Oxide growth on silicon (100) in the plasma phase of dry oxygen using an electron cyclotron resonance source

Department of Physics and Semiconductor Physics Research Center, Jeonbuk National University, Jeonju 560-756, Korea

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Silicon dioxide films were grown using an oxygen plasma generated by an electron cyclotron resonance (ECR) source at several low temperatures. The plasma oxidation rate was investigated by varying the growth parameters. The oxide thickness parabolically increases with microwave power but decreases with increasing pressure or flow rate. A complementary model of the Deal–Grove oxidation theory is suggested for the plasma oxidation, and kinetic parameters are compared with the other plasma and thermal oxidation cases. The diffusion rate constant in O2 plasma oxidation at room temperature is enhanced up to the level of the diffusion rate in thermal oxidation and the reaction rate constant is much larger than the thermal oxidation case. This may imply that, due to oxygen atoms dissociated by the ECR plasma, plasma oxidation is related to the atomic diffusion through oxide layer and the atomic chemical reaction at the Si–SiO2 interface. The high quality of the ultrathin oxide film was characterized with a breakdown field of 14.8 MeV/cm and an interfacial state density of $1.2 \times 10^{10}$ eV$^{-1}$ cm$^{-2}$. © 1996 American Vacuum Society.

I. INTRODUCTION

In silicon technology, the quality of ultrathin oxide films becomes a crucial factor for ultralarge scale integration (ULSI) devices because of decreasing sizes of integrated circuits. The conventional thermal oxidation of silicon gives rise to questions about applications in ULSI technology. At high temperatures, potential problems of the thermal oxidation such as dopant diffusion, impurity redistribution, defect formation, and thermally induced stress can seriously degrade the device performance.1 Therefore, the low-temperature oxidation process is highly desirable for high quality ultrathin dielectric films. In order to reduce the processing temperature and to increase the growth rate, many studies on the sputtered gate oxide films and the films deposited by the plasma enhanced chemical vapor deposition (PECVD) were undertaken.2 However, the deposited films show interfacial instability with large gap states generated by hydrogen atoms which are included in the deposition process, and so the degraded electrical property is not comparable with that in thermal oxides.

High quality films can be grown by low-temperature plasma oxidation. As one kind of plasma oxidation process, plasma anodization has improved the low oxidation rate of the plasma oxidation. Anodization with two electrodes that apply the external positive bias to the sample enhances the diffusion of oxygen ions into oxide layer. Unfortunately, the contamination caused by electrode sputtering is unavoidable.3 O2 plasma oxidation without an external bias shows an even larger oxidation rate than the thermal oxidation case. Plasma oxidation without external bias increases as the device geometry of the ULSI decreases. Recently, an electron cyclotron resonance (ECR) plasma source has been developed and has several advantages such as a low plasma potential, a high ionization rate (10%), dissociation of oxygen in low pressure (mTorr), and a long plasma lifetime. ECR plasma oxidation shows that the dielectric property of the film is comparable to that of thermal oxides.4–6

Usually, the driving force for both the chemical reaction and the diffusion process is the thermal activation energy in the thermal oxidation of silicon. Instead of using the thermal energy, plasma oxidation utilizes a highly activated oxygen plasma including excited neutral oxygen atoms and reactive radicals of oxygen ions. In an ECR plasma, there are optical emission spectra for neutral oxygen atoms ($O_1$) and molecular oxygen ions ($O_2^+$).4,5 Without the ECR condition, the oxygen plasma emits spectra not only from $O_1$ and $O_2^+$, but also from $O^+$.7 However, Kimura et al.5 suggested the migration of $O^+$ into the oxide. Carl, Hess, and Lieberman3 also suggested that the strong electric field induced by the plasma self-bias on the oxide layer can conduct $O^+$ ions through the oxide. Vinckier et al.8 showed that charged species generated from the microwave discharge in afterglows have no effect on the oxidation rate due to poor ionization efficiency. Joseph, Hu, and Irene9 demonstrated the effect of applied bias, suggesting $O^+$ as the main oxidizing species. These experimental findings contradict each other and provide little explanation for the mechanism of the plasma oxidation without an external bias. The plasma oxidation kinetics parameters derived from the Deal–Grove model10 are still controversial. The reaction rates have been reported with a positive value by Carl et al. but with a negative value by Kimura et al.

