Suboxide characteristics in ultrathin oxides grown under novel oxidation processes

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(Received 28 August 2003; accepted 26 July 2004; published 7 October 2004)

Interfacial suboxide ($\text{SiO}_x, 0 < x < 2$) between Si and its stable SiO_2 is observed to be a key factor to affect the ultrathin-oxide quality. SiO_2 grown by anodic oxidation (anodization) or by repeated-spike oxidation (RSO) presents a better dielectric characteristic than conventional rapid-thermal oxidation (RTO). This improvement can be attributed to two reasons: (1) A thinner transition region and/or (2) more stoichiometric S–O bonds under the same oxide thickness. Anodic SiO_2 presents a thinner suboxide width (interface region) and RSO SiO_2 demonstrates the existence of less suboxide existence at the near-surface region (oxide bulk). The reduction of the imperfect bonding structure in suboxide gives an abrupt Si– SiO_2 interface and consequently, the reduction of electron tunneling probability through oxide. © 2004 American Vacuum Society. [DOI: 10.1116/1.1795824]

I. INTRODUCTION

As the dimension of silicon complementary metal-oxide semiconductor (CMOS) devices shrink further into the deep-submicron range, ultrathin SiO_2 is necessary to maintain the gate-driving current. When the oxide is thinner than ~ 3 nm, the dominant tunneling mechanism changes from Fowler–Nordheim (FN) tunneling to direct tunneling (DT). A reduction of ~ 2 Å in oxide thickness (T_{ox}) leads to an order of magnitude increase in DT current, which is a problematic issue for limiting T_{ox} scaling.¹ At the same time, the interfacial transition region's fraction becomes larger of the total oxide layer. The presence of defects in the suboxide becomes crucial to the oxide quality. These defects can function as oxide traps, oxygen vacancies, dangling bonds, and voids. These defects would lead to an increase of trap-assisted tunneling current and also the introduction of catastrophic oxide breakdown.² Ultrathin-oxide quality is controlled by the complex combination of oxidation methods, growth kinetics, and equilibrium energies. Therefore, many studies have been proposed to enhance the ultrathin gate-oxide quality by improved growth conditions or by additional process treatments.^{3–5} The results reveal that the interfacial transition region is both nonstoichiometric and improvable. Furthermore, it is known that a thin and reliable SiO_2 interlayer is beneficial for maintaining high interface quality and carrier mobility in future devices with high-k dielectrics. Therefore, we believe this transition region would be of great technological importance and is worthy of studying in gate-dielectric engineering.

From the literature,^{6,7} the interfacial transition region, i.e., the suboxide region ($\text{SiO}_x, x < 2$), is composed of crystalline Si, SiO_2 and a high ratio of void that were formed during the competition process between Si monomer creation and SiO production. When the suboxide arrangement extends into the

oxide, localized tunneling current occurs and the effective oxide thickness is reduced. Many works have been proposed to minimize the transition width, e.g., post-oxidation annealing and interfacial nitridation. The results imply that the suboxide characteristics are strongly dependent on the growth condition and the addition of process treatment.

In this work, oxides prepared by novel anodic oxidation (anodization) and repeated-spike oxidation (RSO) were examined to verify the suboxide influence. In our previous studies,^{8–11} it was shown that anodic and RSO SiO_2 exhibit improved characteristics with respect to the conventional thermally grown SiO_2 . Briefly, it was observed that the capacitance-voltage (C–V) curves of RSO SiO_2 exhibit less frequency response, and the anodic SiO_2 presents a higher breakdown field and a lower gate-leakage current property. In this work, the layer-by-layer composition from the oxide surface to the inner Si– SiO_2 interface was evaluated by in-depth analysis of x-ray photoelectron spectroscopy (XPS). The results demonstrate that the distribution and concentration of atoms in the suboxide are crucial to the oxide quality.

II. EXPERIMENT

Prior to oxidation, 3-inch p-type Si wafers were treated with standard wafer cleaning. To remove the native oxide, a final hydrofluoric acid (HF) dip was adopted. After cleaning, thin SiO_2 with different thicknesses was grown separately by conventional rapid-thermal oxidation (RTO SiO_2), anodic oxidation (anodic SiO_2), and repeated-spike oxidation (RSO SiO_2). For anodic SiO_2 films, the wafer acts as an anode electrode. A constant electrolyzing field of 10 V/cm was applied by using deionized (DI) water as an electrolyte. After anodization, post-anodization annealing (PAA) was treated at 850 °C in N_2 ambient. For the RSO films, oxidation temperature was set to ramp up and cool down between 750 °C and 850 °C in the rapid-thermal process (RTP) system in an O_2 ambient. The temperature profile is described in Sec.

