Correlation between Si–H/D bond desorption and injected electron energy in metal–oxide–silicon tunneling diodes

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(Received 28 August 2000; accepted for publication 22 November 2000)

Metal–oxide–silicon tunneling diodes with SiO_2/Si interface passivated by hydrogen or deuterium are stressed under various constant current conditions. When the energy of injected electrons exceeds a threshold value (~3 eV), both hydrogen and deuterium passivated devices reveal similar soft breakdown behaviors. On the contrary, when the injected electrons with low energy (<3 eV) at high current density stress, a giant isotope effect is observed in the deuterated devices due to the resonance between the Si–D bond bending mode and the transverse optical phonon of bulk silicon.
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The reliability of ultrathin gate oxide under electrical stress is an important issue for future ultralarge scale integration (ULSI) technology. Anomalous increases of gate leakage current and the occurrence of fluctuations in gate current, so-called soft breakdown, have been reported for several years.[1–4] Multiple tunneling via generated electron traps in the ultrathin gate oxide layer may be the physical mechanism of the electron transport after soft breakdown.[2] Remote hydrogen plasma experiments, reported by DiMaria and Cartier,[5] have shown a strong evidence that trap creation is related to the release of hydrogen by hot electrons. Therefore, the hot-carrier-induced depassivation of the SiO_2/Si interface is believed to be a dominant component of metal–oxide–silicon (MOS) device degradation. The scanning tunneling microscopy (STM) experiment on hydrogen passivated silicon surface under ultrahigh vacuum conditions[6] inspired the idea to use deuterium instead of hydrogen in a MOS system, and a giant isotope effect between hydrogen and deuterium was reported.[7–10] Due to similar vibrational frequency of the bending mode of the Si–D bond (~460 cm^{-1}) and silicon transverse optical phonon states (~463 cm^{-1}), replacing hydrogen with deuterium during the postmetal-anneal process greatly reduces hot electron degradation in MOS transistors by the relaxation of excited Si–D bond energy through the optical phonons.[7,8] In this letter, we investigate H_2-treated and D_2-treated *n*-channel MOS (NMOS) diodes at the constant current stress (CCS) to study the desorption mechanism of Si–H and Si–D bonds under different energies (gate bias voltage) and impact rates (current density) of tunneling electrons from gate electrodes to SiO_2/Si interface. Heavily doped *p*-type silicon substrate (0.01–0.05 Ω cm) is used to reduce the series resistance effect.

The ultrathin gate oxide of the NMOS diode was grown by rapid thermal oxidation (RTO) on heavily doped *p*-type substrate (0.01–0.05 Ω cm) at 900 °C. The gas flows were 500 sccm nitrogen and 500 sccm oxygen at reduced pressure. *In situ* hydrogen or deuterium prebake at 1000 °C for 2 min was performed before the growth of RTO oxide. After the growth of the ultrathin oxide, the sample was *in situ* annealed in hydrogen/deuterium and nitrogen for 10 min each at 900 °C. The oxide thickness was measured by ellipsometry. NMOS diodes had Al gate electrodes with various circular areas defined by photolithography. In this experiment, the constant current stress measurement was carried out using an HP4156A semiconductor parameter analyzer. The experimental results are confirmed by measuring more than ten devices with the area size of 3×10^{-4} cm^2 on the same run.

Figure 1 shows the gate voltage variation as a function of stress time for H_2-treated NMOS diode (tox = 2.5 nm) under low injected current density stress (about -3×10^{-4}–-3×10^{-2} A/cm^2). The magnitude of CCS is designed carefully to make the proper initial gate bias voltage (from −2 to −5 V), and the total injected charge density is kept constant. The devices remain intact even after 3.3 C/cm^2 fluence stress if biased at low voltage ($|V_g|<4$ V). Only when the initial gate bias exceeds −4 V (−10 μA stress in Fig. 1), the devices reveal soft breakdown and the current–voltage ($I-V$) characteristics of NMOS diodes after stress change dramatically, as shown in the inset of Fig. 1. This gate bias threshold indicates that only the injected hot electrons from gate to SiO_2/Si interface with energy above ~3 eV (the difference between the gate voltage and flat band voltage) can break the

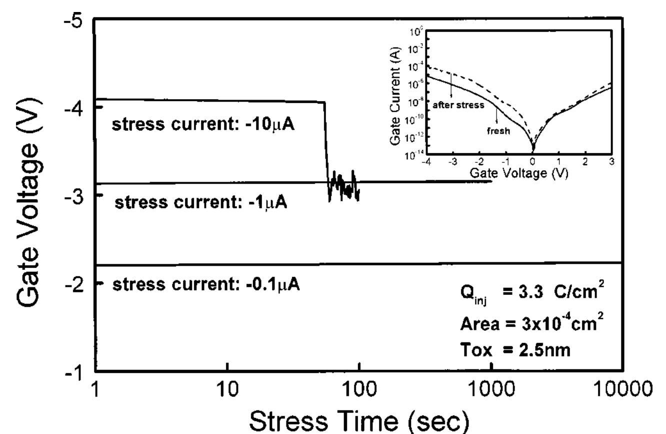

FIG. 1. The gate voltage vs stress time plot of H_2-treated NMOS diodes under different low current density injection. The inset is the current–voltage characteristics of device before and after −10 μA CCS.

