Direct evidence of multiple vibrational excitation for the Si—H/D bond breaking in metal–oxide–semiconductor transistors

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Experiments based on substrate hot-electron generation due to impact ionization are designed to reveal whether the hydrogen/deuterium (H/D) isotope effect is caused by the density of electrons or their energy. It is found that the H/D isotope effect for hot-electron degradation is strongly dependent on the density of hot electrons presented at the interface. This suggests that the multiple vibrational excitation (heating) plays a major role in hot-carrier degradation of metal–oxide–semiconductor (MOS) transistors. Because of the unique nature of multiple vibrational excitation (heating), low-energy electrons are able to break Si—H/D bonds in MOS devices. This implies that hot-electron degradation is still an important reliability issue even if the drain voltage is scaled down to below 1 V. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1516863]

The study of the desorption of hydrogen (H) and deuterium (D) on silicon in an ultrahigh vacuum (UHV) by Scanning Tunneling Microscopy (STM) led to the discovery of the giant H/D isotope effect.[1–3] It was later used in passivation of the SiO_2/Si interface, leading to a large improvement of hot-electron lifetime of metal–oxide–semiconductor (MOS) transistors.[3–7] It is known that the desorption mechanisms for the Si—H/D bonds by STM are multiple vibrational excitation at low voltage and direct excitation at high voltage.[8,9] However, the chemical environment of the SiO_2/Si interface in the MOS devices is very different from that of Si in an UHV, because in the MOS transistors, the electrons not only directly excite the Si—H/D bonds, but also are injected into the oxide. Recently, we showed that electrons that are injected into the oxide may not break Si—H/D bonds and only electrons that remain in the channel (not overcome the oxide/Si barrier) break the Si—H/D bonds.[10,11] Although it was suggested that the mechanisms for breakage of Si—H/D bonds in MOS transistors should be analogous to the explanation of the STM experiments,[3,4] there is no direct experimental evidence to support the suggestion. The multiple vibrational excitation mechanisms suggest that the interface trap generation at the Si/SiO_2 is strongly dependent on the current density not the voltage. In this letter, we present experimental results to show the quantitative H/D isotope effect is dependent on the channel current density, which supports the multiple vibrational excitation mechanisms.

In the experiments, 0.35 μm 3.3 V n-type MOS (n-MOS) transistors with a gate oxide with thickness of 65 Å were used. The devices consist of phosphorus-implanted low-doped drain source and drain, oxide spacers, and three levels of metallization. Two groups of identical n-MOS transistors were used. One group was annealed in 100% H_2 at 450 °C for 3 h, and the other one annealed in 100% D_2 at 450 °C for 3 h. The experiment was designed to produce hot electrons by impact ionization at the interface from the depletion region in the substrate. As shown in Fig. 1, the source and drain were grounded, 1 V was applied to gate, and V_B ranging from -10 to -11 V was applied to the substrate. The experiment was carried out in dark. The degradation behavior and the isotope effect were studied using G_m degradation and charge pumping test. The degradation test was carried out on an automatic system consisting of Agilent 4155B semiconductor parameter analyzer, Agilent E5250A switching matrix, and HP8160A pulse generator.

It is critical to create a scenario where the number of electrons increases rapidly while their energy is relatively constant. In this way, any effect that appears in this situation can be ascribed to the number of electrons rather than electron energy. The experiment shown in Fig. 1 is exactly what we need. Because the source and drain are grounded and the substrate is biased at ~ -11 V, the surface potential between the SiO_2/Si interface and the substrate is 10 V,[12] which is

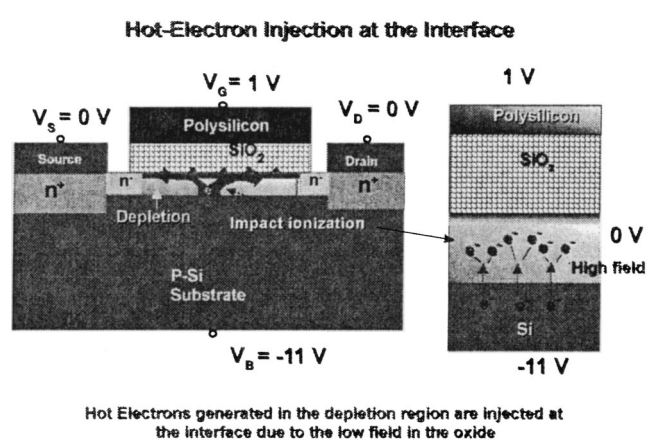

FIG. 1. Electrical configuration of the MOS device and the principle for the experiments.

