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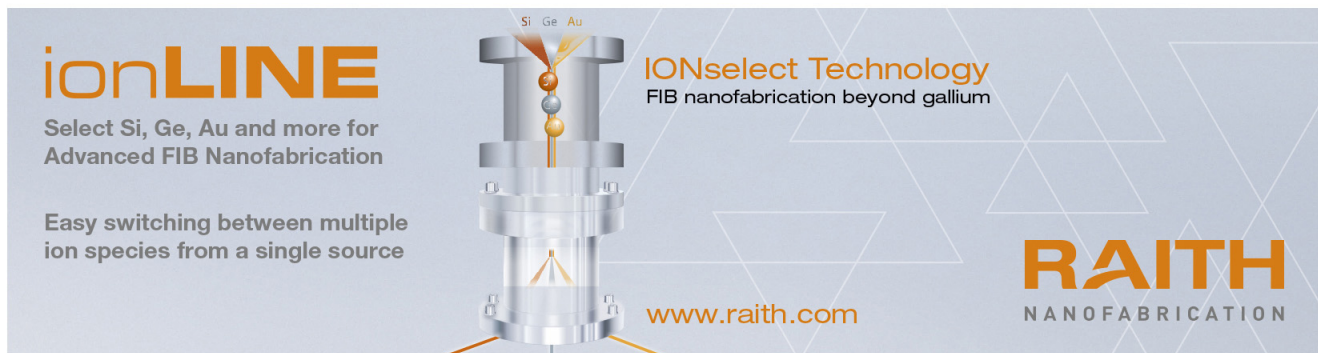
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# Characterization of the Si/SiO<sub>2</sub> interface formed by remote plasma enhanced chemical vapor deposition from SiH<sub>4</sub>/N<sub>2</sub>O with or without chlorine addition

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The Si/SiO<sub>2</sub> interface formed by remote plasma enhanced chemical vapor deposition (RPECVD) at low temperature with SiH<sub>4</sub>/N<sub>2</sub>O or SiH<sub>4</sub>/N<sub>2</sub>O/Cl<sub>2</sub> was studied and compared with thermal oxidation. The interface of the CVD SiO<sub>2</sub> without chlorine addition is rougher than that with chlorine addition. But the surface roughness of CVD SiO<sub>2</sub> films increases with chlorine addition. The thermal oxidation induces strong interface strains, and the strains generated by the CVD SiO<sub>2</sub> without chlorine addition are stronger and are distributed more nonuniformly than those by the chlorinated SiO<sub>2</sub>. It is believed that chlorine addition during RPECVD affects the initial stages of deposition, and chlorine is combined with Si dangling bonds existing at the Si/SiO<sub>2</sub> interface through the formation of Si-Cl<sub>x</sub> bonds. It was also found that with chlorine addition during RPECVD, the strained layer thickness, interface trap density, and suboxide density could be lowered significantly.

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## I. INTRODUCTION

The Si/SiO<sub>2</sub> interface plays a crucial role in microelectronic devices and has been the subject of intense study for over 40 years. During the past decade, remote plasma enhanced chemical vapor deposition (RPECVD) has emerged as a viable technique for depositing SiO<sub>2</sub>.<sup>1,2</sup> Many applications of SiO<sub>2</sub> films require low temperature processing. For example, in active matrix liquid crystal display (AMLCD) applications, low temperature deposition of SiO<sub>2</sub> films is required to utilize low cost glass substrates.

The incorporation of halogen compounds during thermal oxidation of Si results in a significant improvement in the electronic properties of the oxide and the interface formed with underlying Si.<sup>3-10</sup> However, for high halogen concentration and high temperature, a volatile phase begins to form at the interface, which may lift the oxide from the silicon, form bubbles, etch the silicon substrate, and increase the interface roughness.<sup>11</sup> Therefore, the determination of an appropriate amount of halogen compounds is important to optimize an oxidation window.

The effect of the addition of halogen compounds on the Si/SiO<sub>2</sub> interface and bulk properties in the PECVD process of SiO<sub>2</sub> film deposited at low temperature below 500 °C is still, to a large extent, unknown. Recently, Falcony and co-workers have reported on SiO<sub>2</sub> films deposited using a halogen chemistry, i.e., SiF<sub>4</sub>/H<sub>2</sub>/N<sub>2</sub>O, SiF<sub>4</sub>/SiH<sub>4</sub>/N<sub>2</sub>O, and SiCl<sub>4</sub>/O<sub>2</sub>, in order to reduce the incorporation of Si-H and Si-OH bonds and improve the breakdown field.<sup>12,13</sup> They could effectively decrease a significant amount of these

bonds and improve the breakdown field up to 4-6 MV/cm.

In the present article, the interface between the Si substrate and the SiO<sub>2</sub> film obtained by RPECVD at low temperature with SiH<sub>4</sub>/N<sub>2</sub>O and SiH<sub>4</sub>/N<sub>2</sub>O/Cl<sub>2</sub> was studied using transmission electron microscopy (TEM), high frequency (1 MHz) capacitance-voltage (C-V) measurement, x-ray photoelectron spectroscopy (XPS), and electron spin resonance (ESR). The surface and interface roughness and morphology of deposited oxide films were observed by atomic force microscopy (AFM). For comparison, the Si/SiO<sub>2</sub> interface obtained by thermal oxidation was also studied.

