Evidence for energy coupling from the Si–D vibration mode to the Si–Si and Si–O vibration modes at the SiO_2/Si interface

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In order to verify Van de Walle and Jackson's theory on the isotope effect of the Si–H/D bonds resistant to hot-electron excitation [C. G. Van de Walle and W. B. Jackson, Appl. Phys. Lett., **69**, 2441 (1996)], we measured the Si–H, Si–D, and other vibrational modes in the oxidized silicon wafers annealed in hydrogen and deuterium using Fourier-transform infrared (FTIR) spectrometry. Our FTIR data suggest that the frequency for the Si–D bending mode at the SiO_2/Si interface is $490\ cm^{-1}$. Our experimental data support Van de Walle and Jackson's theory with some modification. Their theory is correct for the experiments of breaking Si–H/D bonds using scanning tunneling microscope where no oxide involves. In the SiO_2/Si case, the de-excitation of the Si–D bond may be due to the energy coupling from the Si–D bending mode to two vibrational modes, i.e., Si–O TO mode and the Si–Si TO phonon mode. Van de Walle and Jackson only pointed out coupling to Si–Si TO phonon mode. The strongest coupling might happen between the Si–D mode and the Si–O TO mode. Therefore, the oxide may play a crucial role in energy dissipation of the Si–D bond in metal–oxide–semiconductor devices. © *2003 American Institute of Physics.*
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The giant hydrogen/deuterium (H/D) isotope effect was discovered in the study of the desorption of hydrogen (H) and deuterium (D) on silicon in UHV using scanning tunneling microscopy (STM).[1,2] This effect was later used in passivation of the SiO_2/Si interface, leading to large improvement of the hot-electron-related lifetime of metal–oxide–semiconductor (MOS) transistors using the deuterium process.[3–9]

Van de Walle and Jackson[10,11] proposed a theory to explain this remarkable isotope effect, i.e., the Si–D bond is more resistant to hot-electron excitation than the Si–H bond. The Si–H/D bond breaking at the SiO_2/Si interface is caused by two competing processes. One is that the energy of the bonds is accumulated through excitation by energetic hot electrons. The other process is de-excitation where the bond energy is taken away by coupling between the Si–H/D vibrational modes and substrate phonons. Van de Walle and Jackson[10] suggested that the vibrational frequency of Si–D bending mode is close to the Si–Si TO phonon mode ($460\ cm^{-1}$), resulting in energy coupling between the Si–D bending mode and the Si–Si TO phonon mode. This de-excitation efficiently strengthens the Si–D bond. On the other hand, because the vibrational frequency of the Si–H bond is far away from the Si–Si TO phonon mode, there is no energy coupling between the Si–H bending mode and the Si–Si TO phonon mode, leading to Si–H bonds more vulnerable to hot-electron excitation.

However, no experimental data exist regarding vibrational frequency of the Si–D bond at the SiO_2/Si interface to support the earlier theory. Although the vibrational frequency ($510\ cm^{-1}$) of the Si–D bond is reported for deuterated amorphous Si (α-Si),[12] the chemical environment in the oxidized single crystal Si (SiO_2/Si structure) is very different from that in α-Si. In order to understand fundamental mechanisms of isotope effect of hot-electron degradation of MOS transistors, it is of great importance to measure the vibrational frequency of the Si–D bond and other chemical bonds in the SiO_2/Si structure and study the energy coupling from the Si/H(D) bonds to other vibrational modes. In this letter, we present the experimental measurement of vibrational modes at the SiO_2/Si interface by Fourier-transform infrared (FTIR) spectrometry and study the correlation between the vibrational modes and energy dissipation of the Si–D bond.

The n^+ silicon wafers with (100) orientation, 50 mm (2 in.) in diameter, and ~0.3 mm in thickness were used in our experiments. Because high-density electrons are present at the SiO_2/Si interface in MOS transistors, we use n^+ silicon wafers. The wafers were prepared using conventional Radio Corporation of America (RCA) cleaning. The thermal oxidation was performed in dry O_2 at a constant temperature of 1050 °C (1323 K) for 15 min. The thickness of oxide layer was measured to be 32 nm. Some of the oxidized wafers were annealed at 450 °C in 100% H_2 and 100% D_2 for 60 min separately. Because it is unlikely to have the same oxide for each wafer, in order to have accurate comparison, the oxidized wafer was cut into two half-wafers. One half-wafer was annealed in H_2 or D_2 and the other half was used for comparison. Infrared absorbance spectra of the processed wafers were obtained immediately by a FTIR spectrometer (Thermo Nicolet 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 $8\ cm^{-1}$. All spectra were base line corrected after proper correction for CO_2 peaks from the air by using the OMNIC software.

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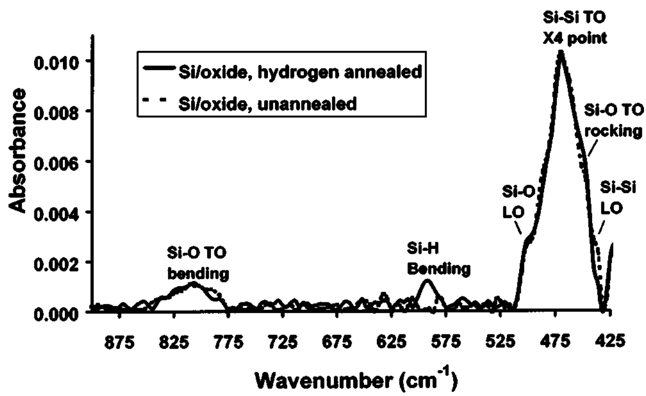

FIG. 1. FTIR spectra of Si/SiO_2 wafers before (dashed) and after hydrogen annealing (solid), oxide thickness 32 nm, spectral resolution $8\ cm^{-1}$, 128 scans, 65° grazing angle.