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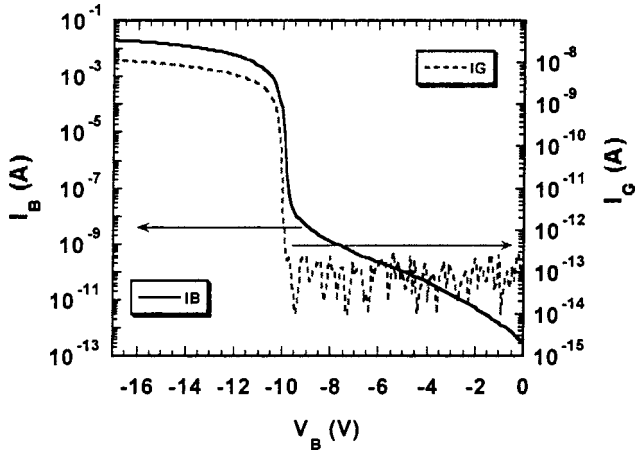

FIG. 2. Substrate current and gate current. The substrate current passes through the source and drain ($I_B = I_S + I_D$).

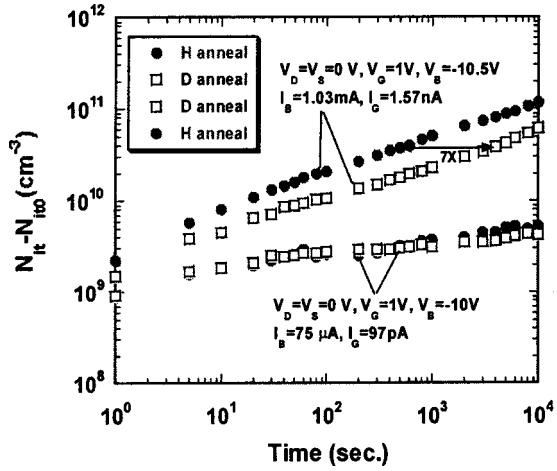

FIG. 3. Interface trap generation vs the stress time. The current presented at the SiO_2/Si interface is 75 μA and 1.03 mA. (Note: Although only two points are shown here, more data can be found in Fig. 4.)

only 1 V lower than that at the source and drain. The electric field E_s at the SiO_2/Si interface is 9.6×10^5 V/cm and the electric field at the $p-n$ junction of the source and drain is 1×10^6 V/cm.[12] The electric field E_s across the depletion region is high enough to produce strong impact ionization in the depletion region near the SiO_2/Si interface as shown in Fig. 1. Because of the low gate voltage (1 V), the amount of hot electrons injected into the gate oxide is limited and majority of hot electrons can be collected at the source and drain, i.e., $I_B \approx I_D + I_S$. The substrate current I_B represents the amount of hot electrons that are present at the SiO_2/Si interface. Therefore, the substrate current is equal to the channel current. Figure 2 shows the substrate current I_B and gate current I_G as V_B varies from 0 to -17 V. There is a rapid increase in hot electrons from 75 μA to 1.03 mA when V_B varies from -10 to -10.5 V by impact ionization in the depletion region. It should be noted that from 75 μA to 1.03 mA, the hot-electron energy only increases by 0.5 eV while number of electrons is increased by over ten times. This is a case that shows an effect caused by the number of hot electrons not by their energy.

As shown in Fig. 2, from the substrate voltage of -9.5 to -10.5 V, both the channel current and gate current increase by approximately 5 orders of magnitude. This scenario is similar to the impact ionization inside the pinch-off region near drain for regular hot-carrier stress (For example, $V_G = 1/2V_D$, $V_D = 5$ V, $V_S = V_B = 0$ V) where the substrate current increases exponentially.[13] As shown in Fig. 1, electrons (the minority carrier) in p-Si substrate are injected into the depletion region where the electric field is established. When the field is low, the injected electrons do not gain enough energy to produce electron–hole pairs. Therefore, the current is small until V_B reaches -9.5 V (See Fig. 2). As suggested by Ning *et al.*,[14] the increase in the drain current at large substrate voltage was due to multiplication inside the depletion region. Because our experiments were carried out in the dark and the minority carrier in the p-Si substrate was the only source, a large substrate voltage (>9 V) was needed to produce multiplication inside the depletion region. Although the average energy of electrons in the depletion region might be smaller than qV_B as suggested by DiMaria[15] but still correlated with V_B. For qualitative comparison, as long as the variation of the substrate voltage is small (5% or 0.5 V/10 V), the variation of energy of electrons should be small, too.