## II. EXPERIMENTAL PROCEDURE

### A. Film preparation

The deposition of SiO<sub>2</sub> on Si was performed in a RPECVD reactor as shown in Fig. 1. N<sub>2</sub>O (99.999% pure) was introduced into a quartz tube, excited by the induction with 13.56 MHz RF power to produce activated oxygen, and flowed into the deposition zone. SiH<sub>4</sub> (99.99% pure) mixed with Ar (99.9999% pure) diluent was introduced into the region 10 cm downstream of the plasma, through the gas dispersal ring. This then mixed with the excited oxygen species and flowed toward the substrate, 20 cm downstream of the plasma. Cl<sub>2</sub> (99.99% pure) in Ar diluent was also introduced into the region, 12 cm downstream of the plasma. Commercially supplied 10-20 Ω cm *p*-type Si wafers of (111) orientation were used as substrates. The modified RCA method, (i) dipping in H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>=3:1 solution for 10 min and deionized (DI) water rinse, (ii) dipping in HF:H<sub>2</sub>O=1:7 solution for 30 s and DI water rinse, was used for the predeposition cleaning. After the substrate was loaded in the reaction chamber, it was baked for 30 min to eliminate moisture from the wet cleaning. Thermal oxidation was carried out at 1000 °C in a furnace using ultrahigh-purity oxygen. Deposi-

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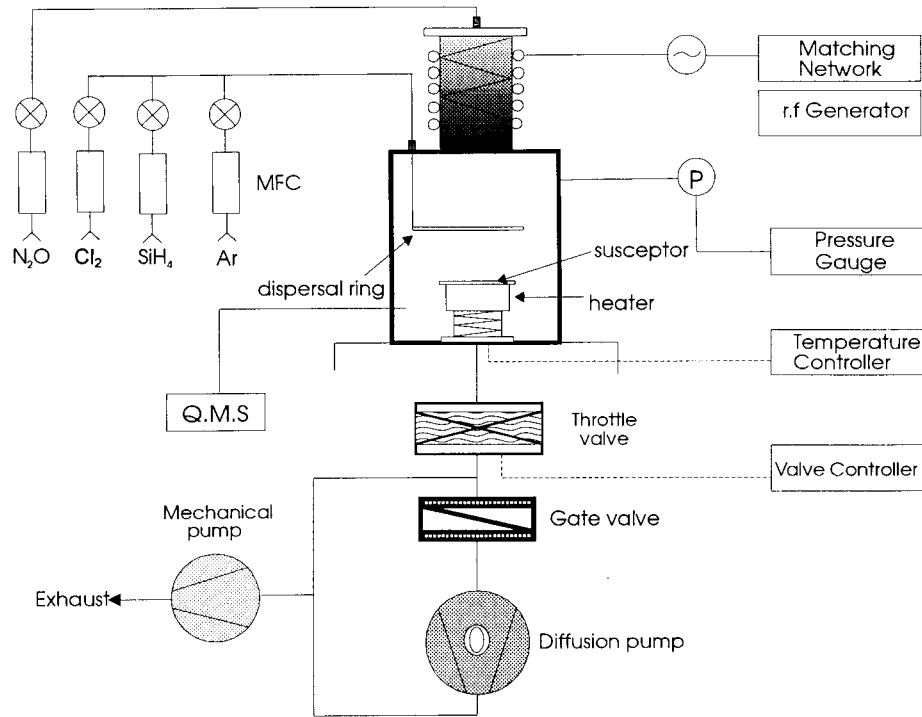


FIG. 1. Schematic diagram of the RPECVD system.

tion was performed at 250–300 °C. The amount of Cl<sub>2</sub> addition was 0 and 10 vol % of total gas flow. The total gas flow rate including Ar was 100 sccm, the N<sub>2</sub>O flow rate was 12 sccm, and the SiH<sub>4</sub> flow rate was 3 sccm. The reactor pressure was 400 mTorr and the plasma power was 50 W.

### B. Film characterization

The oxide thickness and refractive index were measured with an ellipsometer (NIIC EL-101A). As for the AFM observation of the Si/SiO<sub>2</sub> interface, optimization of the oxide stripping condition is essentially required. We used the HF-dipping method and showed the interfacial morphology in a three-dimensional real space. The chemical etch of the oxide

film was performed in the buffered HF solution (49% HF:H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH=1:10:110) at room temperature.<sup>14</sup> The replica of the Si/SiO<sub>2</sub> interface may be preserved by such a treatment, because bare Si was not attacked by the diluted HF-based solution. After the HF dipping, the substrates were rinsed in DI water for 4 min and dried by blowing with dry N<sub>2</sub> gas. It is thought that the Si dangling bonds on the surface are terminated by hydrogen, which prevents surface reoxidation in air and damage of the original Si/SiO<sub>2</sub> interface morphology.

Cross-sectional specimens for TEM were first glued face to face, cut, then ground, dimpled, and thinned by ion milling. TEM observations were conducted using JEOL JEM-