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FIG. 1. Evolution of XPS Si 2p spectra from the oxide surface to the Si substrate for oxides with 40 Å thickness. These were grown by (a) typical RTO and (b) anodic oxidation. A faster spectra transformation is observed in the anodic SiO₂ near the interface.

III B. For comparison, conventional SiO₂ prepared by RTO at 850 °C was prepared. Finally, a metal-oxide-semiconductor (MOS) capacitor structure with an Al metal gate of 150 μm × 150 μm was fabricated for the measurement of device characteristics. All oxides were examined by high-resolution Auger electron spectroscopy (AES) and XPS to characterize the depth profile and bonding condition, respectively. In addition, C-V and current-voltage (I-V) measurements were utilized to analyze the electrical characteristics of ultrathin SiO₂. The oxide thickness was obtained from C-V measurement, while considering the series resistance and quantum mechanical (Q.M.) effects.^{12,13}

III. RESULTS AND DISCUSSION

A. Suboxide characteristics of RTO SiO₂ and anodic SiO₂

1. XPS spectra and AES depth profiles of 40 Å SiO₂

Figures 1(a) and 1(b) show the XPS Si 2p spectra of RTO SiO₂ and anodic SiO₂ with $T_{ox}=40$ Å, respectively. The spectra were merged by each detected spectrum under various T_{ox} . For example, the first spectrum was detected on the oxide surface, and then a very low and constant sputter rate (by controlling the ion-gun current) was employed to remove the surface oxide (about 1.5–2 Å SiO₂ was removed for

FIG. 2. (a) Intensity ratio of Si^0 to the background silicon $\text{Si}^0\text{-BG}$ for RTO and anodic SiO_2 from the surface (~ 0.1) to the substrate (~ 1) showing the sputter rate is controllable and that every T_{ox} is identical. In addition, XPS $\text{Si } 2p$ intensities at Si^{x+} , $x=2-4$ at each step are shown in Figs. 2(b)–2(d), respectively.

each sputter duration). After sputtering, the second spectrum was then detected. By this sequence, when the oxide layer was totally removed, only the signal from the bulk Si (Si^0) could be detected. The small deviation of the standard binding energy of 99.4 eV (Si^0 , bulk Si) that occurred on each spectrum may be attributed to a residual charge on the film. However, the deviation does not affect the binding energy of the intermediate-oxidation states relative to the bulk Si (Si^0). During the sequential sputtering, more suboxide might be created on the surface region and localized nonuniform etching might take place on the bombarded area. However, because the sputter rate is quite low, signals come from the 10 nm layer below the surface and the near-surface region ($5\text{--}8 \text{ \AA}$) contribute to the main intensity. Hence, we think the bombardment-induced surface damage would not create a noticeable effect on the final XPS spectrum.

The stoichiometric SiO_2 (Si^{4+}) and Si (Si^0 , bulk Si) spectra correspond to distinguishable binding energies of 103.3 and 99.4 eV, respectively, and the peaks among Si^{4+} and Si^0 can be attributed to the intermediate oxidation states. By inspecting the spectra from the SiO_2 surface to the Si substrate, it can be seen that the peaks gradually shift and transform from Si^{4+} to Si. Also, it is obvious that the suboxide distributes mainly around the interface. In contrast to the anodic SiO_2 spectra, a smoother transformation from Si^{4+} to Si is observed for the RTO SiO_2 spectra when the spectrum gets close to the interface. It reveals the greater existence of suboxide in the RTO SiO_2 . The faster transformation of anodic SiO_2 infers the more abrupt Si– SiO_2 interface.