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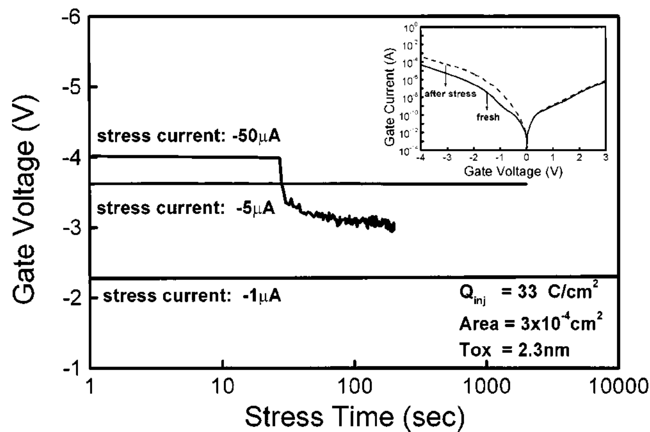

FIG. 2. The gate voltage vs stress time plot of D_2-treated NMOS diodes under different low current density injection. The inset is the current–voltage characteristics of device before and after -50 μA CCS.

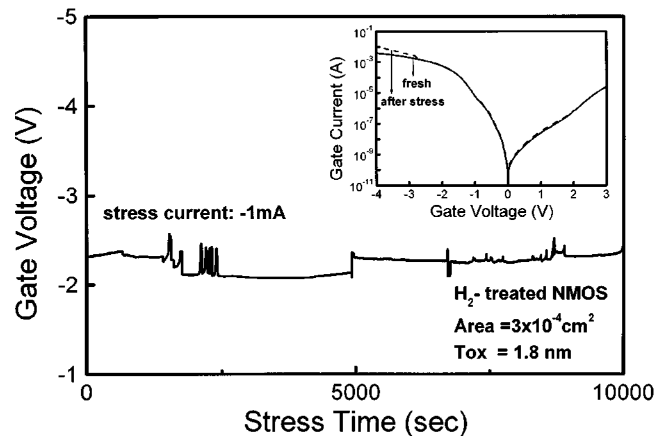

FIG. 3. High current (low initial gate bias) stress of H_2-treated NMOS. Soft breakdown occurs after ~1000 s stress. The inset is the current–voltage characteristics of device before and after stress.

Si–H bond. The value is close to the energy that is required to remove hydrogen from a dangling bond and to place it in an interstitial site (2.5 eV).[11] To confirm the effect of injected electron energy, the MOS devices with thinner oxide (1.5 nm), etched from previous 2.5 nm oxide, is stressed under the same current (-10 μA), and the initial gate bias voltage is -1.3 V. There is no apparent change of gate voltage and $I-V$ characteristic after stress. This indicates the injected electrons with lower energy (bias at -1.3 V) cannot desorb the Si–H bond. Consequently, at high electron energy (>~3 eV), we proposed that the desorption of Si–H bond is mainly due to the direct excitation of hydrogen over the barrier to a mobile transport state by injected high-energy electrons. The speculative mechanism is shown in Fig. 5(a).

The experimental results of constant current stress on D_2-treated NMOS diodes (tox = 2.3 nm) are shown in Fig. 2. Compared to previous results of H_2-treated samples, the same phenomena are observed for D_2-treated NMOS diodes under low injected current densities (about -3×10^{-3} to -1.5×10^{-1} A/cm^2). This implies that the mechanism of the desorption of Si–D bond stressed at low current density is similar to Si–H bond. No apparent isotope effect for D_2-treated device is observed. This indicates that both Si–D and Si–H bond breakage at high electron tunneling energy (>~3 eV) is due to the direct excitation of hydrogen and deuterium over the barrier, and this excitation is not coupled with the phonon relaxation, which is responsible for the giant isotope effect.[12]

The H_2-treated NMOS diodes with thinner oxide thickness (1.8 nm) is stressed at high injected current density (-3 A/cm^2), at least two order of magnitude larger than previous current density, to increase the impact rate of electrons, and the initial gate bias is -2.3 V (Fig. 3). The gate bias voltage is plotted as a function of stress time during constant current stress. Though the bias voltage does not exceed the threshold voltage (-4 V) described previously, the fluctuations in gate voltage under constant current stress and an anomalous increase of current in the $I-V$ curve after 10 000 s stress imply that soft breakdown occurs even the gate bias voltage smaller than -4 V. In this case, we propose that the desorption of the Si–H bond is mainly via multiple vibrational excitation by injected electrons within the lifetime of the excited Si–H bond. This speculative mechanism is also illustrated in Fig. 5(b).