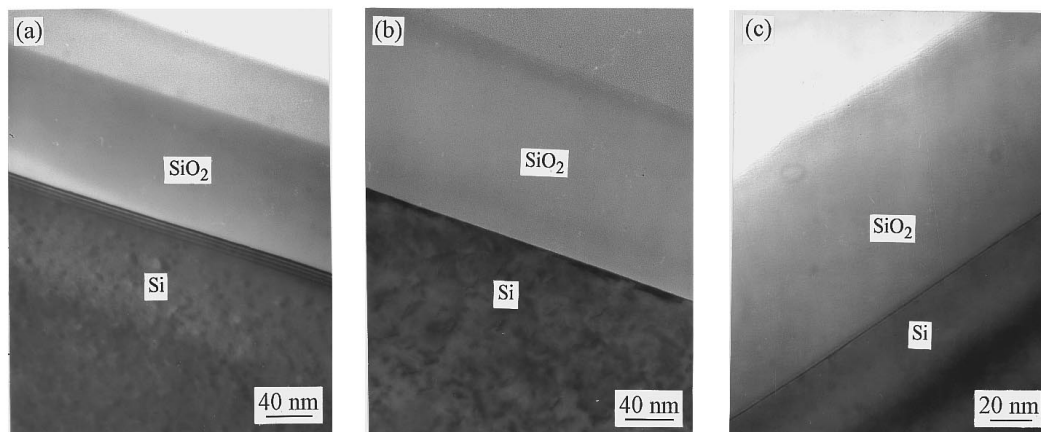


FIG. 2. TEM images of the Si/SiO<sub>2</sub> interface including the interface formed by (a) thermal oxidation, (b) CVD without chlorine, and (c) CVD with chlorine addition (6 vol %). PECVD oxides were deposited at the temperature of 300 °C with SiH<sub>4</sub>:N<sub>2</sub>O=3:12 sccm. The pressure was 0.4 Torr.

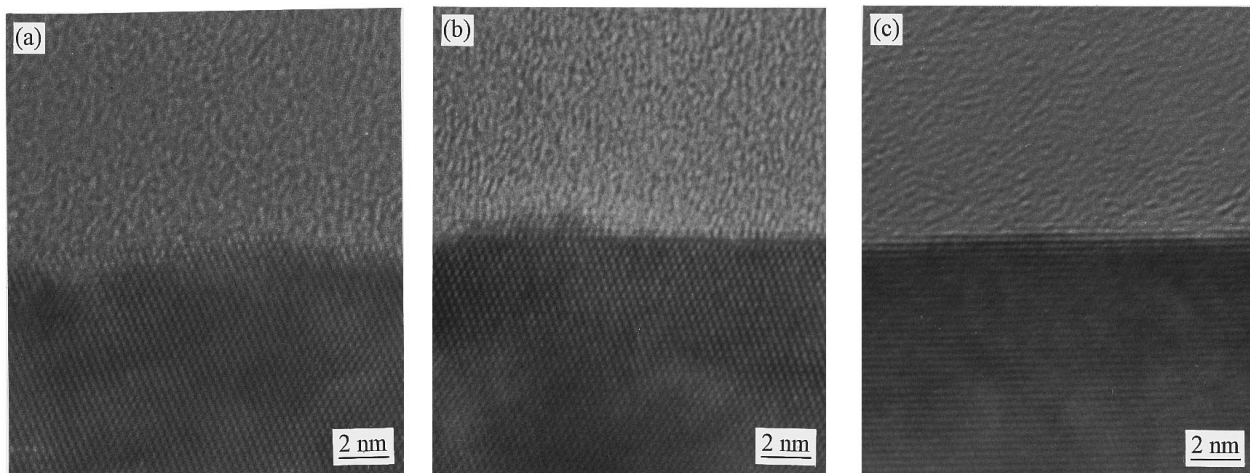


FIG. 3. High resolution TEM lattice images of the Si/SiO<sub>2</sub> interface formed by (a) thermal oxidation, (b) CVD without chlorine, and (c) CVD with chlorine addition (6 vol %). PECVD oxides were deposited at a temperature of 300 °C with SiH<sub>4</sub>:N<sub>2</sub>O=3:12 sccm. The pressure was 0.4 Torr.

4000FX transmission electron microscope operating at 400 kV. The surface roughness of the SiO<sub>2</sub> film was measured by AFM using a Park Science Instrument (PSI) Autoprobe-CP. The photoelectrons were detected using a Perkin Elmer PHI 5400 XPS with Al K $\alpha$  radiation. The photoelectrons were collected by hemispherical analyzer at a 45° take-off angle. Sputtering for the depth profile was performed at 3.5 kV with Ar ions. Si 2*p* core levels were measured and analyzed using a least-square curve-fitting method. The paramagnetic defects were examined by electron spin resonance using a Bruker ER 200D X-band (microwave frequency: 9.45 GHz) spectrometer at room temperature.

For electrical characterization, metal–oxide–semiconductor (MOS) capacitors were fabricated with deposited oxides. The aluminum dot electrode, 0.05 cm in diameter, was deposited by thermal evaporation through a metallic mask. The *C–V* characteristics were analyzed at high frequency (1 MHz) using a Hewlett–Packard 4275 multifrequency LCR meter with a sweep voltage range of +10 to –10 V. The flat band voltage and the concentration of oxide fixed charges were obtained from the high frequency *C–V* data. The interface trap density at the Si/SiO<sub>2</sub> interface was also obtained from the *C–V* data using the Terman method.<sup>15</sup>

### III. RESULTS AND DISCUSSION

Figure 2 shows the TEM images of the Si/SiO<sub>2</sub> interface formed by thermal oxidation and chemical vapor deposition (CVD) from SiH<sub>4</sub>/N<sub>2</sub>O and SiH<sub>4</sub>/N<sub>2</sub>O/Cl<sub>2</sub>. Sections with homogenous oxide thickness were obtained with these three samples. The thickness of the SiO<sub>2</sub> sample was found to be about 96, 140, and 100 nm, respectively. The pattern of thickness fringes was observed in the Si substrate below the oxide in these three samples, indicating oxide-induced strains in the lattice.<sup>16</sup> For the thermally oxidized sample, three straight fringes with clear contrast exist in the depth range from the surface of the Si substrate to a depth about 12 nm, whereas only one fringe with poor contrast was ob-

served for the SiO<sub>2</sub> samples by CVD with and without chlorine. This indicates that the thermal oxidation induces strong interface strains. The fringe in the SiO<sub>2</sub> sample with chlorine addition is thicker and more nonuniform than that in the