In this work, we systematically analyze the kinetic parameters from the complete form of the oxidation model. Furthermore, the ECR plasma oxidation experiment without an applied bias on samples was carried out to confirm the plasma oxidation kinetics, and the oxidation rate was studied in terms of processing pressure, microwave power, substrate temperature, and oxidation time. The experimental results for plasma oxidation were fitted by the present formalism of oxidation theory. Furthermore, the electrical properties of the
breakdown field and the interfacial state density were characterized from metal–oxide–semiconductor (MOS) capacitor structures.

II. EXPERIMENTAL METHODS

A cross-sectional schematic view of the ECR system of Astex, Inc. is shown in Fig. 1. A microwave generated by a magnetron was guided through the waveguide to the ECR cavity. The waveguide was separated from the ECR cavity by a quartz disk. The ECR condition was adjusted by the three-stub tuner and accordingly the electromagnetic mode could be changed. In order to reproduce the process, it was important to choose a distinct electromagnetic mode that could provide a stable plasma. The ECR source was excited by a microwave power supply at 2.45 GHz with the range 50–1000 W. The ECR source was surrounded by magnetic solenoids to get the resonance condition. Sufficient electron kinetic energy could be obtained by introducing a steady magnetic field $B = 875$ G for the electron cyclotron frequency $\omega_e = eB / mc$ in the resonance chamber, which could resonate with the applied microwave frequency $\omega = 2.45$ GHz.

Pure oxygen gas (99.99%) entered the ECR source through a shower ring. The distribution of magnetic flux was of mirror type in the resonator and of divergent type in the discharge chamber. This divergent magnetic field could accelerate the activated oxygen radical stream to the sample by a magnetic longitudinal force regardless of the species charge. The samples were negatively self-biased with 12 V from the induced sheath potential of the ECR plasma without the applied bias. The distance between the shower ring to the sample stage was adjustable and set to 7.5 cm to optimize the uniformity of the plasma density. The sample stage was made of stainless steel and the temperature was measured using a resistance temperature detector placed directly underneath the stage. The temperature of the substrate holder could be controlled from room temperature up to 400 °C. The reflected power was kept below 10% of the forward microwave power. To maintain the low pressure, the system was evacuated by a 1000 l/s turbomolecular pump. The chamber was pumped out to a base pressure of $2 \times 10^{-6}$ Torr before each run. Plasma oxidation was processed in the pressure range of about $(1–2) \times 10^{-4}$ Torr. The processing pressure is directly related to the oxygen flow rate.

The samples used for oxidation were boron doped Si(100) with a resistivity of $3–10$ Ω cm and 7.5 cm in diameter. These samples were cleaned with a standard RCA-type wet chemical clean. The organic material on the surface could be dissolved in a boiling 4:1 mixture of H2SO4 and H2O2 at 110 °C for 10 min. The samples were dipped in a 20:1 diluted solution of H2O2 :HF for 10 s to etch the native oxide layer. The wafer oxide was also rinsed in deionized H2O at room temperature after each of these steps. However, in spite of the wet chemical cleaning, native oxides with a thickness of 10 Å still existed. The oxide thickness was measured by a Rudolph ellipsometer II. A nominal index of refraction of 1.462 was used for oxide thickness measurements. The breakdown field and interface charge trap density were obtained from $I–V$ and $C–V$ measurements on MOS capacitors. These MOS capacitor structures were fabricated by depositing 1-μm-thick Al on both sides of wafers. The dot size of the capacitors was $7.85 \times 10^{-3}$ cm² in area.