Figure 3 shows the interface trap generation of hydrogenated and deuterated MOS transistors stressed at $I_B = 75\ \mu$A ($V_B = -10$ V) and $I_B = 1.03$ mA ($V_B = -10.5$ V). It can be seen that at a lower level of hot-electron current ($I_B = 75\ \mu$A), the interface trap generation rate is smaller than that at $I_B = 1.03$ mA. It is notable to see that at low substrate current, the interface trap generation rate for the deuterated transistor is the same as that of the hydrogenated transistor, i.e., *there is no isotope effect*. Here, the isotope effect is defined as the ratio of the stress time for the deuterated transistor over that for the hydrogenated transistor for the same amount of trap generation. When I_B is increased to 1.03 mA while $|V_B|$ is increased to 10.5 V, *the isotope effect* ($7\times$) *is clearly seen* as shown in Fig. 3. *This shows that isotope effect is dependent on the density of hot electrons, which is the indicator of multiple vibrational excitation*. The multiple vibrational excitation mechanisms suggest that defect generation at the Si/SiO_2 is strongly dependent on the current density not the voltage. The multiple vibrational excitation mechanisms were proposed to explain the experimental phenomena in scanning tunneling microscope induced desorption of H/D on Si. We can not directly compare experimental data such as the dependence of the desorption rate on current density in the STM system with those in the Si/SiO_2 system, because the situation in the Si/SiO_2 system is completely different from that in the STM experiments. The fundamental principle of multiple vibrational excitation lies in its strong dependence on current density. The several orders of magnitude increase in current indeed suggest that the isotope effect is correlated with the multiple vibrational excitation.

Figure 4 shows more experimental data when I_B varies from μA level to mA level. For the channel current less than 75 μA or 0.075 mA, there is no isotope effect ($1\times$). When the channel current is increased to near 1 mA, larger isotope effect ($4\times-7\times$) appears. Based on numerous experiments, the error bars are indicated in Fig. 4. These errors might be caused by nonuniformity of devices fabricated on large wafers. From the large statistical data, it is clear that large num-

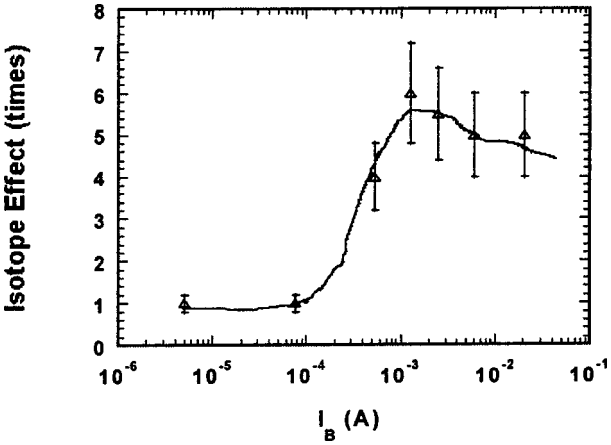

FIG. 4. Isotope effect vs substrate current. The isotope effect is defined as the ratio of the stress time for the D-processed transistor over that for the H-processed transistor for the same amount of the trap generation.

ber of electrons is essential to produce the isotope effect. The largest isotope effect is $\sim 7\times$ at $V_B = -10.5$ V ($I_B = 1.03$ mA). When we continue increasing $|V_B|$, the isotope effect begins to decrease slightly. Because of the very high electric field across the depletion region, a large number of hot electrons ($I_G = 2.7$ nA at $I_B = 1.03$ mA) are still injected into the oxide close to the interfacial region due to their high energy. The hot-electron injection into oxide can create nonhydrogen related interface traps as discovered in our previous experiments.[10,11] These nonhydrogen related interface traps when increased to a certain amount may mask out the H/D related interface traps. This may also explain why there is more isotope effect ($>20\times$) for normal hot-carrier stress (similar to normal operation with higher drain voltage), where much less hot electrons are injected into the oxide (I_G is only in pA level).[10–12]

Although the hot-electron degradation was observed at drain voltage as low as 1.75 V,[16] it is not clear what the mechanism is behind this phenomenon. It was suggested that hot electrons in the high-energy region of the energy distribution might be responsible for the interface trap creation.[16] Our experiments might suggest that low-energy electrons might also contribute to the interface trap generation through multiple vibrational excitation because the characteristic energy of vibration is only 0.25 eV for Si—H bonds.[17] Therefore, even if the drain voltage is scaled down to less than 1 V, hot-carrier degradation is still an important reliability issue for MOS devices.

In summary, the H/D isotope effect for hot-carrier degradation is strongly dependent on the number of hot electrons presented at the interface. This suggests that the multiple vibrational excitation (heating) play a major role in hot-carrier degradation of MOS transistors although other mechanisms including direct excitation and injection into oxide may also play roles. Because of the nature of multiple vibrational excitation (heating), low-energy electrons can still break Si—H/D bonds in MOS devices.

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