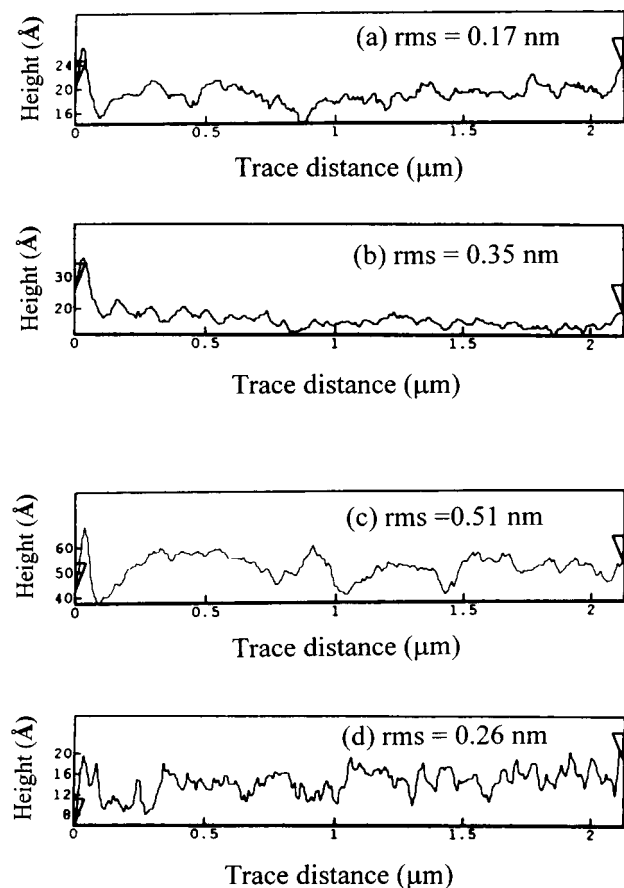


FIG. 4. Two-dimensional line scanning of AFM on the Si surface after stripping SiO<sub>2</sub>: (a) bare Si, (b) thermal oxidation, (c) CVD without chlorine, and (d) CVD with chlorine addition (6 vol %). PECVD oxides were deposited at a temperature of 300 °C with SiH<sub>4</sub>:N<sub>2</sub>O=3:12 sccm. The pressure was 0.4 Torr.

