

## Oxidation rate and surface-potential variations of silicon during plasma oxidation

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We have studied the effect of dc bias ( $-60$  to  $+60$  V) on the plasma oxidation of silicon surfaces to understand the role of ions, neutral atoms, and electrons, using real-time ellipsometry. The real-time observation shows a strong dependence of the plasma oxidation on the dc bias. The results clearly reveal an enhancement of the oxidation rate by positively charged species in the ultrathin oxide film region, in addition to that by negatively charged species in conventional anodic oxidation. The plasma oxidation rate shows a minimum at around  $+27$  V, which corresponds to the plasma potential. The evolution of the surface potential during the plasma oxidation is discussed.

### I. INTRODUCTION

Oxidation of silicon is a key process in metal oxide semiconductor device fabrication.<sup>1-4</sup> Low-temperature processing of semiconductors is of interest because the thermally activated defect production and redistribution of impurities are greatly suppressed. Plasma oxidation is a technique currently being used for growing insulator films on semiconductor surfaces at lower temperatures than when using thermal oxidation.<sup>4-11</sup> However, the plasma oxidation mechanism is still not well understood since active chemical species and electrons in the presence of a potential profile in the growing oxide make it complicated.

In thick silicon oxides ( $>3-5$  nm), negatively charged oxygen species formed at the plasma-oxide interface are known to be the primary oxidation species under anodic oxidation conditions and the electric field produced in the oxide may lead to rapid transport of the ionic species through the film.<sup>4-9</sup>

The plasma oxidation rate depends on the plasma parameters, the sample temperature, and the electric field in the oxide films.<sup>4,6,8,12,13</sup> The effect of the applied bias on the plasma oxidation was pointed out by several authors. Carl *et al.*<sup>4</sup> have studied the effect of the dc bias on the growth rate of the oxide ( $3-300$  nm). They have reported that the silicon oxides with the best thickness uniformity were formed under anodic conditions (with positive biases) in an electron cyclotron resonance (ECR) plasma and that the oxide growth stops at some thickness ( $\approx 5$  nm) under cathodic conditions (with negative biases). Hu and co-workers<sup>7-9</sup> have studied the kinetics of the ECR-plasma oxidation of silicon using *in situ* spectroscopic ellipsometry and real-time single wavelength ellipsometry. They reported that beyond a film thickness of  $\approx 3$  nm a positive bias enhances the oxidation rate but a negative bias does not significantly enhance the rate. On the other hand, in the early stage of the oxide growth, within  $3$  nm, the plasma oxidation is virtually bias independent.<sup>8,9</sup> The experiments in the literature, however, do not focus on the very early stage of the oxidation, and the

very rapid initial oxidation process for thin films is not yet well understood.

Plasma oxidation occurs under the presence of an electric field in the oxide films and/or the sheath between the plasma and the surface. The plasma potential can be measured by a Langmuir probe and the sample substrate potential can be controlled by the applied bias voltage. Changes in the overall potential drop in the oxide film have been reported for thick oxide growth ( $3-300$  nm) in a ECR plasma.<sup>4</sup> However, surface-potential changes in the early stage of the plasma oxidation have not been studied in detail.

In this paper, we report the effects of dc biasing ( $-60$  to  $+60$  V) on the plasma oxidation rate of silicon surfaces in the early stage using real-time ellipsometry techniques. The purpose is to find out whether a bias dependence of the oxidation rate of silicon exists in the early stage of the oxide growth and to elucidate the roles of charged and neutral species as well as the role of electrons in the thin oxide. The plasma density of the radio frequency (rf) oxygen plasma used in our experiments was much lower than those of conventional ECR plasmas leading to slower oxidation rates. The bias dependence of the rapid initial changes of the ellipsometry data could then be measured more easily. We have also examined the effects of the characteristics of the plasma on the oxidation and we discuss the surface-potential variations during the oxidation.

### II. EXPERIMENT

Plasma oxidation of silicon was performed in an ultrahigh vacuum system with a base pressure of  $5 \times 10^{-8}$  Pa.<sup>12,13</sup> The oxygen plasma was generated by a rf discharge at  $13.56$  MHz with a power of  $300$  W. The oxygen pressure was  $1.3$  Pa. The chamber is approximately  $0.15$  m in diameter and  $1.5$  m in length. The distance between the substrate and the rf coil is approximately  $1$  m. The applied dc bias to the sample was varied from  $-60$  to  $+60$  V relative to ground. The total plasma oxidation time was around  $15\,000$  s.