III. GROWTH PROPERTIES IN PLASMA OXIDATION

Instead of using thermal activation in conventional high-temperature oxidation, the ECR plasma enhances oxidation by increasing the activated oxygen species, and so plasma oxidation is useful for a low-temperature process in semiconductor technology. When a low-pressure gas is introduced, the gas breaks down and a discharge forms inside the chamber. The oxygen plasma diffuses along the expanding magnetic field lines into a process chamber toward a wafer holder. The oxidation rate asymptotically decreases with increasing pressure or O2 flow rate as shown in Fig. 2. This is due to the higher plasma density at lower pressure as mentioned by other groups.6,11 However, at very low pressure, the oxidation rate decreases with increasing intensity of the O2 ion peak.6

The optical emission spectroscopy (OES) shows several peaks of excited neutral atomic oxygen (O I) and positively charged molecular oxygen (O2+). There are several spectrum lines associated with O I in plasma at 4368, 6158, 5329, 3947, 7775, and 8446 Å.4,5 There are also a number of relatively broad bands associated with ionized molecular oxygen (O2+), the most prominent of which are at 5251, 5597, 5973, and 6351 Å.4,12 In particular, Kimura et al. demonstrated the oxygen pressure dependence of the emission intensity from O I (436.8 nm) and O2+ (525.1 nm). The maximum intensities of two species are located at 0.1–0.2 mTorr, consistent with our pressure dependence of the oxide thickness as shown in Fig. 2. They showed that the dissociation of O2 molecules into O I with an energy of 5 eV likely occurs in the high-pressure region due to low electron cyclotron energy, while
the electron energy is high enough to give rise preferentially to ionization (13 eV) in the low-pressure region.

The effect of microwave power on the oxide thickness is shown in Fig. 3. The oxide films were grown under conditions such that the flow rate was 10 sccm with a pressure of 0.1 mTorr and a 7.5 cm distance to source for 30 min. The parabolic behavior of the oxidation rate to the incident microwave power\( P_W \) is observed and fitted with the curve of
\[
x - x_0 = a_0 P_W^{1/2},
\]
where \( x, x_0, \) and \( a_0 \) are the oxide thickness grown for 30 min, the native oxide thickness, and the proportional constant, respectively. According to experimental data of present work, Sung and Pang\(^6\) and Vinckier et al.\(^8\) the native oxide thicknesses are given by 10, 15, and 18.7 Å, respectively. The constant \( a_0 \) is fitted to 0.5 for both the present work and the work of Sung and Pang and 0.86 for the work of Vinckier et al. The experiment on the dependence of the O-atom concentration on the applied microwave power was carried out by Vinckier et al. They showed that the atomic oxygen concentration linearly increases with microwave power and that the oxide thickness is proportional to the O-atom concentration \( C_O \) with the following relation:
\[
x^{2.17} - x_0^{2.17} = A C_O,
\]
where \( A \) is a constant. The oxide thickness and power relationship may support that the belief that the O atom is diffused into the interface as the oxidant. The oxidation rate may be directly related to the mass transport or the momentum of the O atom. Vinckier et al.\(^8\) also showed that the voltage applied on samples has no effect on the oxidation rate. This implies that charged species generated from the oxygen plasma do not play a role in the oxidation process of silicon and that the major oxidizing species is the O atom. On the other hand, Joseph, Hu, and Irene\(^10\) demonstrated the effect of applied bias on the oxidation rate. They suggested that the positive bias on samples provides significant enhancement of the oxidation process and that the most probable oxidizing species is \( O^- \). The oxidation kinetics by charged species in the limit of a low electric field is compatible with the Cabrera–Mott theory, which purports oxidation occurs from the movement of both Si outward as a cation in the interlayer and the oxidant species \( O^- \) inward as an anion. However, there is still no evidence on optical emission spectra of \( O^- \) ions in the ECR oxygen plasma without an external bias.