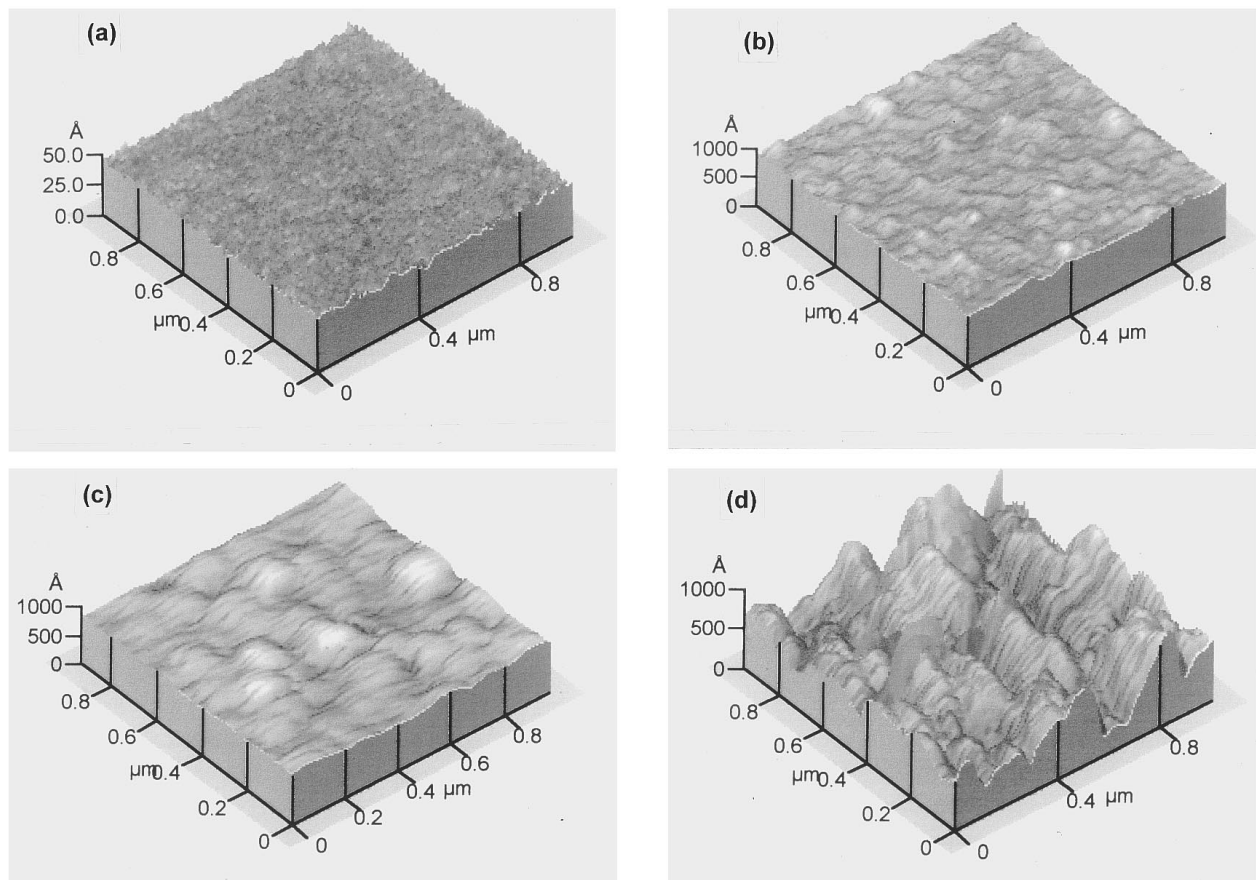


FIG. 5. Three-dimensional AFM for the deposited SiO<sub>2</sub> surfaces from (a) thermal oxidation, (b) CVD without chlorine, (c) CVD with chlorine addition (6 vol %), and (d) CVD with chlorine addition (10 vol %). PECVD oxides were deposited at a temperature of 250 °C with SiH<sub>4</sub>:N<sub>2</sub>O=3:12 sccm. The pressure was 0.4 Torr.

sample without chlorine addition, indicating that the strains generated by the chlorine-free CVD SiO<sub>2</sub> are stronger and are distributed more nonuniformly than those by the chlorine-added CVD SiO<sub>2</sub>.

Figure 3 shows the high resolution TEM lattice images of the Si/SiO<sub>2</sub> interface formed by thermal oxidation and chemical vapor deposition from SiH<sub>4</sub>/N<sub>2</sub>O and SiH<sub>4</sub>/N<sub>2</sub>O/Cl<sub>2</sub>. Taking the largest protrusion or step height observed in a sample as a measure of the Si/SiO<sub>2</sub> interface roughness, one sees that the interface roughnesses of the thermally oxidized, chlorine-free, and chlorine-added CVD SiO<sub>2</sub> samples are about 1, 0.67, and 0.33 nm, respectively. For the thermal oxidation, it has been reported that the interface roughness results from protrusions of Si into the SiO<sub>2</sub> rather than oxidized valleys in the silicon surface.<sup>17</sup> This is suggestive of locally retarded oxidation rather than a local acceleration of the reaction rate. The interface protrusions lead directly to a variation in oxide thickness. The local thickness variation is indicative of nonuniform oxidation.

Compared with thermal oxidation, RPECVD affects the underlying substrate much less.<sup>18</sup> It is obvious that Cl<sub>2</sub> addition decreases interface roughness [Fig. 3(c)]. Lattice strain fields in Si near the interface were observed in these three samples. The lattice strain field in the thermally oxidized

sample is more irregular than those in the CVD SiO<sub>2</sub> samples. The strain field in the RPECVD sample with chlorine addition is weaker than that in the chlorine-free CVD SiO<sub>2</sub> sample. It seems that the Cl<sub>2</sub> addition can relax the interface strain by breaking the strained SiO<sub>2</sub> ring structure. Beyond the Si/SiO<sub>2</sub> interface roughness, there were no apparent structural defects or irregularities associated with the thin oxide films. We did not observe any evidence of Si inclusions in the SiO<sub>2</sub>, amorphous oxide regions in the near interface Si, crystalline patches of oxide, metallic or other precipitates, or oxide pinholes. In thermal oxidation, Si is consumed to generate the oxide film, so that the Si/SiO<sub>2</sub> interface is located in the bulk of the Si, below the original Si surface. Similarly, the Si/SiO<sub>2</sub> interface deposited by remote PECVD is also formed by a subcutaneous oxidation of Si substrate that occurs at the initial stage of the film deposition.<sup>19,20</sup> This generates unwanted interfacial oxide thickness of 0.5–1 nm. At deposition temperatures above 300 °C and deposited oxide thicknesses above 25 nm, the amount of subcutaneous oxidation increased significantly, and the electronic quality of these interface rapidly degraded. The mechanism for defect generation may be related to a buildup of stress in the subcutaneous layer. This stress derives from a molar volume mismatch between Si and SiO<sub>2</sub>

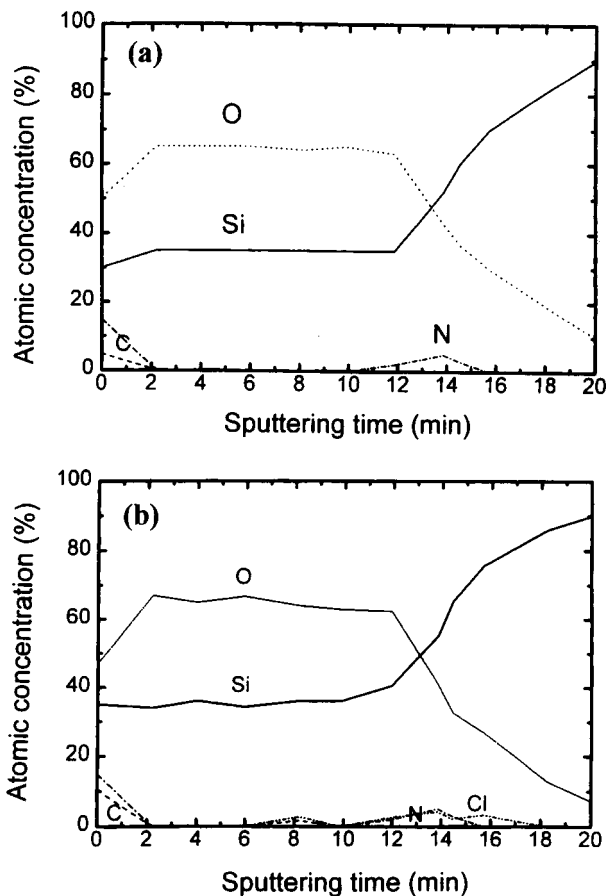


FIG. 6. XPS depth profile of chlorinated SiO<sub>2</sub> samples: (a) CVD without chlorine and (b) CVD with chlorine addition (6 vol %). PECVD oxides were deposited at a temperature of 300 °C with SiH<sub>4</sub>:N<sub>2</sub>O=3:12 sccm. The pressure was 0.4 Torr.

and cannot be relieved through a viscoelastic relaxation process at low temperatures in this RPECVD process. However, when chlorine was added into this RPECVD process gases, chlorine can strongly adsorb to an initial Si surface and prevent further subcutaneous oxidation from active oxygen species generated by remote plasma. It is believed that chlorine addition improves the surface states by reducing surface roughness and interface trap density.

