Mechanism for generation of the phonon-energy-coupling enhancement effect for ultrathin oxides on silicon

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Large leakage-current reduction of SiO_2 due to the phonon-energy-coupling enhancement effect was confirmed by measuring the oxide thickness using a cross-sectional transmission electron microscopy. There is a critical temperature T_c. Rapid thermal processing (RTP) of SiO_2 at $T>T_c$ in pure N_2 leads to a destructive structure with large leakage current, while RTP at $T<T_c$ in pure N_2 does not change the oxide structure. After introducing a little amount of oxygen during RTP, the destructive structure can be converted to a constructive one by repairing the defects created during RTP at $T>T_c$. This leads to reduced leakage current. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2820383]

Recently, using Fourier transform infrared (FTIR) spectroscopy, my co-workers and I discovered phonon-energy coupling enhancement (PECE) between Si–O and Si–Si bonds, when SiO_2/Si samples were annealed using rapid thermal processing (RTP), leading to dramatic reduction of gate leakage current of SiO_2.[1–3] The leakage current of SiO_2 is reduced by two to five orders.[1–3] In addition, we also reported that the leakage current of high-*k* HfSiON is reduced by over one order of magnitude.[4] However, many people have been suspecting its authenticity. This is because there are several puzzling issues regarding the PECE effect. For example, in our early publications,[1–4] we did not present both the *I-V* and *C-V* curves of the same sample. People may be wondering whether this is caused by wrong measurement. Also, the mechanism for generation of the PECE effect was not clear at that time, so that even we could not reproduce the results using another piece of RTP equipment on a different location. It is unlikely that other researchers can reproduce our results. The key question is "what is the key factor that produces the PECE effect?"

In this paper, I will present the first cross-sectional TEM image of a RTP-processed SiO_2 sample to confirm the authenticity of the PECE effect. I will show the key factor that generates the PECE effect so that other researchers can reproduce it. I will also propose a possible mechanism for the generation of the PECE effect.

Si (100) wafers ($n=1\times10^{16}$ cm^{-3}) were prepared using conventional RCA cleaning. The wafers were loaded in furnace at 900 °C and oxidized at 900 °C in 100% O_2 for 5–20 s. After oxidation, one quarter of a wafer was used as a control sample without further processing and the other three quarters were subjected to RTP processing under various conditions. The front sides of samples were covered with a positive photoresist (PR) (Shipley 1813), which was then hard baked at 140 °C for 2 min. The backsides of the substrates were etched in buffered oxide etch for 30 s to remove the back oxide without damaging the front oxide. After thermal evaporation of 1000-Å-thick Al on the backsides of the samples, the positive PR was removed using PR remover (Shipley 1165). The samples were then annealed in 10% D_2 at 450 °C for 30 min. Finally, top electrodes (circular dots of Al) were formed by thermal evaporation of 1000-Å-thick Al through a shadow mask. No postmetal annealing (PMA) was carried out because for ultrathin oxides (<2.5 nm) PMA causes short circuit of Al metal-oxide semiconductor (MOS) capacitors. The oxide thickness was measured using an ellipsometer (Gaertner Scientific Co.).

Figure 1 shows *J-V* curves of a control SiO_2 sample without RTP and a sample processed in RTP at 1100 °C for 45 s. The oxide thickness is 24 Å before RTP and 25 Å after RTP. There are three orders of magnitude leakage-current reduction. Since for ultrathin oxide (<25 Å), it is very difficult to obtain correct *CV* curves, we usually use ellipsometry to measure the oxide thickness. In order to verify the oxide thickness obtained by ellipsometry, cross-sectional transmission electron microscope (TEM) imaging of the RTP-processed SiO_2 sample was carried out. The TEM image in Fig. 2 shows that the oxide thickness after RTP processing is 25 Å, which is in agreement with the ellipsometry measurement. This also suggests that the leakage current reduction is not due to the oxide thickness increase.

In our early publications,[1–3] we reported that RTP processing of SiO_2 in pure N_2 at 1050 °C for 60 s produces the PECE effect or leakage current reduction. However, when I began to reproduce the results using another piece of RTP

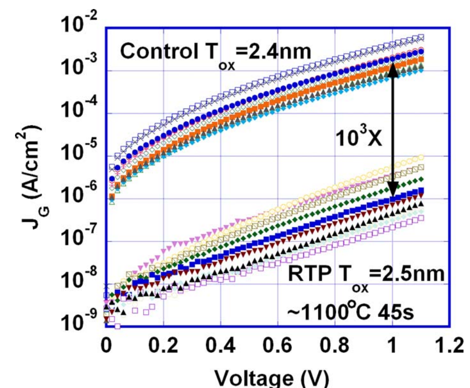

FIG. 1. (Color online) Current density–voltage curves of a control SiO_2 sample on *n*-type Si without RTP and that processed in RTP at ~1100 °C for 45 s. The V_{FB} is 0 V for the $Al/SiO_2/n$-Si MOS capacitors.

