Understanding a New Effect: Correlation between Phonon-Energy-Coupling Enhancement and the Energy-Band-Structure Change of the SiO_2/Si System

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1. INTRODUCTION

The SiO_2/Si system is of technological importance because metal-oxide-semiconductor (MOS) transistor, a key component in modern integrated circuits, uses SiO_2 as a gate insulator. Because of increased integration, the gate insulator of MOS transistors is becoming thinner and thinner (currently ~1-2 nm), leading to large leakage current through the gate insulator, which contributes to a major portion of power consumption of integrated circuits. Currently high permittivity (high-k) oxides are used for reduction of the gate leakage current. However, an interfacial SiO_2 layer is required for high-k oxides for improving electron mobility. Therefore, a method for reducing leakage current and improving reliability of SiO_2 is very important. It is therefore necessary to understand and the Si-O and Si-Si bonds in the SiO_2/Si system.

Recently a new effect, phonon-energy-coupling enhancement (PECE), induced by rapid thermal processing (RTP) of SiO_2, was reported to cause a large leakage-current reduction of SiO_2 (10^2-10^5 fold) [1-6]. Leakage current reduction of a high-k gate oxide HfSiON on Si was also reported due to existence of Si-O bonds in HfSiON [7]. The basic theory for the PECE effect (See Fig. 1) is the extension of the Van de Walle and Jackson theory on hydrogen/deuterium isotope effect for hot-electron degradation [8]. However, this theory can only explain why the Si-O bonds become stronger when the phonon-energy coupling between the Si-O rocking mode (~480 cm^{-1}) and the Si-Si TO mode (~468 cm^{-1}) is enhanced. There is a missing link between the tunneling current reduction and the strength of chemical bonds. How could stronger Si-O bonds cause a tunneling-current reduction of SiO_2? In this abstract, using the Fourier transformed infrared (FTIR) spectroscopy and electrical characterization, we will show that there is a correlation between the phonon-energy-coupling enhancement and the energy-band-structure change of the SiO_2/Si system. It is well known that the energy band structure of a solid is determined by its crystal structure, temperature, and pressure [9]. It is therefore very important from the viewpoint of fundamental science that there is another way to alter the energy band structure of a solid!

2. EXPERIMENTAL

In our experiments, for FTIR studies, we used n^+ silicon wafers ($n=1\times10^{19}$ cm^{-3} and $\rho=5\times10^{-3}$ Ω-cm) with (100) orientation, 2 inch in diameter, and ~0.3 mm in thickness. The wafers were prepared using conventional RCA cleaning. Thermal oxidation was performed in 100% O_2 at 900°C. Because it is unlikely to have the exact same oxide for each wafer, in order to have accurate comparison, the oxidized wafer was cut into two half-wafers. One half-wafer was used as a control sample without further processing and the other half was subjected to rapid thermal processing (Modular Process Technology Co. RTP-600S). The detailed process can be found in reference [4]. Infrared absorbance spectra of the processed wafers were obtained immediately using a Fourier Transform Infrared (FTIR) Spectrometer (Thermo Electron Co., Nexus 470), in conjunction with a variable angle specular reflectance accessory (Pike VeeMax II). The spectral range was selected from 400 to 900 cm^{-1}, with a resolution of 8 cm^{-1}. After this, the RTP processed wafer was annealed in furnace in 100% D_2 or 100% H_2 at 450 °C for 30 minutes, and then infrared spectra of the sample were obtained again. The MOS capacitors were also fabricated by direct evaporation of 120-nm-thick aluminium layer on top of the oxide using a shadow mask and 100 nm-thick Al layer at the back of the exposed n^+-substrate. The oxide at the back of the wafer was removed in buffered oxide etch (BOE) after RTP. The MOS capacitors were annealed at 450°C in 100% D_2 or 100% H_2 for 30 min. The oxide thickness was measured using an ellipsometer (Gaertner Scientific Co.). The current-voltage curves were measured using Agilent 4155B semiconductor analyzer. High frequency C-V curves of MOS capacitors were measured using Keithley 590 CV analyzer.