Figure 4 shows two-dimensional line scanning for the Si/SiO<sub>2</sub> interface using AFM after the oxide film was removed. Compared with bare Si (rms=0.17 nm) after HF dipping, the rms values of surface roughness are 0.35 nm for thermal oxidation and 0.51 and 0.26 nm for CVD without and with chlorine addition, respectively. The AFM result for the Si/SiO<sub>2</sub> interface roughness gives us a better guide because high resolution TEM is focused only on a very small spot. CVD with chlorine addition has the lowest interfacial roughness. The roughness at the interface reduces the mobility of charge carriers in MOS-based devices, and a local field enhancement across the oxide lowers the oxide breakdown field strength. Interface states and also protrusions or hillocks can act as electron emitters, thus reducing the positive charge centers near the interface.<sup>21</sup>

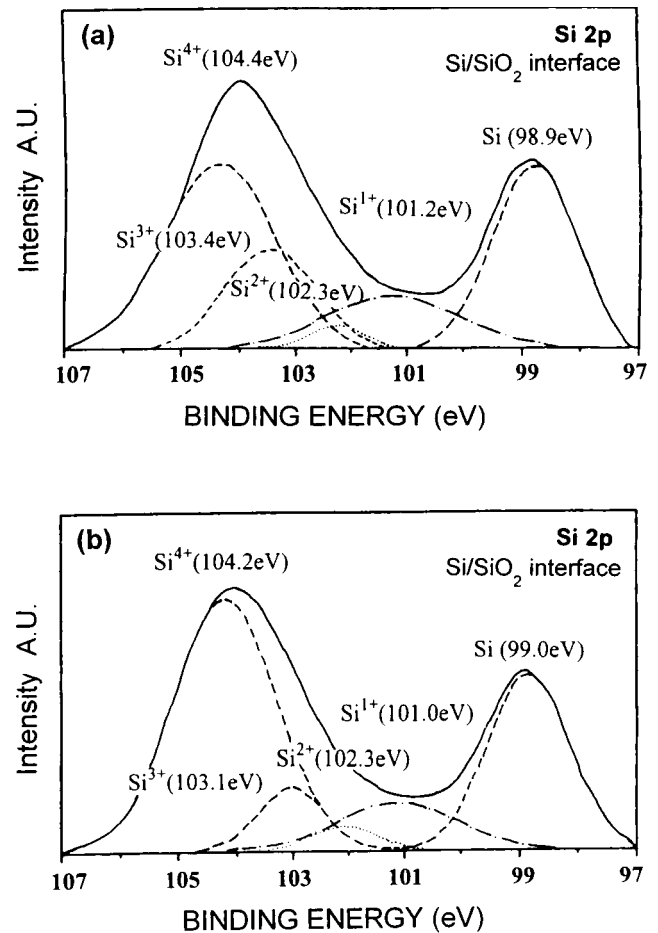


FIG. 7. XPS curve fitting for the Si 2p core level: (a) CVD without chlorine and (b) CVD with chlorine addition (2 vol %). PECVD oxides were deposited at a temperature of 300 °C with SiH<sub>4</sub>:N<sub>2</sub>O=3:12 sccm. The pressure was 0.4 Torr.

Figure 5 shows three-dimensional (3D) AFM images of CVD oxide surface with chlorine addition. It can be seen that the oxide surface roughness was dependent on the amount of chlorine addition and the deposition temperature. The rms values of surface roughness for thermal oxide and CVD SiO<sub>2</sub> without chlorine addition were 0.2 and 1.6 nm, respectively. When the chlorine was added, the rms value was increased from 3.1 nm (2 vol % addition) to 4.2 nm (6 vol % addition) at a deposition temperature of 300 °C. The rms value was 15.2 nm with 10 vol % addition. Surface roughening was mainly due to the surface desorption of halide groups such as Si-Cl<sub>x</sub> and O-Cl.

Figure 6 shows the XPS depth profile with Ar ion sputtering. With chlorine addition, about 5 at. % chlorine atoms, irrespective of the amount of chlorine addition, piles up at the Si/SiO<sub>2</sub> interface. It is believed that chlorine addition affects the initial stages of deposition, i.e., neutralizes the Si dangling bonds through the formation of Si-Cl bonds. The substitution of the stronger Si-Cl bonds for the weak Si-O bonds can relax the strains at the Si/SiO<sub>2</sub> interface. The film stoichiometry, defined by the O/Si ratio, was still lower than 2, and there is no detectable chlorine in the bulk oxide. It

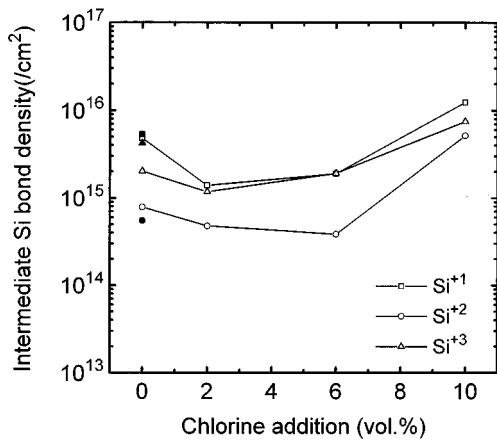


FIG. 8. The density of various intermediate Si states as a function of chlorine addition. The closed symbols represent the thermal oxide. PECVD oxides were deposited at a temperature of 300 °C with SiH<sub>4</sub>:N<sub>2</sub>O=3:12 sccm. The pressure was 0.4 Torr.

seems that the chlorine in the bulk oxide etches out the SiO<sub>2</sub> ring structure and desorbs out.