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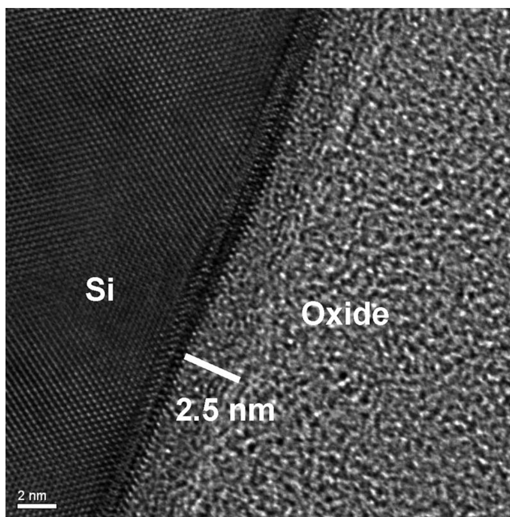

FIG. 2. Cross-sectional TEM of the same RTP-processed sample shown in Fig. 1. The oxide thickness is the same as that measured using ellipsometry. This verifies that the leakage current reduction is not caused by thickness increase.

equipment at a different location, I found that I could not reproduce the results published in Refs. 1–3. On contrary to the results in Refs. 1–3, I obtained negative results using pure N_2. In order to understand the mystery, I began to study the phenomenon extensively and quickly using oxynitiride (SiON) wafers provided by Mattson Co., because I have large quantity of Mattson oxynitride samples available. The Mattson SiON samples have only 14%N. Thus, they are mainly SiO_2. Therefore, the conclusion drawn from the oxynitride samples can be applied to SiO_2 samples and vise versa. Figure 3 shows the effect of RTP processing temperature on 20-Å-thick oxynitride [equivalent oxide thickness (EOT)=15 Å] on p-type Si using pure N_2 (research grade). After RTP processing at 960 and 980 °C, J_g of the oxynitride is very similar to that of the control oxynitride. After RTP processing at $T>990$ °C in pure N_2 leads to larger leakage current. Therefore, there is a critical temperature, which is 990 °C for oxynitride samples. For $T<990$ °C, the RTP process does not damage the oxynitirde. For $T>990$ °C, RTP process damages the oxynitride, causing high leakage current. These results suggest that high temperature RTP in pure N_2 induces a destructive structure.

In order to reproduce our early results in Refs. 1–3, I also explored various RTP process parameters including

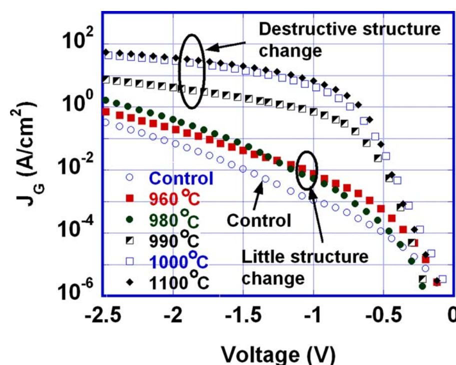

FIG. 3. (Color online) Leakage current density of silicon oxynitride with ~14%N (EOT~15 Å and physical thickness=20 Å) on p-Si with a flatband voltage $V_{FB}=-1.5$ V annealed using RTP in pure N_2 (research grade).

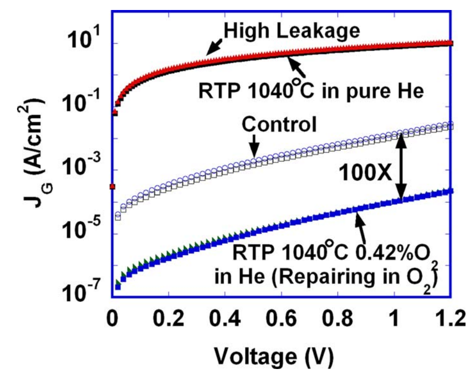

FIG. 4. (Color online) RTP treatment of SiO_2 (2.2 nm) on n-Si at 1040 °C for 60 s in pure He leads to high leakage current while RTP treatment at 1040 °C for 60 s in He mixed with 0.42% O_2 leads to reduced leakage current. T_{ox} is 2.3 nm after RTP. The V_{FB} is 0 V for the Al/SiO_2/n-Si MOS capacitors.

ramp up rate and cooling rate. All efforts led to negative results, i.e., either the leakage current was higher or remained the same as that of the control sample. There was not any leakage reduction after RTP. I strongly felt that a key factor was missed. Finally, I noticed that in our early research, after RTP, the oxide always had slight thickness increase (1–2 Å).[1–3] In the new RTP setup, there is no thickness increase at all after RTP. Therefore, I realized that there must be something in N_2, causing the leakage current reduction.