The growth of the silicon oxide films was monitored by a real-time rapid ellipsometry. The two ellipsometric param-

eters  $\Delta$  and  $\Psi$  were measured *in situ* by a photoelastic modulator dual lock-in ellipsometer (JASCO PME-30p) using a He-Ne laser [632.8 nm (1.96 eV)], having an 8-ms resolution.<sup>13,14</sup> In this experiment, the data were taken at a 1.0-s resolution and interval. The polarized laser was reflected by the sample with angles of incidence and reflection at 70°. The samples used were *p*-type Si(111) with resistivities of  $1 \times 10^{-4} \sim 3 \times 10^{-4} \Omega \text{ cm}$ . They were etched by immersion in an HF solution for 5 min, rinsed in water, and annealed at  $\cong 873 \text{ K}$  in vacuum ( $5 \times 10^{-8} \text{ Pa}$ ) to obtain a clean substrate surface.

The chemical state of the oxide films formed by plasma oxidation was examined *ex situ* by x-ray photoelectron spectroscopy (XPS). In order to examine the effects of the plasma characteristics on the oxidation rate, the electron temperature, the plasma density, and the plasma potential were measured by the Langmuir probe (LP) method. A disk-shaped Langmuir probe, 1.5 cm in diameter, was placed  $\cong 2 \text{ cm}$  from the substrate. From the LP measurements, the electron temperature  $T_e$ , the plasma density  $n_p$ , the plasma potential  $V_p$ , and the floating potential  $V_f$  were found to be 5–6 eV,  $2\text{--}4 \times 10^7/\text{cm}^3$ , 23–27 V, and 9–10 V, respectively. Little bias dependence was observed in the plasma parameters. To observe chemical species in the oxygen plasma, optical emission spectroscopy and mass detection using a quadrupole mass sector without additional ionization were performed. The measurements showed the existence of  $\text{O}_2^+$  and  $\text{O}^+$  ions, and O atoms in the oxygen plasma.

Spectroscopic ellipsometric studies have showed that the thickness of the interfacial damage layer is constant during the ECR plasma oxidation and nearly bias independent, and it is straightforward to monitor the oxide growth by single wavelength ellipsometry.<sup>8,15</sup> The temperature of silicon wafers floats up to about 80 °C (from room temperature) without applied heating during an exposure to an ECR oxygen plasma (at an oxygen gas pressure  $6 \times 10^{-2} \text{ Pa}$  and a power of 300 W).<sup>15</sup> The dielectric function of most substrate materials is temperature dependent. For semiconductor materials, however, there is a photon energy regime in which the optical properties do not vary appreciably with temperature. By using a wavelength of 340 nm (3.65 eV) for the single wavelength ellipsometry measurements, the temperature changes in the optical properties can be ignored in an ECR experiment.<sup>8,15</sup> In this paper, we used an rf oxygen plasma in which the plasma density is much lower ( $\approx 1/10\,000$ ) than that of an ECR plasma. The sample temperature was found to increase only by 5° (from room temperature) under the most severe conditions: an exposure of 15 000 s at an applied bias of +60 eV. At a wavelength of 632.8 nm, we observed no change in  $\Delta$  and  $\Psi$  over a temperature range of 20–40 °C. Therefore, we need not consider the variations of the optical properties due to the substrate temperature changes during the plasma oxidation.

Figure 1 shows how the ellipsometric parameters  $\Delta$  and  $\Psi$  vary with time during the plasma oxidation. We observe a sudden decrease in  $\Delta$  upon the plasma ignition while  $\Psi$  remains almost constant. The values of  $\Delta$  and  $\Psi$  before starting the plasma oxidation were 179.26° and 10.75°, respectively.  $\Delta$  and  $\Psi$  depend on the material, the wavelength, and the angle of incidence. Under our experimental conditions, the above values correspond to a refractive index of 3.880–

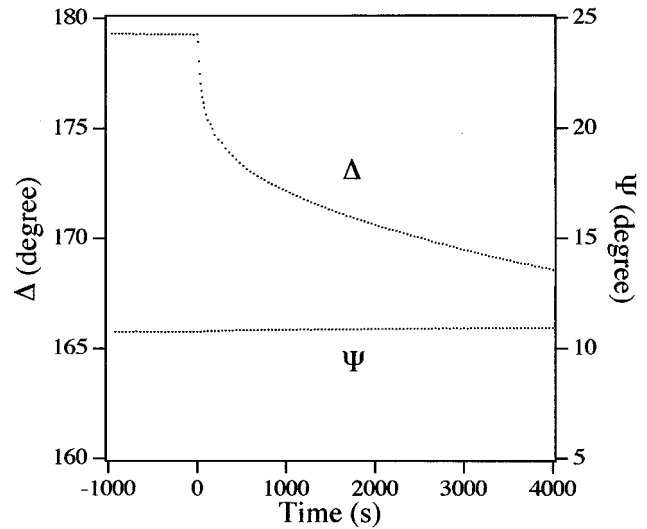


FIG. 1.  $\Delta$  and  $\Psi$  as a function of time before starting plasma oxidation and during the first 4000 s of the oxidation for a 45-V applied bias.