Figure 7 shows Si 2*p* spectra at the interface for CVD SiO<sub>2</sub> without and with chlorine addition. Si 2*p* peaks at the Si/SiO<sub>2</sub> interface show the chemical binding state of Si at the Si/SiO<sub>2</sub> interface at various deposition conditions. As mentioned in the TEM result, the transition (strained and mismatched) layer consisted of nonbonded silicon in a nonstoichiometric oxide and chloride with intermediate oxidation states, i.e., Si<sup>1+</sup>, Si<sup>2+</sup>, and Si<sup>3+</sup>. The Si 2*p* peak was deconvoluted into intermediate oxidation states, which determine the microscopic oxide interface properties such as interface trap density.<sup>22</sup> The silicon–chlorine bond is located at 100.15 eV for Si–Cl, 101.22 eV for Si–Cl<sub>2</sub>, and 102.34 eV for Si–Cl<sub>3</sub>, respectively,<sup>23</sup> but no attempt is made to deconvolute silicon suboxides and subchlorides.

Figure 8 shows the intermediate Si bond density obtained by XPS based on the well established method of calculating the suboxide density,  $N_{\text{SiO}_x}$ ,<sup>24</sup>

$$N_{\text{SiO}_x} = n_{\text{Si}} \lambda_{\text{Si}} \frac{I^{+x}}{I^0} \frac{\sigma_{\text{Si}}}{\sigma_{\text{SiO}_x}} \sin(\theta), \quad (1)$$

where  $n_{\text{Si}}$  ( $5.0 \times 10^{22} \text{ cm}^{-3}$ ) is the atomic density of silicon,  $\lambda_{\text{Si}}$  (0.33 nm) is the photoelectron mean free path in silicon,<sup>25</sup>  $I$  is the integrated peak intensity of the suboxide or the bulk silicon,  $\theta$  (45°) is the photoelectron take-off angle,  $\sigma$  is the photoionization cross section ( $\sigma_{\text{SiO}_x}/\sigma_{\text{Si}} = 1.0, 1.1, \text{ and } 1.7$  for Si<sup>1+</sup>, Si<sup>2+</sup>, and Si<sup>3+</sup>, respectively).<sup>25</sup> The calculated values for the intermediate densities may not be absolute but are useful in showing relative changes as a function of deposition parameter. For the Si/SiO<sub>2</sub>-based devices, properties of interfaces will certainly be affected by the microscopic structure at the Si/SiO<sub>2</sub> interface. With increasing chlorine addition, the intermediate silicon bond density is decreased compared with the thermal oxide and the CVD oxide without chlorine addition. The decrease of the intermediate silicon bond density means that chlorine at the interface reduces the

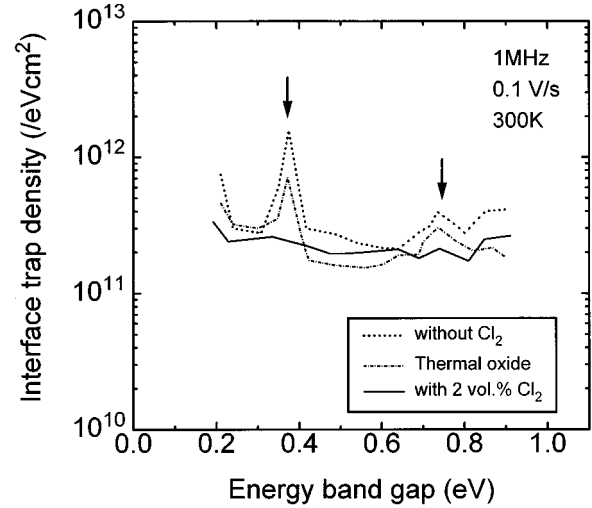


FIG. 9. Interface trap density distributions in the Si energy band gap: (---) thermal oxidation, (···) CVD without chlorine, and (—) CVD with chlorine addition (2 vol %). PECVD oxides were deposited at a temperature of 300 °C with SiH<sub>4</sub>:N<sub>2</sub>O=3:12 sccm. The pressure was 0.4 Torr.

mismatched suboxide density. At high chlorine partial pressure, however, the intermediate silicon bond density increased because the etching process dominantly occurs in competition with deposition as shown in the AFM image [Fig. 5(d)]. It shows that the deposited SiO<sub>2</sub> film surface is also roughened due to the desorption of halide group. Therefore it is possible that too much chlorine addition in the SiO<sub>2</sub> deposition process may cause the degradation of bulk properties as well as interface properties.