3. RESULTS AND DISCUSSION

Based on the theory shown in Fig. 1, the phonon coupling enhancement occurs at ~480 cm^{-1} (Si-O rocking mode), not at ~1080 cm^{-1} (Si-O the stretch mode). In experiments, the absorbance of Si-O stretch mode (See Fig. 2) is only slightly increased (~10%) while that of the Si-O rocking mode is increased by 36% (See Fig. 3a). This agrees very well with the theory. As shown in Fig. 3, there is also a one-to-one correlation between the IR absorbance enhancement of the Si-O rocking mode and the leakage current reduction. This strongly suggests that phonon-energy-coupling enhancement causes the leakage current reduction. For ultrathin oxide (<3 nm), the leakage current is dominated by direct tunneling current, for which there is not any well-accepted model. In order to understand the physics behind the leakage current reduction, we studied the leakage current of thick oxide (~10 nm) using the well-known Fowler-Nordheim tunneling model. Figure 4 shows the leakage current of a control SiO_2 (T_{ox} =10.2 nm) and that of SiO_2 (T_{ox}=10.6 nm) after RTP processing in trace O_2. There is only ~4% increase in oxide thickness, but there is a leakage current reduction of over 2 orders of magnitude after RTP. This slight thickness increase can not explain the large leakage-current reduction. By fitting the leakage currents shown in Fig. 4 using the Fowler-Nordheim tunneling current model, it can be found in Fig. 5 that the slope of the line is increased after RTP. If the leakage-current reduction were caused by oxide thickness increase, the slope would remain the same. The slope represents the product of the effective mass of electrons and the conduction band offset, which are both related to the energy band structure. Assuming that the effective mass remains the same, we found that the conduction band offset of SiO_2/Si is increased by 0.2 eV after RTP (See Fig. 5). Therefore, the above experiments strongly suggest that phonon-energy-coupling enhancement causes energy band-structure change of the SiO_2/Si system.

Because there is no theory for energy-band-structure change due to phonon-energy coupling, we may propose a simple analogy to understand this phenomenon. For a large bandgap material like SiO_2, tightly bound electron model is more suitable. Electrons are largely bounded to the atomic core and the band structure is closely related to the discrete energies of electrons in isolated atoms, similar to what was described in the molecular orbital theory [10,11]. Thus, the valence band of a solid state material is equivalent to the energy of valence electrons in isolated atoms and the conduction band of a solid state material is equivalent to the energy of free electrons in isolated atoms. Therefore, bandgap may be considered as the energy needed to free a covalence electron in two bounded atoms (Si-O bond). In order to free the electrons, the Si-O bonds have to be broken. Because of phonon coupling, additional energy is needed to break the Si-O bonds. Therefore, the energy bandgap of SiO_2 is increased due to the enhanced phonon coupling. Additional supporting evidence is that larger band gap semiconductors such as SiC and GaN have higher breakdown fields (stronger bonds).

4. CONCLUSION

In this paper, we showed evidence to link the phonon energy coupling to the energy band structure change of the SiO_2/Si system. This may provide better understanding of the new effect, phonon-energy coupling enhancement, and its implication to the tunneling current reduction.

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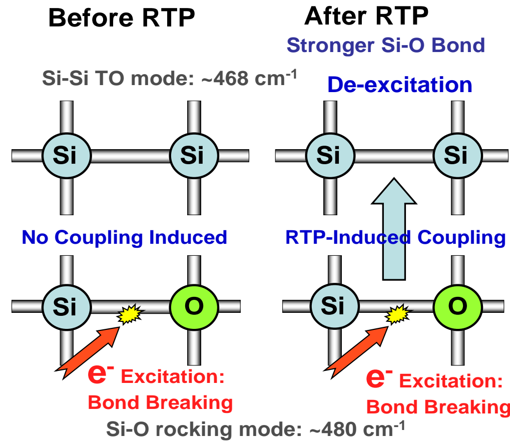

Figure 1 Schematic theory of the PECE effect: electron excitation causes Si-O bond breaking and de-excitation by phonon coupling strengthens the Si-O bonds. Proper RTP processing induces the enhanced coupling at the Si-O rocking mode.

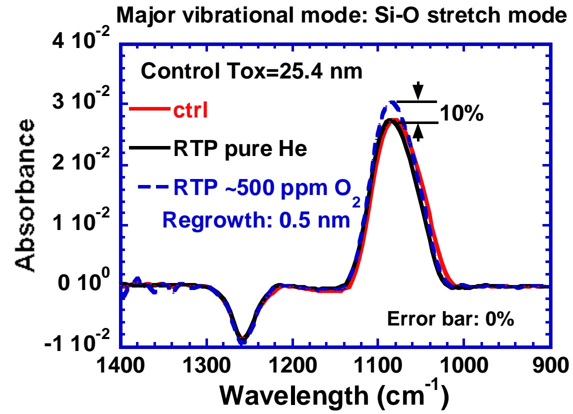

Figure 2 FTIR spectra of Si-O stretch mode. No vibrational frequency shift suggests that there is no stoicheometric change after RTP. There is only slight increase in absorbance of stretch mode after RTP in trace O_2, suggesting no coupling for the stretch mode.

