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

Zhi Chen
Department of Electrical and Computer Engineering and Center for Nanoscale Science and Engineering, University of Kentucky, Lexington, Kentucky 40506, USA

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Large leakage-current reduction of SiO₂ 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 SiO₂ at $T > T_c$ in pure N₂ leads to a destructive structure with large leakage current, while RTP at $T < T_c$ in pure N₂ 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 SiO₂/Si samples were annealed using rapid thermal processing (RTP), leading to dramatic reduction of gate leakage current of SiO₂.¹–³ The leakage current of SiO₂ 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 publications¹–³ we did not present both the $J$-$V$ 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 SiO₂ 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 ($n=1 \times 10^{16}$ cm$^{-3}$) were prepared using conventional RCA cleaning. The wafers were loaded in furnace at 900 °C and oxidized at 900 °C in 100% O₂ 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 back sides 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 back sides of the samples, the positive PR was removed using PR remover (Shipley 1165). The samples were then annealed in 10% D₂ 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 SiO₂ 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 SiO₂ 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 publications¹–³ we reported that RTP processing of SiO₂ in pure N₂ 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. 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 N₂. In order to understand the mystery, I began to study the phenomenon extensively and quickly using oxynitride (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 SiO₂. Therefore, the conclusion drawn from the oxynitride samples can be applied to SiO₂ samples and vice 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 N₂ (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 N₂ 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 oxynitride. For T > 990 °C, RTP process damages the oxynitride, causing high leakage current. These results suggest that high temperature RTP in pure N₂ induces a destructive structure.

In order to reproduce our early results in Refs. 1–3, I also explored various RTP process parameters including 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). In the new RTP setup, there is no thickness increase at all after RTP. Therefore, I realized that there must be something in N₂, 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 N₂ or using pure He, although the RTP cooling rate is faster by using He. In this experiment, 22-Å-thick SiO₂ samples on n-Si substrates were used. As shown in Fig. 4, RTP of SiO₂ at 1040 °C for 60 s in pure He leads to high leakage current, consistent with that of the oxynitride samples in pure N₂. The leakage current density (L) of V_D=1 V is 8.1 A/cm², which is two and half orders of magnitude higher than that of the control oxide (1.3 × 10⁻² A/cm²). By introducing 0.42% O₂ 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/cm² at V_D=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 N₂ containing a small amount of O₂, 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 T_c, the RTP process induces a destructive structure by regrowth of ~1 Å oxide.
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 O2 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 (Jg). For example, a control oxide with Tox of 23–24 Å grown at 800–850 °C has a Jg of 1.0–1 × 10−1 A/cm². After proper RTP processing, it becomes 1 × 10−5–1 × 10−6 A/cm², leading to five order reduction. However, for a good oxide with Tox=23–24 Å, Jg is only 1 × 10−2–1 × 10−3 A/cm². After RTP, it is still 1 × 10−2–1 × 10−3 A/cm², resulting in only three order reduction. Good oxide can be either SiO2 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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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% O2, as shown in Fig. 4. The diameter of the circular dots is 150 μm.