$i0.019$ . This value of the refractive index is in good agreement with the accepted value for silicon at 632.8 nm ( $3.881 - i0.018$ ).<sup>16</sup> This shows that the silicon substrate surface before starting the plasma oxidation is clean.

For thick-film growth one can estimate the refractive index  $\tilde{N} (=n + ik)$  and the thickness from the ellipsometry measurements using the optically homogeneous and isotropic film model with parallel-plane boundaries (using the Fresnel coefficients).<sup>17–19</sup> The calculated refractive index of our oxide films using this model was found to be  $1.465 (\pm 0.005) - i0.0005 (\pm 0.0005)$  after a long-time oxidation at positive biases (+30, +45 and +60 V), in very good agreement with the literature value for bulk  $\text{SiO}_2$  (1.46).<sup>16</sup>

For very thin films one should be careful when the optically homogeneous and isotropic film model is used to evaluate film thickness. The dielectric function  $\epsilon$  is a quantity related to the electronic orbital deformation (polarization) caused by the electric field of the incident light. Electronic structures are influenced by the substrate, and the refractive index of very thin films is different from that of the bulk. The thickness, which is calculated assuming a homogeneously continuous thin film with a bulk refractive index, is questionable for very thin films (nanometer films).<sup>20</sup> Many authors use the raw relative changes of the ellipsometric parameter  $\Delta$  ( $\delta\Delta$ ) with respect to the bare substrate as the optical thickness (or ellipsometric thickness) to evaluate the growth of very thin surface layers.<sup>18,21–27</sup> Fortunately the  $\text{SiO}_2/\text{Si}$  interface is one of the best for which the homogeneous isotropic film model is applicable. The errors due to inhomogeneity (e.g., density deficits, strains, or presence of suboxides) in evaluating thickness using the bulk value of the refractive index for thin films are small ( $\pm 0.5 \text{ nm}$  or less).<sup>7,15,28</sup> In this paper, we directly converted the  $\Delta$  and  $\Psi$ , measured with real-time ellipsometry, to film thickness assuming a one-layer homogeneous isotropic  $\text{SiO}_2$  model to monitor the growth of the oxide films on the silicon substrate.

### III. RESULTS

Figure 2 shows the evolution of the film thickness ( $d$ ) of the oxide for different bias values obtained from the real-

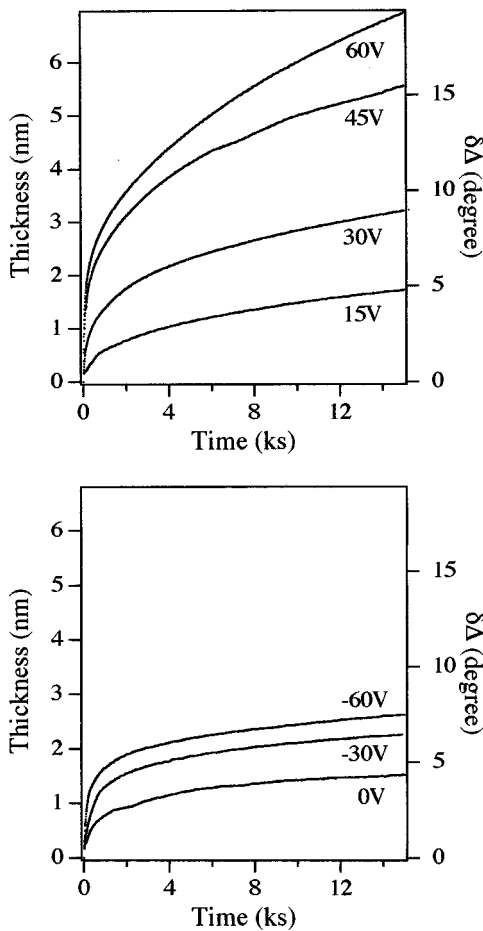


FIG. 2. Time dependence of the thickness ( $d$ ) of the oxide film obtained from the *real-time* rapid ellipsometry at different applied biases: (a) positive bias, and (b) zero and negative bias. The thicknesses were calculated assuming a one-layer homogeneous isotropic  $\text{SiO}_2$  model for the oxide film [the refractive index of the bulk  $\text{SiO}_2$  was 1.46 (Ref. 16)]. A scale for the relative change  $\delta\Delta$  ( $\equiv \Delta_0 - \Delta$ , where  $\Delta_0$  is the value of  $\Delta$  at the beginning of the discharge, that is, for bare silicon substrate) is also added in this figure on the right-hand axis for comparison. Note that the calculated thickness does not exactly correspond to  $\delta\Delta$  for thin oxide films less than  $\approx 3$  nm.