Our concern is for the ECR system without the applied bias on samples and so the sheath potential of −12 V is self-biased between the plasma and the sample. This implies that the \( O^- \) ions are repelled by the negative potential on the silicon surface. Therefore, without bias on samples, the primary oxidizing species is concluded to be the neutral excited oxygen atoms generated from the dissociation of \( O_2 \) molecules by the ECR source. Some dissociated \( O \) atoms can be recombined with electrons on the silicon surface to reduce the large electronegativity of the oxygen atom. Even though growth parameters are different for available experimental data, the oxidation rate as the function of substrate temperature is shown in Fig. 4. Kimura et al.\(^4\) and Carl, Hess, and Lieberman\(^5\) demonstrated that the oxidation rate increases with increasing temperatures higher than 350 °C. Sung and Pang\(^6\) showed the low rate at a room temperature of 16 °C and also Lee et al.\(^11\) did for the data at 400 °C. Our measurement of the rates below 350 °C shows that the rate slightly decreases with increasing temperature. This may imply that the dissociated neutral oxygen atom is simultaneously diffused into the oxide layer below 350 °C and then thermalized above 350 °C, indicating the inclusion of the thermal diffusion effect on plasma oxidation at high temperatures.

**IV. PLASMA OXIDATION KINETICS**

Many authors introduced the Deal–Grove model in order to understand plasma oxidation kinetics.\(^4\)–\(^6,11\) Deal and
Grove proposed that the oxidation rate was determined by a combination of two processes. One is the actual chemical reaction of oxygen with silicon at the interface, and the other is the diffusion of oxygen through the previously formed oxide film. The combination of these processes resulted in the linear–parabolic relationship between the oxide thickness \( x \) and the oxidation time \( t \),

\[
x = \frac{A}{2} \left( 1 + \frac{4B(t + \tau)}{A} \right)^{1/2} - 1,
\]

where

\[
A = \frac{2D}{k},
\]

\[
B = 2D \frac{C_0}{C_{ox}},
\]

and

\[
\tau = \frac{x_0^2 + Ax_0}{B},
\]

where \( k \) is the first-order reaction rate constant for the oxidation, \( C_0 \) the concentration of oxidant at the oxide surface, \( C_{ox} \) the concentration of oxygen molecules incorporated the oxide layer, and \( D \) the effective diffusivity of oxygen in the silicon dioxide. \( x_0 \) is the native oxide thickness and \( \tau \) is the corresponding oxidation time. In Eq. (5), \( B \) is the parabolic rate constant while the ratio of \( B/A \) is the linear rate constant. The rate constants obtained from several groups are summarized in Table I. Since the experimental conditions of the references given in Table I are different from each other, the comparison of the rate constants in terms of the substrate temperature can be arguable. However, the negative value of the reaction rate of \( B/A \) is strange even for plasma oxidation, because the negative rate is unphysical. Otherwise, the negativeness of the reaction rate is perhaps a unique characteristic of plasma oxidation, which may differ from thermal oxidation. This may imply that the Deal–Grove theory is not valid for plasma oxidation kinetics, which is involved with the atomic diffusion of O atoms.

According to a modified Deal–Grove model proposed by Tiller,\(^ {13} \) it is shown that \( B/A \) can be negative if migration of oxygen ions is considered. In Tiller’s model, the effect of field-aided ion migration is added into \( B/A \), \( B \), and \( \tau \) terms. However, Kimura \textit{et al.} argued that the index of the power law relation exceeds 2, in contrast to Tiller’s results of the Deal–Grove model. Note that the index of the exponent in the Deal–Grove model is varied from 1 to 2 according to a change of the mechanism from the linear region in a thin oxide to the parabolic region in a thick oxide. Vinckier \textit{et al.} used an exponent index of 2.17 for their model calculations of the silicon dioxide growth rate\(^ 8 \) from the following relation:

\[
x^n - x_0^n = bt,
\]

where \( x_0 \) is the initial thickness of the native oxide layer and \( b \) a constant independent of the oxidation time \( t \). This indicates that before analyzing the plasma oxidation kinetics, the validity of the Deal–Grove model has to be examined fundamentally. We consider again the analysis of the silicon oxidation kinetics of the Deal–Grove model in order to apply it to the plasma oxidation mechanism.