Interpretation of the suboxide states has been widely discussed.^{14–16} In spite of the impurity disturbance, changes in peak intensity provide a crude means of suboxide distri-

FIG. 3. AES depth profiles of (a) 1000 Å SiO₂ and (b) 40 Å SiO₂ grown by RTO and anodic oxidations. Very low ion-gun current is used for sputtering of 40 Å SiO₂ (~2 Å/step). Steeper distribution slope is observed in the 40 Å anodic SiO₂.

bution. From previous study,¹⁴ the Si 2*p* spectrum can be deconvoluted to five admitted bonding configurations, i.e., Si^{x+}_{x=0-4} at 99.4, 100.4, 101.2, 102.1, and 103.3 eV, respectively. From Fig. 1, it can be seen that when oxide was totally removed, the Si⁰ signal from the substrate presents a constant value, which can be referred to as substrate background (Si⁰-BG). As shown in Fig. 2(a), we can see the slopes of Si⁰/Si⁰-BG of RTO and anodic SiO₂ were fairly overlapped from step 1 (surface) to step 20 (substrate). That overlap implies the sputter rate is quite controllable and the oxide thicknesses are the same for this comparison. In Figs. 2(b) and 2(c), we can see that the XPS intensities of Si²⁺ and Si³⁺ exhibit similar distributions from the oxide surface to the interface. However, in Fig. 2(d), the anodic SiO₂ shows a relative steeper slope in Si⁴⁺ distribution than RTO SiO₂. This reveals the greater stoichiometric Si⁴⁺ existence around the SiO₂-Si interface. In the suboxide region, the lack of oxygen leads to the presence of dangling bonds and traps. We suppose that unlike the RTO SiO₂ grown by the interaction of high-kinetic and massive oxygen, anodic SiO₂ is formed by the reaction of OH⁻ and Si at room temperature. Layer by layer, the low-kinetic oxidant reacts with the silicon. At that time, the oxygen vacancies are easier to compensate. Therefore, we believe incorporating more oxygen in the film is helpful for reducing the imperfect suboxide bonding.

Furthermore, depth profiles of RTO SiO₂ and anodic SiO₂ were detected by high-resolution AES. The atomic concentration of 1000 Å SiO₂ shown in Fig. 3(a) presents a quite stoichiometric proportion of Si and O (1:2) in the bulk. On the right side, depth profiles of RTO SiO₂ and anodic SiO₂ with *T*_{ox}=40 Å are shown in Fig. 3(b). By controlling the ion-gun current (~2 Å per step), the anodic SiO₂ demonstrated a relatively steeper profile that implies two contributions: (i) A thinner transition region between SiO₂-Si and

(ii) a higher stoichiometric SiO₂ fraction under the same *T*_{ox}. Here, we can see this result is identical to the previous XPS analysis.

2. Electrical characteristics of anodic and RTO SiO₂

Gate-leakage current density of RTO and anodic SiO₂ versus *T*_{ox} ranging from 18 to 30 Å (gate bias at *V*_G-*V*_{FB}=-1 V) is shown in Fig. 4. In this work, high-frequency C-V curves of 100 K and 1 MHz were measured and corrected to eliminate the series-resistance effect.¹² Afterward, the two frequency-corrected C-V curve was taken to fit the quantum mechanical (Q.M.)-considered C-V curves to obtain the *T*_{ox}.¹³ Under the same *T*_{ox}, we can see that the leakage current of the anodic SiO₂ presents an order of magnitude lower than that of RTO SiO₂. This indicates that a thinner transition

FIG. 4. Gate leakage current densities versus oxide thickness of RTO and anodic SiO₂ with a gate bias of *V*_G-*V*_{FB}=-1 V. Weibull plot of TZDB characteristic for RTO and anodic SiO₂ samples is shown in the inset.

FIG. 5. Electron-barrier height (Φ_B) versus the oxide thickness for RTO and anodic oxides. As shown in the inset, each Φ_B is extracted from FN plots.

region can effectively reduce the tunneling probability of electrons through oxide. The time-zero dielectric breakdown (TZDB) shown in the inset illustrates that to break down an anodic SiO_2 could require a field ~ 2 MV/cm higher than RTO SiO_2 . One may wonder if more OH bonds in the anodic oxide would cause a difference of interfacial Al_2O_3 between the Al gate and SiO_2 . Our previous study found that most of the hydrogen in the anodic film could be removed after the subsequent annealing process and the excess oxygen may react with the silicon or be evaporated from the film. Therefore, if the subsequent annealing temperature is high enough to remove the excess OH bonds, we think the variation might be suppressed. From this result, it is believed that the less-extended suboxide in anodic SiO_2 is responsible for the higher endurance observed in the breakdown field.