time ellipsometry. The thickness exhibits a steep increase immediately after starting the discharge and a slow increase at long times. The existence of different oxidation regimes was also reported for silicon oxide growth in the ECR oxidation.<sup>8</sup>

For both positive and negative biases, the value of  $d$  increases as the absolute value of the bias increases. For all values of the bias, the rate of change of  $d$  decreases with oxidation time. Positive and negative applied biases exhibit different evolution of  $d$ . The total increases in  $d$  for positive biases are larger than those for negative biases. For the ECR oxidation, positive biases also enhance the oxidation more than negative biases.<sup>4,7-9</sup> The continuous increase in  $d$  at long oxidation times means that the oxidation also occurs for the negative biases. This is different from the results in the ECR plasma oxidation,<sup>4,8,9</sup> where the oxide growth stops after a long-time oxidation for the negative biases (this is discussed later in more detail).

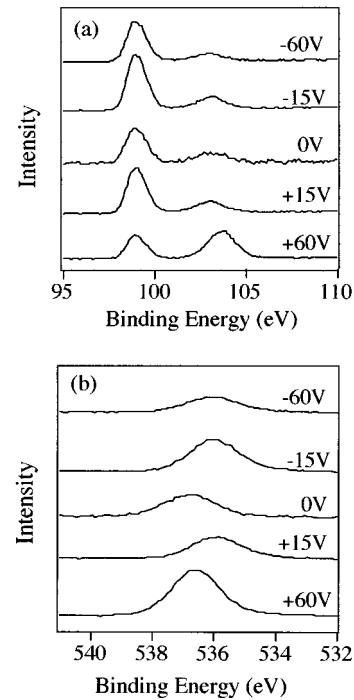


FIG. 3. XPS spectra of silicon after plasma oxidation (15 000 s) at different applied biases. (a)  $\text{Si}(2p)$ , and (b)  $\text{O}(1s)$ .

Figure 3 shows the XPS spectra of silicon surfaces after plasma oxidation (15 000 s) at different biases. The peak in binding energy near 99 eV of  $\text{Si}(2p)$  is due to the silicon substrate under the silicon oxide film [ $\text{Si}(2p)_{\text{Si}}$ ]. The other peaks near 103.5 eV [ $\text{Si}(2p)_{\text{ox}}$ ] [Fig. 3(a)] and near 536.5 eV [ $\text{O}(1s)$ ] [Fig. 3(b)] confirm the presence of silicon oxide.<sup>29-31</sup> We have observed no feature that might indicate the presence of impurities. Figure 4 shows the binding energy of the  $\text{Si}(2p)_{\text{ox}}$  and the  $\text{O}(1s)$  peaks in the XPS spectrum as a function of applied bias. The shift in peak position of the  $\text{Si}(2p)_{\text{ox}}$  is larger for the positive bias than for the negative bias. For stoichiometric  $\text{SiO}_2$  on a Si substrate, the  $\text{Si}(2p)_{\text{ox}}$  peak shift from the  $\text{Si}(2p)_{\text{Si}}$  peak was reported to be 4.72 eV.<sup>29</sup> In the present work, the peak shift was about 4.7 eV for positive biases (+30, +45 and +60 V), showing that the thicker silicon oxide formed by the rf plasma under positive bias is  $\text{SiO}_2$ . The ellipsometry results also showed that the refractive index of the oxide films formed using positive biases was very close to that of  $\text{SiO}_2$  (Sec. II). The decrease in binding energy for thinner oxides grown using less positive biases suggests the formation of lower oxidation states (between III and IV). The peak position of  $\text{O}(1s)$  also moves to higher binding energy for larger positive biases. The binding energy of  $\text{O}(1s)$  is known to decrease as the oxygen concentration decreases,<sup>30</sup> corresponding to the decrease in the  $\text{Si}(2p)_{\text{ox}}$  peak position. The decrease in both peak shifts may be related to the formation of suboxides like  $\text{SiO}$  and  $\text{Si}_2\text{O}_3$  at the substrate-film interface.<sup>29-31</sup>