For the diffusion process of O atoms in the oxide layer, Fick’s first law is written by

\[
F_D = -D \frac{dC(x^+)}{dx^+},
\]

where \( D \) is the effective diffusivity of the O atoms in the oxide layer and \( C(x^+) \) is the oxidant concentration at any

---

**Table I.** Comparison of rate constants for several plasma oxides and thermal oxides. The experimental data were fitted by the Deal–Grove model for 16, 400, and 640 °C (Refs. 4, 6, and 11) and by the power law for 350 °C (Ref. 5). The present experimental result at 27 °C was fitted by the present theory.

<table>
<thead>
<tr>
<th>Oxidation</th>
<th>( T ) (°C)</th>
<th>( B ) (( \mu m^2/h ))</th>
<th>( B/A ) (( \mu m/h ))</th>
<th>( \tau ) (h)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma</td>
<td>27</td>
<td>1.94×10(^{-3} )</td>
<td>0.388</td>
<td>3.16×10(^{-3} )</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>8.01×10(^{-5} )</td>
<td>−4.47×10(^{-3} )</td>
<td>−1.57</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>1.26×10(^{-2} )</td>
<td>0.21</td>
<td>0.03</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>9.80×10(^{-4} )</td>
<td>−0.14</td>
<td>−0.34</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>640</td>
<td>4.92×10(^{-4} )</td>
<td>−1.23×10(^{-2} )</td>
<td>−1.44</td>
<td>4</td>
</tr>
<tr>
<td>Thermal</td>
<td>920</td>
<td>4.90×10(^{-3} )</td>
<td>2.08×10(^{-2} )</td>
<td>1.40</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1.20×10(^{-2} )</td>
<td>0.07</td>
<td>0.37</td>
<td>10</td>
</tr>
</tbody>
</table>
where the x’ of the diffused species. It is valuable to note that the above diffusion equation is fundamentally valid for a steady state process.\(^{14,15}\) The variable of integration of the above diffusion equation is fundamentally valid for a steady state process.\(^{14,15}\) The variable of integration of the above diffusion equation is fundamentally valid for a steady state process.\(^{14,15}\) The variable of integration \(x_i\) is any arbitrary distance from the gas/oxide interface in the position \(0 \leq x' \leq x_i\). In this work, however, our concern is limited only to the position of the interface \(x_i\) because oxidation is assumed to occur at the interface. As shown in Fig. 5, the diffused flux at the interface can be represented from the gradient of the concentration of oxygen for an infinitesimal element of the interfacial position \(x_i\).

$$F_D = -D \lim_{\Delta x_i \to 0} \frac{C_i(x_i + \Delta x_i) - C_i(x_i)}{(x_i + \Delta x_i) - x_i},$$

$$= -D \frac{dC_i(x_i)}{dx_i},$$  (9)

where the \(x_i\) denotes the position of the interface and \(C_i\) is the concentration of oxygen species at the interface. We again remind ourselves that this time-invariant flux at the interface in a steady state. It is noted that Deal and Grove approximated Fick’s law to the linear form of the concentration gradient from the assumption of steady state oxidation. This led to the difference form of the diffusion flux at any point of the interface with the surface concentration \(C_O\).

$$F_D = -D \frac{C_i(x_i) - C_O}{x_i}.$$  (11)

The flux involving the oxidation reaction at the interface is related to the interfacial oxidant concentration with the linear reaction coefficient \(k\),

$$F_R = kC_i(x_i).$$  (12)