Fowler–Nordheim (FN) conduction is well known as one of the SiO_2 tunneling mechanisms. Many studies have been devoted to the tunneling regime.^{17,18} The potential barrier height (Φ_B) is the most important parameter in this conduction. From the FN model, Φ_B can be evaluated from the I–V measurement. However, in such a thin oxide region, the DT effects become impossible to ignore. The emergence of the DT current (J_{DT}) leads to the lowering of effective Φ_B . However, while the suboxide extends into the film, localized tunneling enhances the J_{DT} that leads to the more severe lowering of Φ_B . Therefore, effective Φ_B extracted from the FN model can provide the suboxide information. Besides, when Bell *et al.* comprehensively researched SiO_x ($0 < x < 2$) alloys,¹⁹ the bandgap value was found to be proportional to the oxygen-incorporation level. This result is in consensus with the Φ_B lowering phenomenon shown in Fig. 5. Effective Φ_B between the metal gate and SiO_2 is obtained from the FN tunneling formula of the slope of $\ln(JF^{-2})$ vs F^{-1} as shown in the insets, where J is the FN tunneling-current density and F is the oxide field. As shown, 1.5 eV decreased in Φ_B is observed for both samples when T_{ox} decreased from 30 to 20 Å. This experimental evidence explains the bandgap roll-off phenomenon when T_{ox} scales into the DT region.

FIG. 6. Schematic diagram of suboxide-induced bandgap lowering of RTO and anodic SiO_2 . The lower bandgap is employed at the region where suboxide exists.

Here, anodic SiO_2 still retains a higher Φ_B than RTO SiO_2 under the same T_{ox} . It is reasonable to assume that when the DT effect becomes less important, the oxide grown by RTO and anodic oxidation should have identical Φ_B . However, in our previous study, anodic SiO_2 exhibited properties of lower gate-leakage current and higher Φ_B than the thermally grown SiO_2 in thicker region. When FN tunneling dominates the gate-tunneling current, fewer tunneling paths through the oxide would keep an ideal Φ_B value. We think the greater suboxide existence in the bulk could provide more tunneling paths, i.e., trap-assisted tunneling. Anodic SiO_2 maintains higher effective Φ_B than RTO SiO_2 under the same oxide thickness. This can be attributed to less suboxide. The less suboxide that exists in the bulk oxide would effectively reduce the probability of trap-assisted tunneling, thus the higher Φ_B is observed in anodic SiO_2 .

Here we propose a schematic diagram to describe the suboxide-induced Φ_B lowering phenomenon shown in Fig. 6. The suboxide region exhibits a lower conduction-band offset than stoichiometric oxide based on the XPS results.⁴ The lower bandgap profile is employed to separate the suboxide region from the stoichiometric region. The more oxygen incorporated in the anodic SiO_2 , the more perfect the bandgap profile. According to the Deal-Grove model, the diffusive flux is dominated by the interface reaction in the thin-oxide regime. Hence a low and stable interface reaction is important during oxidation. Standard techniques such as RTO will have difficulty in producing such a short transition width. This difficulty is due to the high-kinetic O mass generated during the slow ramp-up time. Anodic SiO_2 , grown by field-enhanced oxidation layer by layer, presents a thinner transition region than RTO SiO_2 .

Fig. 7. Setting and measured temperature profiles of (a) typical RTO and (b) RSO.

B. Suboxide characteristics of RTO SiO_2 and RSO SiO_2

In addition to the anodic SiO_2 , our previous works also revealed that SiO_2 prepared by RSO exhibits better electrical characteristic than RTO SiO_2 .¹¹ The temperature profiles of RTO and RSO are shown in Figs. 7(a) and 7(b), respectively. In Fig. 7(a), the oxidation temperature was kept at 850 °C, and in Fig. 7(b), the temperature profile was set to vibrate from 750 °C to 850 °C. In our previous work, it was found that by using RSO technology the absorption of the radiated heat in two different temperature zones could be compensated on a wafer to form a more uniform oxide.¹⁰ The better uniformity in T_{ox} could effectively reduce the probability of local-oxide thinning. Thereby, it is believed that when temperature ramps up and cools down within a short time, the residual atomic oxygen in the oxide layer has a greater chance to fill the silicon dangling bonds.