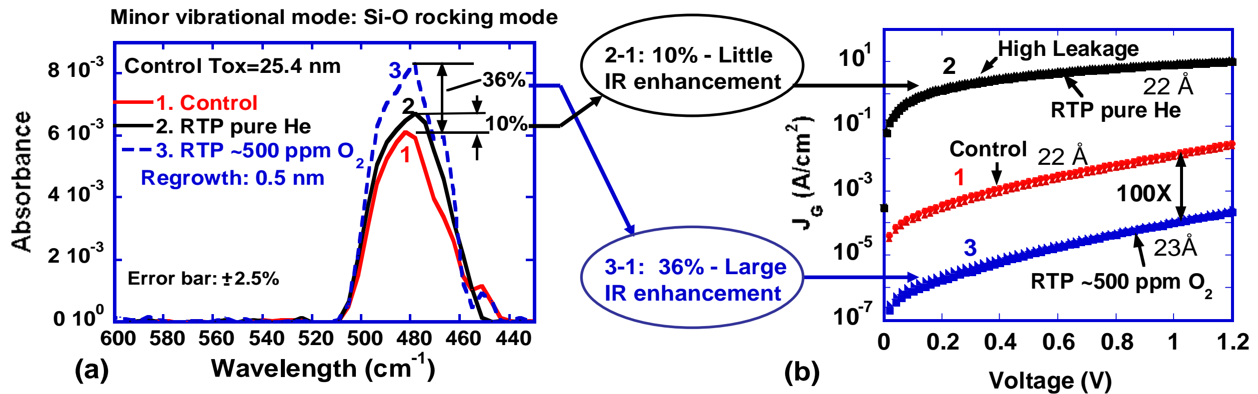

Fig. 3 (a) FTIR spectra of the Si-O rocking mode of SiO_2 samples processed by RTP in pure He and in trace O_2 and (b) their corresponding leakage currents. More IR absorbance enhancement leads to leakage current reduction, suggesting phonon-energy coupling causes the leakage current reduction.

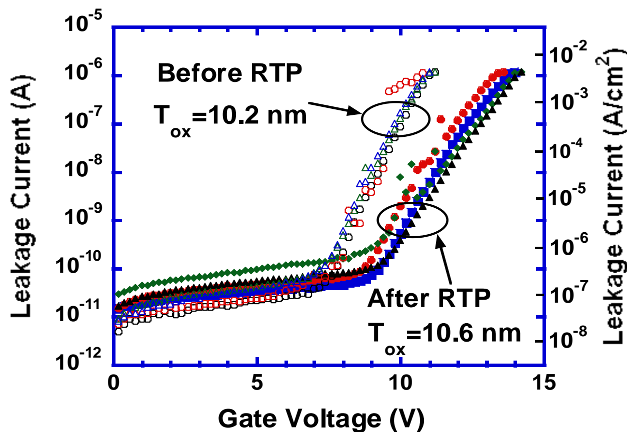

Figure 4 Gate leakage (tunnelling) currents of silicon MOS capacitors on n-Si with area of 4.24×10^{-4} (cm^2) for a control sample and for the RTP sample (1050°C in trace O_2 for 4 min.).

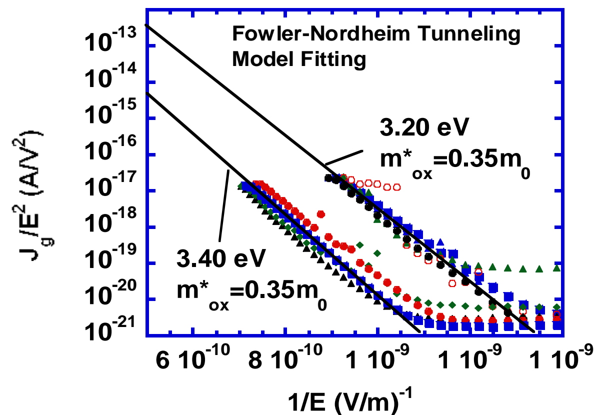

Figure 5 Fitting the tunneling current data in Fig. 4 using the Fowler-Nordheim tunneling model. After RTP, the slope has been changed, suggesting that the energy band structure of SiO_2 has been changed, i.e. either the conduction band offset or the effective mass has been changed.