## IV. DISCUSSION

### A. Initial oxidation process

In the ECR plasma oxidation, no bias dependence was found in the initial growth regime below 3 nm.<sup>7,8</sup> We have

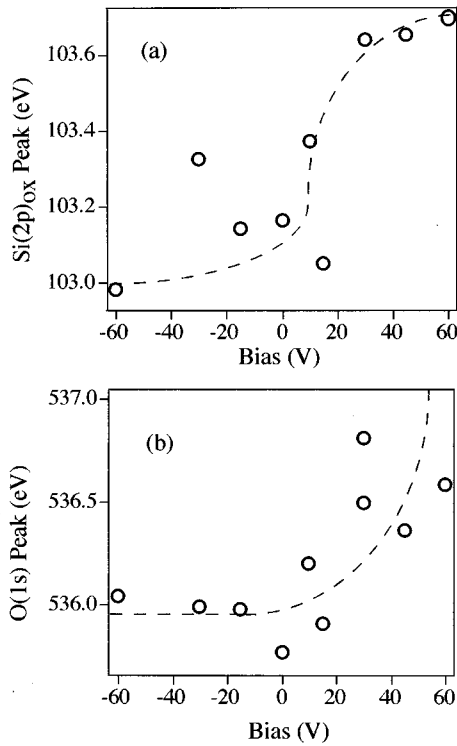


FIG. 4. Plot of the binding energy of (a) Si(2p)<sub>ox</sub> and (b) O(1s) as a function of the applied bias voltage.

found a significant bias dependence in this regime for the rf plasma oxidation. Figure 5 shows the plasma oxidation rate  $\partial d/\partial t$  (nm/s) for the first 300 s of oxidation. The plasma oxidation rate decays with time, and it shows different decay curves with different applied biases, which is, in particular, remarkable for the first several tens of seconds. Figure 6 shows the plasma oxidation rate as a function of applied bias at different plasma oxidation times. We can see that the plasma oxidation rate depends strongly on the bias applied to the sample. The oxidation rate increases as the absolute value of the bias is increased (both positive and negative) with a minimum near +27 V for very short oxidation times. This result shows that negatively charged species (electrons or negative ions) dominate the plasma oxidation at positive biases  $\geq +27$  V and positively charged species (such as  $O_2^+$ ) dominate at less positive biases. The direct contribution of negative ions from the plasma to the oxidation is negligible since the mobility and the density of the negative ions in the plasma are quite low. Most of the flux of negative charges from the plasma is probably due to electrons. For the thick oxide, the transport of the negative ions, which are formed at the plasma/silicon interface through an attachment of the electrons to adsorbed oxygen ( $O_2$  and O),<sup>7-10</sup> through the oxide is thought to be the rate-limiting process of the plasma oxidation.<sup>4,6,7-10</sup> On the other hand, for the very thin oxide the transport process could be unimportant because the oxide is too thin to act as a diffusion barrier,<sup>7,12</sup> and collision of electrons may promote chemical reactions of oxygen species with the solid surface through the excitation of the adsorbed oxygen (O or  $O_2$ ) in the positive-bias side. On the other hand, direct reaction of the surface with positive ions is suggested to occur for the negative bias.

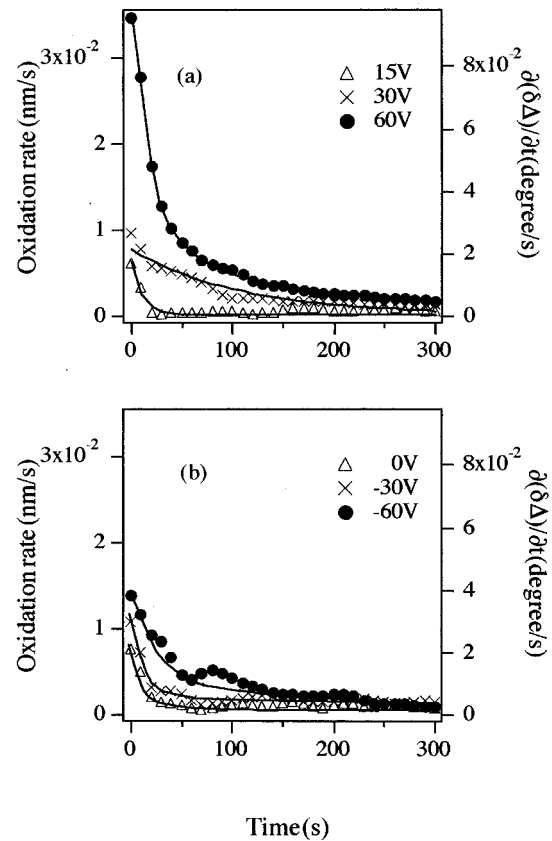


FIG. 5. Time dependence of the plasma oxidation rate at different applied biases: (a) positive bias, (b) zero and negative bias. The differential coefficient  $\partial(\delta\Delta)/\partial t$  is also shown (see the caption of Fig. 2).