For the same reason, we believe the suboxide has played a major role in improving of the RSO technique. To sustain this supposition, the same procedure is utilized to examine the suboxide distribution, as shown in Fig. 8. Figures 8(a) and 8(b) show the XPS spectra of RTO SiO_2 and RSO SiO_2 with $T_{\text{ox}}=40$ Å, respectively. Unlike the anodic SiO_2 spectra shown in Fig. 1, the RSO spectrum does not show a distinct difference in the interface-spectrum transformation. However, under the same T_{ox} , the ratio of $\text{Si}^{4+}-\text{Si}^0$ is observed to exhibit a relatively higher value for the RSO SiO_2 on the surface. In the same sequence, when oxide was totally re-

Fig. 8. Evolution of XPS Si 2p spectra from the oxide surface to the Si substrate for oxides with 40 Å thickness. These were grown by (a) typical RTO and (b) RSO. The RSO SiO_2 exhibits a relatively higher $\text{Si}^{4+}-\text{Si}^0$ intensity value on the surface under the same T_{ox} .

moved, we refer to the constant Si^0 intensity as $\text{Si}^0\text{-BG}$. As shown in Fig. 9(a), the curves of $\text{Si}^0\text{-Si}^0\text{-BG}$ are shifted to become fairly overlapped from step 1 (surface) to step 22 (substrate) to make sure that the oxide thicknesses are identical in this comparison. Relative intensity ratios of $\text{Si}^{x+}-\text{Si}^0$, $x=2-4$ at each step are shown in Figs. 9(b)–9(d), respectively. Unlike anodic SiO_2 , it is obvious that the RSO SiO_2 exhibits less suboxide component at the near-surface region [Figs. 9(b) and 9(c)]. However, the intensity of Si^{4+} [Fig. 9(d)] shows more stoichiometric bonding existence at the near-surface region (oxide bulk) in the RSO SiO_2 . This evidence apparently validates the previous assumption. During the temperature vibration, the reactive residual O has more chance to compensate the imperfect Si–O arrangement. The residual oxygen captured by the dangling bonds results in a more stoichiometric Si–O network. Thus the lower gate leakage can be observed in Fig. 10. RSO SiO_2 shows approximately one order of magnitude lower gate leakage than RTO SiO_2 .

FIG. 9. XPS intensity ratios of (a) $\text{Si}^0\text{-Si}^0\text{-BG}$, (b) $\text{Si}^{2+}\text{-Si}^0$, (c) $\text{Si}^{3+}\text{-Si}^0$, and (d) $\text{Si}^{4+}\text{-Si}^0$ evaluated from surface (step 0) to silicon substrate (step 22). In (a), the constant intensity from bulk Si is referred to as $\text{Si}^0\text{-BG}$, curves of the intensity ratio ($\text{Si}^0\text{-Si}^0\text{-BG}$) from the surface (~ 0.1) to the substrate (~ 1) show the sputter rate is controllable, and the T_{ox} 's are the same for the RTO and RSO SiO_2 . From (b)–(d), the RSO SiO_2 exhibits the less imperfect suboxide ($\text{Si}^{2+}, \text{Si}^{3+}$) and more stoichiometric oxide (Si^{4+}) at the near-surface region.

From the above discussion, XPS provides strong evidence to verify the reduction of suboxide in RSO SiO_2 . Compared to the anodic SiO_2 , we can see that the different growth conditions could cause variations in suboxide distribution. The more stoichiometric Si–O fraction accounts for the better insulator characteristics.

IV. CONCLUSIONS

In this work, suboxide characteristics are widely studied under different oxidation procedures. We found that the oxidation methods and the reaction kinetics greatly affect the suboxide distribution and concentration. From the layer-by-

FIG. 10. Gate leakage current densities versus oxide thickness of RTO and RSO SiO₂ with a gate bias of $V_G - V_{FB} = -1$ V.

layer composition analyses, we see that field-enhanced oxidation produces a thinner suboxide transition width for anodic SiO₂. We may attribute this finding to the low and stable reaction of silicon and oxidant under room temperature. In another aspect, SiO₂ prepared by RSO was examined in the same sequence to verify our previous supposition. It is supposed that temperature vibration can provide the high-kinetic O with more residual time to fill the suboxide dangling bonds. The gate-insulator property is strongly dependent on the oxide stoichiometry. The anodic SiO₂ exhibits a thinner transition region and the RSO SiO₂ exhibits a more-stoichiometric bulk oxide. Consequently, we believe that as oxide thickness is continuously reduced, the understanding

of the suboxide and the control of its distribution will become a major issue in gate-dielectric engineering.

ACKNOWLEDGMENT

The authors thank the National Science Council of the Republic of China for supporting this work under Contract No. NSC-92-2215-E-002-005.

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