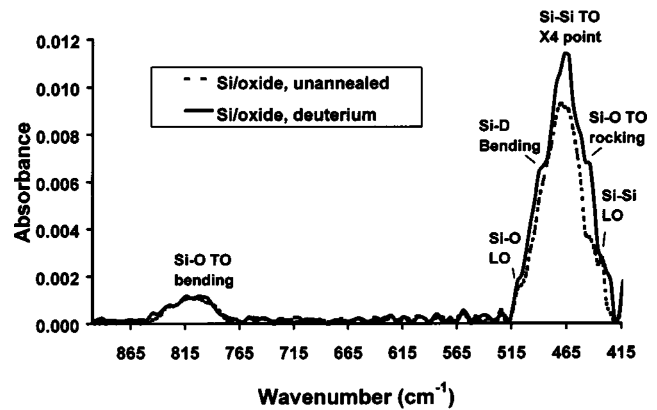

FIG. 2. FTIR spectra of Si/SiO_2 wafers before (dashed) and after deuterium annealing (solid), oxide thickness 32 nm, spectral resolution $8\ cm^{-1}$, 128 scans, 65° grazing angle.

Figure 1 shows the FTIR spectra of a SiO_2/Si sample with oxide thickness of ~32 nm before and after hydrogen anneal. The two curves (before and after hydrogen anneal) are very similar. The peak ($592\ cm^{-1}$) appears uniquely in the H-annealed sample, which is determined to be Si–H bending mode. There are five other peaks appearing in both curves with a slight difference in magnitude, which might be ascribed to the slight structure change due to the thermal process in annealing. The main peak at $468\ cm^{-1}$ may be ascribed to the Si–Si TO phonon mode as suggested by Van de Walle[10,11,13] and Lin.[14] The wave number of $806\ cm^{-1}$ is Si–O TO bending mode.[15,16] The peak at $505\ cm^{-1}$ is Si–O LO mode[16] and at $448\ cm^{-1}$ is Si–O TO rocking mode.[15,16] The peak at $435\ cm^{-1}$ is suggested to be Si–Si LO mode.[17] Table I summarizes the vibrational modes of the as-oxidized, H-annealed, and D-annealed SiO_2/Si samples.

Figure 2 shows the FTIR spectra of a SiO_2/Si sample with oxide thickness of ~32 nm before and after deuterium anneal. The peak at $490\ cm^{-1}$ uniquely appears in the D-annealed SiO_2/Si sample, which should be the Si–D bending mode. The other five peaks are almost the same as those in the as-oxidized samples. It should be noted that there is no experimental data available for Si–H and Si–D vibrational modes in the oxidized single crystal Si samples. The existing data of the Si–H and Si–D vibrational modes were from the amorphous Si samples.[12,18] There is a striking difference between our data from the single crystal Si and the data from amorphous Si.[12,18] At first, the wave number of the Si–Si TO phonon mode in our sample is ~$468\ cm^{-1}$, which is very close to the value ($463\ cm^{-1}$) obtained by other techniques.[13] However, the vibrational mode of the Si–Si TO phonon mode in the amorphous Si sample is $495\ cm^{-1}$ as reported by Wei *et al.*[12] There is a difference of $27\ cm^{-1}$ between the single crystal Si sample and the amorphous Si sample. We believe that this is due to the structure difference between the single crystal Si and amorphous Si. Second, it is more interesting to note that the vibrational frequency of Si–D bond ($490\ cm^{-1}$) in our oxidized single crystal sample (see Fig. 2) is $20\ cm^{-1}$ lower than that ($510\ cm^{-1}$) in the amorphous Si.[12,18] Finally, the Si–H vibrational mode ($592\ cm^{-1}$) in our oxidized single crystal sample (see Fig. 1) is ~$50\ cm^{-1}$ lower than that ($640\ cm^{-1}$) in the amorphous Si sample.[12,18]

Of the most importance, it is found in Fig. 2 that the absorbance of the Si–Si TO phonon mode and the Si–O TO rocking mode are all enhanced significantly (>25%) after deuterium anneal. There is not much difference for absorbance of the Si–Si TO mode and Si–O TO rocking mode after hydrogen anneal (see Fig. 1). This exclusively suggests that there is energy coupling from the Si–D vibrational mode to the Si–Si TO phonon mode and the Si–O TO rocking mode. This proves that Van de Walle and Jackson's theory is correct for experiments of STM-induced breaking of Si–H/D bonds where no oxide involves.[1,2] For the MOS transistor case, there may be two channels for de-excitation of Si–D bonds: energy coupling to the Si–O TO mode and to the Si–Si TO mode. The strongest coupling may happen between the Si–D mode and the Si–O TO mode rather than Si–Si TO phonon mode because more enhancement of absorbance of the Si–O TO mode (~60%) than the Si–Si TO phonon mode (~25%) is found in the deuterium-annealed samples (see Fig. 2).

In summary, our FTIR data support the basic point of

TABLE I. Vibrational modes obtained by the FTIR measurement.

Wave number (cm^{-1})	806	592	505	490	468	448	435
Type of Vibrational Modes	Si–O TO bending[a]	Si–H bending	Si–O LO[b]	Si–D bending	Si–Si TO[c]	Si–O TO rocking[d]	Si–Si LO[e]
In as-oxidized Si	Yes	No	Yes	No	Yes	Yes	Yes
In H-annealed SiO_2/Si	Yes	Yes	Yes	No	Yes	Yes	Yes
In D-annealed SiO_2/Si	Yes	No	Yes	Yes	Yes	Yes	Yes

[a]References 15 and 16.
[b]Reference 16.
[c]References 10, 11, and 13.
[d]References 15 and 16.
[e]Reference 17.

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