Si bond angle.

ACKNOWLEDGMENT

This work was supported by the Korean Science and Engineering Foundation.

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