We know from Fig. 6(a) that the bias dependence at an oxidation time of 10 s is significant, suggesting that the chemical species readily react with the silicon surface in the

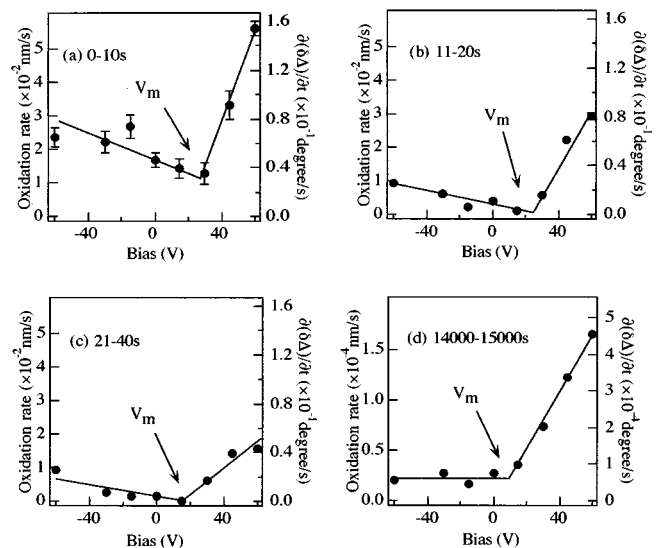


FIG. 6. The dependence of the plasma oxidation rate on the applied bias at different plasma oxidation times. The time for (d) 14 000–15 000 s is 300 times magnified. The differential coefficient  $\partial(\delta\Delta)/\partial t$  is also shown (see the caption of Fig. 2).

initial stage of the plasma oxidation. The bias dependence becomes weaker, in particular in the negative-bias side, as the oxidation time increases [Figs. 6(b)–6(d)]. This shows that direct reactions between the chemical species and the solid surface that dominate at the early stage are suppressed by the oxide film growing on the silicon surface.

It is noteworthy that the plasma potential  $V_p$  (23–27 V) and the applied bias  $V_b$  of the minimum oxidation rate for the short oxidation time ( $\cong 27$  V) are very close to each other. At this bias, the kinetic energy and flux of negatively or positively charged particles from the plasma should be small since the electric field through the sheath is very small, and the oxidation rate shows a minimum. The plasma oxidation should be due to thermal processes of active oxidant species including neutral ones. The main neutral species might be O atoms, which are more chemically active than  $O_2$  molecules. The minimum value of the plasma oxidation rate is about 0.01 nm/s at 10 s, while the rate of thermal oxidation at 400 °C is about 0.002 nm/s.<sup>12</sup> This shows that the plasma oxidation rate is high in the early stage of oxidation (in the ultrathin-film region), because of the presence of active oxidant species such as O atoms.

A negative applied bias increases the positive-ion energy and leads to ion bombardment of the surface. The maximum energy transferred,  $E_{p,max}$ , in an elastic collision between an atom 1 with initial energy  $E$  and an atom 2 with zero initial energy is given by  $E_{p,max} = 4M_1M_2/(M_1+M_2)^2E$ , where  $M_1$  and  $M_2$  are the respective atomic masses (e.g., Ref. 32). From this equation the minimum energy of the incident ions needed to displace the silicon lattice atoms [displacement energy = 15.8 eV (Ref. 33)] is estimated to be around 35 eV, assuming that the positive ions are  $O_2^+$ . This value corresponds to about –10 eV of applied bias, since the plasma potential is +27 eV. We can see no anomalous change near this value of the bias in the dependence of the plasma oxidation rate on the bias for any oxidation time. Production of damage in the oxide film due to ion bombardment may change the chemical state of the silicon oxide and lead to changes in the XPS peak width.<sup>21</sup> Little bias dependence, however, was observed in the full width at half maximum of the Si(2p)<sub>ox</sub> and the O(1s) peak. This suggests that surface damage due to ion bombardment during the plasma oxidation is weak in this bias range.