Under the steady state oxidation of the O-atom diffusion in the equation of continuity,

$$\frac{\partial C_i}{\partial t} = -\nabla F = 0,$$  (13)

the invariant diffusion flux comes into the bulk oxide and finally reaches the Si/SiO\(_2\) interface. Therefore, the continuity equation is valid for the interface as well as in the bulk oxide. Every diffused flux participates in and is completely being used for the chemical reaction that results in growth of the oxide layer at the interface, implying the relationship of \(F_D = F_R = \text{const}\). By equating the diffusion flux at the interface in Eq. (10) to the flux required for the chemical reaction at the interface in Eq. (12), the differential equation provides the oxidant concentration and the flux at the interface from the initial boundary condition of the surface oxidant concentration, \(C_O\),

$$-D \frac{dC_i(x_i)}{dx_i} = kC_i(x_i),$$  (14)

$$C_i(x_i) = C_O \exp\left(-\frac{x_i}{L_D}\right),$$  (15)

and

$$F_R(x_i) = kC_O \exp\left(-\frac{x_i}{L_D}\right),$$  (16)

where \(L_D = D/k\) is represented for the characteristic diffusion length in the exponentially decaying incident flux at the interface.

In addition, the exponential term of the flux equation can be approximated in the form of \((1 + x_i/L_D)^{-1}\) for both limits of thin and thick oxide films \(x_i\). This approximation corresponds to the flux form derived by Deal and Grove,

$$F_R = \frac{kC_O}{1 + kx_i/D},$$  (17)

The steady state oxidation theory requires constant flux at the interface for both processes of diffusion and reaction at any instant. When the oxygen concentration at each point in the oxide no longer changes with time, the quantity of oxygen passing through the oxide per unit time is a constant. However, since the flux is the flow per unit area, it is a function of the oxide thickness and again it cannot be simply approximated to linear form. The difference between the present theory and the Deal–Grove theory is the interpretation of the steady state diffusion flux at the interface. Deal and Grove thought that Eq. (8) is not a steady state form and needed revision due to the relationship of \(-\nabla F_D = 0\). However, this claim may be challenged because the steady state condition applies only to the time variable and the continuity equation provides information on the time-independent flux of \(F_D = -DdC/dx' = \text{const}\), indicating Eq. (8) in a steady state form.\(^{14,15}\) From now on, let us denote the position of the interface \(x_i\) to the oxide thickness \(x\).

The oxidant flux results in oxidation with the growth rate of the oxide layer \(x\) through the relationship

$$F_R = C_{\text{ox}} \frac{dx}{dt},$$  (18)

where \(C_{\text{ox}}\) is the concentration of the oxygen incorporated into the oxide. By equating Eqs. (16) and (18), the following
The results of Carl, Hess, and Lieberman are similar to the thermal oxidation case at 1000 °C for $B$, but much smaller for $B/A$. Our result for the diffusion rate of $B$ shows a value similar to that in the thermal oxidation case at 920 °C. However, the reaction rate of $B/A$ is much larger compared to other thermal and plasma oxidations.

The Deal–Grove model could not overcome the negativeness of the reaction rate of $B/A$ (Refs. 4, 6, and 11) in the plasma oxidation kinetics. Although a spontaneous reaction can occur with a negative reaction energy, the negativeness of the reaction rate is, however, too complicated to understand the oxidation phenomenon, because the reaction rate must be increased without increasing the concentration of the oxidant species at the interface, indicating evidence of the additional process. It is also valuable to note that Deal–Grove estimates fail in predicting even thermal oxidation rates in dry oxygen within the thin film regime (<20 nm). However, for the ultrathin oxide film, our theory clarifies the problem of the negative reaction rate and provides a comparable result for kinetic parameters for thermal oxidation, implying the plasma enhancement of the low-temperature oxidation.