Figure 9 shows the interface trap density distributions of the interface formed by thermal oxidation and CVD without and with chlorine addition. The peaks at the valence band ( $E_v$ )+0.3–0.35 eV and 0.7–0.75 eV mainly appeared and they have been reported to be the trivalent Si dangling bond ( $\cdot\text{Si}\equiv\text{Si}_3$ , where  $\cdot$  denotes an unpaired electron and  $\equiv$  denotes three back bonds to the central atom's nearest neighbors) near the Si/SiO<sub>2</sub> interface.<sup>26</sup> These Si dangling bonds are called  $P_b$  centers. This center is a major source of interface traps in the 0.15–0.9 eV range of the Si energy band gap. The interface trap densities at  $E_v$ +0.3–0.35 eV for the thermal oxidation and CVD without and with chlorine addition are  $1.2 \times 10^{12}$ ,  $8 \times 10^{12}$ , and  $3.5 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ , respectively. The CVD SiO<sub>2</sub> without chlorine addition has the highest interface trap density. It is clear that the Cl<sub>2</sub> addition during the RPECVD decreases the interface trap density greatly. The chlorine incorporation could reduce the interface trap density due to the passivation of positive (Si<sup>1+</sup>) Si dangling bonds through the formation of Si–Cl<sub>x</sub> bonds and inhibit the incorporation of hydrogen and water through the formation of H–Cl or HO–Cl bonds.<sup>10</sup>

Poindexter *et al.*<sup>26</sup> have extensively studied the  $P_b$  center defect using ESR and found a very strong correlation between the  $P_b$  center spin density and the interface trap density in oxide on both Si(111) and (100) surfaces. Figure 10 shows ESR spectra for three differently prepared CVD



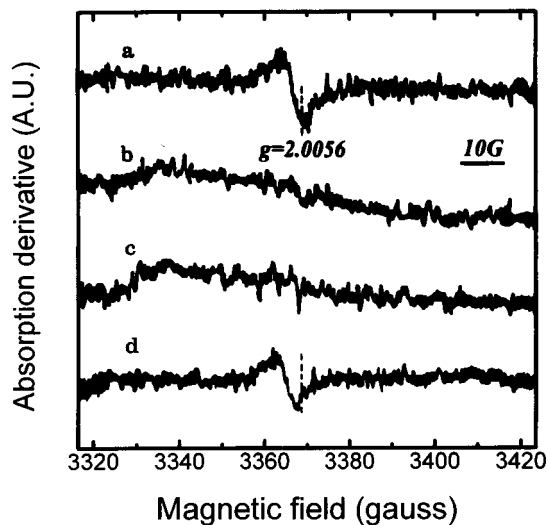


FIG. 10. ESR spectra of (a) CVD without chlorine, (b) and (c) CVD with chlorine (2 and 4 vol %) SiO<sub>2</sub>. PECVD oxides were deposited at a temperature of 250 °C with SiH<sub>4</sub>:N<sub>2</sub>O=3:12 sccm and the pressure was 0.4 Torr. (d) The thermal oxide.

samples compared with the thermal oxide, and peak positions are around  $g=2.0056$ .

The correlation between the interface trap at  $E_v+0.35$  and  $0.75$  eV and the peak amplitude of the  $P_b$  center at  $g=2.0056$  in ESR measurements is shown in Fig. 11. We can conclude that interfacial states, resulting from lattice mismatch, suboxide states, interface roughness, and nonbonded defects are passivated by the addition of small amounts of chlorine during the low temperature CVD process.

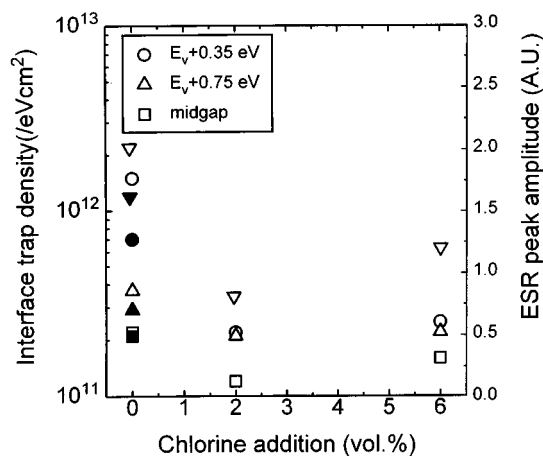


FIG. 11. Correlation between the interface trap density at  $E_v+0.35$  and  $0.75$  eV and ESR amplitude at  $g=2.0056$  for samples shown in Fig. 10. The interface trap density at  $E_v+0.35$  eV ( $\Delta$ ) and  $+0.75$  eV ( $\circ$ ), at midgap ( $\square$ ), and at the peak amplitude of ESR ( $\nabla$ ). The closed symbols represent the thermal oxide ( $\blacktriangle$ ,  $\bullet$ ,  $\blacksquare$ , and  $\blacktriangledown$ ).

#### IV. CONCLUSIONS

We have studied and compared the Si/SiO<sub>2</sub> interfaces formed by thermal oxidation and RPECVD with or without chlorine addition. The thermal oxide has a rough interface and the interface of the CVD SiO<sub>2</sub> without chlorine addition is rougher than that with chlorine addition. The thermal oxidation induces strong interface strains. The strains generated by the CVD SiO<sub>2</sub> without chlorine addition are stronger and are distributed more nonuniformly than with chlorine addition. It was also found out that with chlorine addition during RPECVD, the occurrence of strained layers, the interface trap density, and the suboxide density could be lowered significantly. It is suggested that chlorine addition during RPECVD affects the initial stages of deposition, i.e., neutralizes the Si dangling bonds through the formation of Si-Cl bonds. Although the large amount of chlorine addition roughened the deposited SiO<sub>2</sub> surface, we have discovered the appropriate amount of chlorine addition in order to get device quality low temperature SiO<sub>2</sub> films.

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