### B. Oxide film growth process

We also observed a bias dependence for thicker oxide films formed by a long-time oxidation, although not as pronounced as in the case of thinner oxide. The magnified values of the data at 15 000 s are shown in Fig. 6(d). The plasma oxidation rate shows a constant value of less than  $3 \times 10^{-5}$  nm/s for negative biases, and begins to increase abruptly at around +10 V as the bias is increased. This indicates that negatively charged species dominate the plasma oxidation in the thicker oxide film region. The importance of negative oxygen ions  $O^-$  was pointed out by several authors in the transport limited regime beyond 3 nm in the ECR plasma oxidation of silicon.<sup>4,6–8</sup> Hu and co-workers have analyzed the plasma oxidation in the ECR plasma using the Cabrera-Mott<sup>34</sup> model assuming that transport of oxidant species through the film controls the oxidation rate in the limit of low electric field;<sup>6,8,9</sup> the thickness  $L$  is given by the

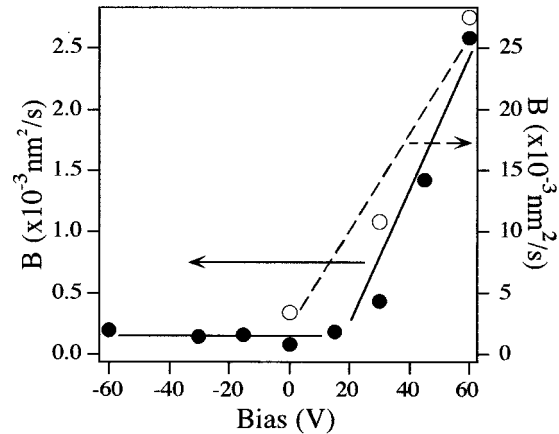


FIG. 7. Parabolic coefficient  $B$  vs applied bias voltage in the thick oxide film region. The solid circles show the present results and the open circles were taken from Hu and co-workers (Refs. 8 and 9). The solid lines are guides to the eye for the present data, and the dashed line is a least-squares fitting line to the three data points of the literature.

parabolic law  $L^2 = Bt + C$ , where  $B$  and  $C$  are constants. For comparison, we analyzed along the same line as they did. Figure 7 shows the parabolic rate constant  $B$  as a function of the applied bias, which was determined by a least-square fit from 5 000 s to 15 000 s. The rate  $B$  increases with bias voltage for positive biases, which is essentially the same as that found in the ECR oxidation.<sup>8,9</sup> The value of the rate constant  $B$  found in this work was about one order lower than that of the ECR plasma oxidation. This may be qualitatively explained from the difference in plasma density [ $\approx 10^7/\text{cm}^3$  for the rf plasma of this work;  $\sim 10^{11}/\text{cm}^3$  for the ECR (Ref. 5)]. In this transport regime, the negative ions  $O^-$  in the oxide are believed to be formed at the surface by the attachment of electrons to the adsorbed neutral  $O_2$  and O.<sup>4,8,10</sup> The ionic carrier density in the oxide film<sup>34</sup> depends on the electron flux from the plasma onto the surface, and the oxidation rate should be lower for the rf plasma than for the ECR plasma.

Carl *et al.*<sup>4</sup> and Hu and co-workers<sup>8,9</sup> have reported that the oxide growth stops at 3–5 nm for long-time oxidation in an ECR plasma with negative applied biases. The present results show that the oxidation occurs even under negative-bias conditions for thicker oxides [Fig. 6(d) and Fig. 7], although the rate is constant and low compared with the rate observed under positive biases:  $B \approx 1.5 \times 10^{-4}$  nm<sup>2</sup>/s below +10 V bias. The independence of the rate of the bias at less positive biases suggests that a transport of neutral oxidant species (like O atoms) may be the important oxidation mechanism under negative bias.

### C. Surface-potential variations

The plasma oxidation rate was found to exhibit a minimum near +27 V at short oxidation times [Fig. 6(a)] and begins to rise at about +10 V for long oxidation times [Fig. 6(d)]. Let  $V_m$  be equal to these specific biases. Figure 8 shows the applied bias  $V_m$  as a function of oxidation time. When the plasma oxidation starts, the surface potential  $V_s$  is equal to the applied bias  $V_b$ : the oxide film is too thin to