V. ELECTRICAL PROPERTIES

The samples used in this study were $p$-type Si(100) with a boron doping concentration of $2.17 \times 10^{16}$ cm$^{-3}$. Silicon wafers were treated with the standard cleaning process before plasma oxidation. After oxidation, aluminum was deposited as the gate metal. The area of contact was $7.85 \times 10^{-2}$ cm$^2$. Postoxidation and premetallization annealing was performed in a rapid thermal process in vacuum at 400 °C for 2 min. The MOS capacitor structure with the thin oxide layer of 77 Å was characterized using $I–V$ and $C–V$ measurements at room temperature.

The breakdown field is defined as the electric field that will introduce 1 µA leakage current across the MOS capacitor. The present average breakdown field of plasma oxide films was found to be 14.8 MeV/cm. This is higher than 7.8 and 12.39 MeV/cm from Salbert, Reinhard, and Amussen$^{16}$ and Sung and Pang,$^{6}$ respectively. The measured 1 MHz capacitance–voltage curve with (real line) and without (dashed line) the low-temperature anneal at 400 °C for 2 min is shown in Fig. 7. The annealing effect lowers the oxide charge from $1.87 \times 10^{-5}$ to $2.54 \times 10^{-5}$ C/cm$^2$ and shifts the flat band voltage from $-2.67$ to $-0.38$ V. The work function difference for the annealed case is $-0.638$ eV. The Si/SiO$_2$ interface state density $D_a$ is determined from the slope of the $C–V$ curve by deep level transient spectroscopy (DLTS) measurements. The trap density of $D_a$ is found to have a minimum of $1.2 \times 10^{10}$ eV$^{-1}$ cm$^{-2}$, as shown in Fig. 8. This is much lower than $10^{11}$ eV$^{-1}$ cm$^{-2}$ from Sung and Pang$^{6}$ and $5 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$ from Salbert, Reinhard, and Amussen.$^{16}$ The low density of interface trapping states is comparable to the thermal oxide MOS capacitors. This indicates that the plasma damage on the oxide layer is not significant and the atomic diffusion of neutral O atoms into the Si/SiO$_2$ interface leads to the layer-by-layer oxidation. Addi-
tually, the large reduction in interface states is attributed to the removal of traps or defects after annealing. We strongly argue that in the ECR plasma oxidation, the boron dopant can be diffused out to the interface from the silicon bulk due to the plasma oxidation environment. The sheath potential attracts the effectively positively charged boron in silicon. The interfacial boron segregation results in the reduction of Si dangling bonds and reflects the asymmetric distribution of the density of the interfacial trapping state just below the conduction band edge as shown in Fig. 8. More study is needed about the dopant behavior at the interface. Note that the ultrathin gate oxide for submicron devices (0.25 μm channel length) is required to be 70 Å in order to reduce the fringe effect. The device quality of the electrical property of the ultrathin gate oxide grown by the ECR oxygen plasma seems to be applicable for ULSI semiconductor technology.

VI. SUMMARY

Plasma oxidation of silicon has been performed by using O₂ gas generated by an ECR source at low temperatures. The oxidation rate was studied in terms of processing pressure, microwave power, substrate temperature, and oxidation time. The oxide thickness was found to increase with microwave power parabolically. The pressure dependence of the oxidation rate is consistent with the maximum intensities of the optical emission spectra of the O atom and O₂⁺ species. Below a 350°C substrate temperature the rate slightly decreases, and it rapidly increases above that temperature. For ultrathin film growth, the plasma oxidation kinetics provides a diffusion rate and chemical reaction rate comparable to the thermal oxidation cases. The proposed model shows a more general formulation of the oxidation kinetics than the Deal–Grove model, especially for plasma oxidation, and gives remarkable agreement with the experimental fit. As a conclusion, in spite of the uncertainty of the contribution of charged atomic species, plasma oxidation is associated with the atomic diffusion process rather than the molecular species related process. The high quality of the MOS capacitor using plasma oxidation films suggests that these films may be suitable for gate dielectrics in ULSI devices.

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