In order to imitate the 1–2 Å oxide thickness increase, I added a little amount of oxygen in the pure He during RTP. It should be noted that there was not any difference in experiments when using pure N_2 or using pure He, although the RTP cooling rate is faster by using He. In this experiment, 22-Å-thick SiO_2 samples on n-Si substrates were used. As shown in Fig. 4, RTP of SiO_2 at 1040 °C for 60 s in pure He leads to high leakage current, consistent with that of the oxynitride samples in pure N_2. The leakage current density (J_g) at V_G=1 V is 8.1 A/cm^2, which is two and half orders of magnitude higher than that of the control oxide (1.3×10^{-2} A/cm^2). By introducing 0.42% O_2 into the pure He during RTP, this destructive structure can be turned into constructive structure by regrowth of ~1 Å oxide. It is amazing that after regrowth of ~1 Å oxide, the leakage current density of the oxide (~23 Å) has been reduced from 8.1 to 1×10^{-4} A/cm^2 at V_G=1 V (see Fig. 4). Compared to the control sample, there is near 100 times reduction of leakage current. The C-V measurement shown in Fig. 5 also suggests that a slight regrowth occurs and the interfacial properties and flatband voltage remain the same as those before RTP. Therefore, our previous published results in Refs. 1–5 were obtained by accidentally using N_2 containing a small amount of O_2, probably leakage from the air into the RTP setup.

These experiments also shed light on understanding of the fundamental mechanism for generation of the PECE effect. As shown in Fig. 3, there is a critical temperature T_c. In this case, T_c=990 °C for the oxynitride with an EOT of 15 Å. It might be different for oxides with different thicknesses. When the RTP processing temperature is lower than T_c, the RTP process does not create any structure change, so that the leakage current remains the same as that of the control sample. Therefore, for $T<T_c$, no PECE effect is generated. When the RTP processing temperature is higher than

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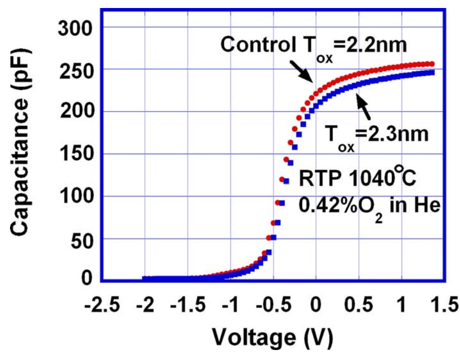

FIG. 5. (Color online) High-frequency (100 kHz) capacitance-voltage curves of the control sample and the sample treated in RTP at 1040 °C for 60 s in He mixed with 0.42% O_2, as shown in Fig. 4. The diameter of the circular dots is 150 μm.

T_c, the RTP process creates the oxide structure change, which is the necessary condition for the PECE effect. The supporting evidence is the FTIR spectra of SiO_2/Si samples.[1–3] After RTP in O_2 at $T=1050$ °C, there was ~45% enhancement of IR absorption at ~460 cm^{-1} (Si–O rocking mode).[1–3] However, after RTP in pure He (without O_2), there was only ~9% enhancement of IR absorption at ~460 cm^{-1} (will be published elsewhere). It should be noted that after high temperature heat treatment of oxide, there might be always some small increase in IR absorption. In addition, after RTP processing in trace O_2, the Si breakdown voltage is also increased by 0.3 V.[5] It is unlikely that the bulk Si structure can be changed in RTP, because it is too thick. Therefore, the only explanation is the energy coupling from Si–Si to Si–O bonds. Meanwhile, this high temperature process also generates defects, causing high leakage current. By adding a little amount of oxygen in N_2 or He, the defects can be repaired so that the full benefit of the PECE effect shows up. The criterion of complete repairing is regrowth of at least 1 Å (because it is hard to measure 1 Å accurately using ellipsometry, 1.5–2 Å regrowth is suggested). Because it is difficult to monitor the concentration of oxygen accurately, the most important parameter for monitoring is the oxide thickness regrowth.

The leakage current reduction is closely related to the RTP temperature in addition to oxygen repairing. After carefully evaluation of all factors in experiments, I found that for control oxides of 20–24 Å, after oxide regrowth of 1 Å in RTP, the leakage current reduction is ~1.5 orders of magnitude at 1040 °C, ~2 orders of magnitude at 1080 °C, ~2.5 orders at 1100 °C, and ~3 orders at 1120 °C. The leakage-current reduction of five orders of magnitude reported in Refs. 1–3 can only be reproduced using lower quality oxide grown in furnace at 800–850 °C. Although our early oxide was grown in furnace at 900 °C,[1–3] substantial part of the thin oxide was actually grown in O_2 from air at 800–850 °C during wafer loading at 800 °C with the quartz tube opened. The lower-quality oxide (bad oxide) has larger leakage current (J_g). For example, a control oxide with T_{ox} of 23–24 Å grown at 800–850 °C has a J_g of $1.0-1\times10^{-1}$ A/cm^2. After proper RTP processing, it becomes $1\times10^{-5}-1\times10^{-6}$ A/cm^2, leading to five order reduction. However, for a good oxide with T_{ox}=23–24 Å, J_g is only $1\times10^{-2}-1\times10^{-3}$ A/cm^2. After RTP, it is *still* $1\times10^{-5}-1\times10^{-6}$ A/cm^2, resulting in only three order reduction. Good oxide can be either SiO_2 obtained by loading a wafer at 900 °C and then oxidizing it at the same temperature or SiON from industry (EOT ~ 15 Å).

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