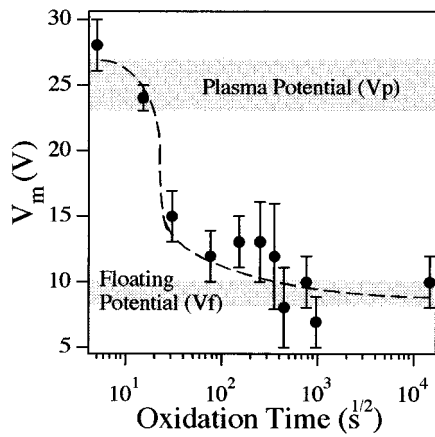


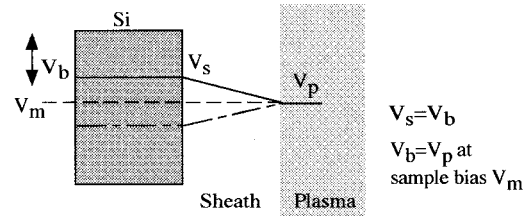
FIG. 8. The specific applied bias  $V_m$  as a function of the oxidation time. At  $V_m$  the plasma oxidation rate exhibits a minimum at short oxidation time and begins to rise at long oxidation times (see Fig. 6). The time dependence of  $V_m$  suggests show the surface potential evolves during the plasma oxidation.

allow charging of the surface. After the oxide thickness is large enough to sustain an electric field,  $V_s$  goes down: the surface potential drops. Thus, the surface potential  $V_s$  will change with time as the oxide grows,<sup>4</sup> and the plasma oxidation rate changes with time. Initially, as mentioned above, the oxidation rate should be very small when the electric field in the sheath becomes zero:  $V_b = V_p$  ( $\equiv V_m$ ) [see Fig. 9(a)]. As the oxide film grows, the plasma oxidation is limited by the negative-ion transport through the film under an electric field  $(V_b - V_s)/L_{ox}$ , where  $L_{ox}$  is the oxide thickness. The plasma oxidation rate is expected to be very low for biases of  $(V_b - V_s) \leq 0$ , and  $V_m$  may correspond to  $V_s$ . For a very thick oxide,  $V_s$  finally reaches the floating potential  $V_f$  [Fig. 9(c)]. Therefore, the time-dependent variation of  $V_m$  may show the evolution of the surface potential during the plasma oxidation. In fact,  $V_m$  has a value corresponding to  $V_p$  ( $\equiv +25$  V) initially and decreases to near  $V_f$  ( $\equiv +10$  V) with time accompanying the surface potential drop, which probably corresponds to a transition from surface limited reactions to diffusion limited reactions.

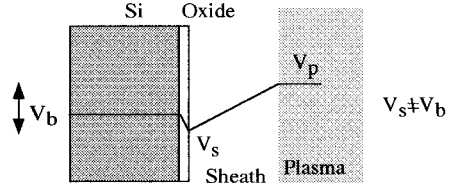
## V. CONCLUSIONS

In this paper, the dependence of the initial process of plasma oxidation of silicon surfaces on the applied dc bias was studied using real-time ellipsometry measurements. The real-time observation showed a strong dependence of the plasma oxidation rate on the bias and a clear enhancement of the oxidation rate by positively charged species, in addition to that by negatively charged species in conventional anodic oxidation. The bias effect depends on the oxidation stage. Initially, the oxidation rate is very sensitive to the applied bias. The oxidation rate increased for both negative and positive biases, showing a minimum near +27 V. For very thin oxide films, negatively charged species contribute to the plasma oxidation under positive biases and positively charged species ( $O_2^+$ ,  $O^+$ ) contribute for negative biases. In the initial stage of the oxidation, the direct reaction of the

(a) Initial; bare surface (or very thin oxide)



(b) Mid way



(c) Thicker oxide

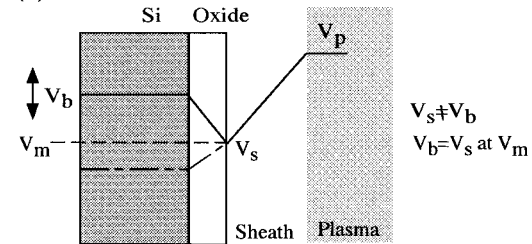


FIG. 9. Potential profiles and bias application schematics during the oxide film growth. Initially (a), the surface potential  $V_s$  is equal to the applied bias  $V_b$  and  $V_m$  equals the plasma potential  $V_p$  (a dashed line). As the oxide film grows [(b) and (c)],  $V_s$  goes down due to the surface-potential drops ( $V_s \neq V_b$ ) and  $V_m$  may correspond to  $V_s$  [a dashed line in (c)].

oxidant species with the silicon surface dominates the process. The bias effect becomes weaker as the oxidation time is increased. For thick oxide films, the plasma oxidation is limited by transport of oxidant species across the oxide. Negative ions  $O^-$  dominate the oxidation under positive biases, and it was suggested that neutral oxidant species (like O) also contribute under negative biases. The specific applied bias  $V_m$  is initially equal to the plasma potential and, after a long oxidation time, equal to the floating potential. The time-dependent change of  $V_m$  shows how the surface potential of oxidized silicon evolves during the plasma oxidation.

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