In the same stress condition (-3 A/cm^2), the D_2-treated NMOS (tox = 1.6 nm) diodes reveal the typical isotope effect. There is no apparent fluctuation in gate voltage during stress, and the current–voltage characteristic of device after stress is almost identical to the fresh one (Fig. 4). The electrons with energy below threshold voltage do not break the Si–D bond despite the high impact rate. Van de Walle and Jackson[8] have reported that due to the frequency of Si–D bending mode close to the vibrational frequency of silicon phonon, the lifetime of an excited Si–D bond is shorter than that of an excited Si–H bond. Therefore, it would be difficult to reach a vibrational excited state of a Si–D bond owing to the rapid decay of the Si–D mode.

The lifetime of Si–H/D bonds can be estimated through the previous experimental results, and is given by

$$\text{impact_rate} \approx \frac{J\text{stress}/1.6\times10^{-19}(\text{coul})}{[\text{H}]\text{or}[\text{D}]},$$

where Jstress is the stress current density, and [H] ([D]) is the concentration of hydrogen (deuterium) at Si/SiO_2 interface. The value of [H] ([D]) is assumed to be $\sim10^{13}$ cm^{-2}.[13] If the lifetime of Si–H/D bonds at excited states exceeds the

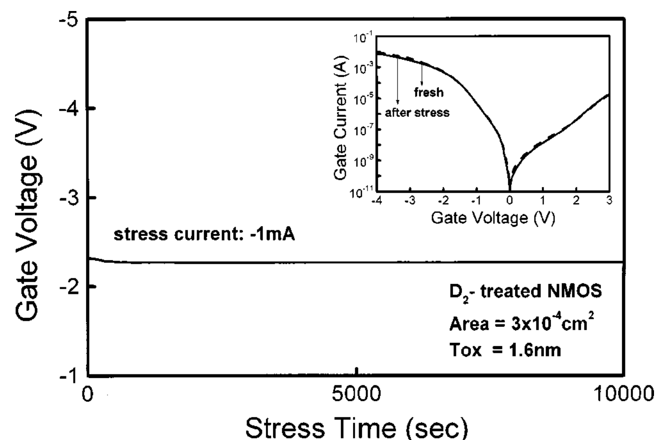

FIG. 4. High current (low initial gate bias) stress of D_2-treated NMOS. No apparent fluctuation in gate voltage is observed. The inset is the current–voltage characteristics of device before and after stress.

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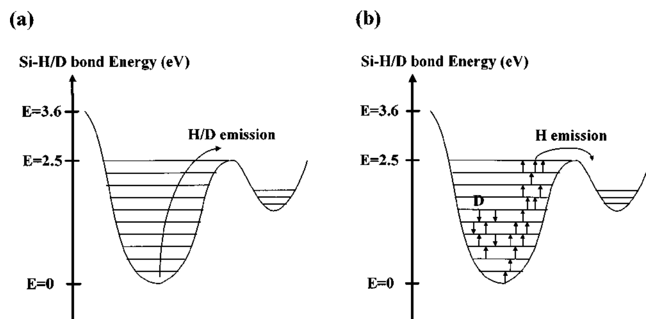

FIG. 5. Schematic diagrams of the speculative mechanism of Si–H/D bonds desorption. (a) The H/D atoms emit over the barrier directly if the initial gate bias exceeds -4 V. (b) At low initial gate bias and high current density stress, the giant isotope effect is observed on the D_2 sample due to the relaxation back to low energy states. The hydrogen is up pumping to the transport mobile states via multiple vibrational excitation.

reciprocal of impact rate, the bonds will be broken by injected electrons via multiple vibrational excitation. On the other hand, if the lifetime of excited states is shorter than the reciprocal of impact rate, the Si–H/D bonds will not be broken due to the relaxation to lower-energy states. At lower bias voltage ($|V_g|<4$ V), the hydrogen-treated devices stressed under high current density condition (-3 A/cm^2) reveal soft breakdown, which is not observed at low stress current density condition (-3×10^{-3} A/cm^2). The reciprocal of impact rates in these two stress conditions are 5×10^{-7} and 5×10^{-4} s, respectively, and the lifetime of an excited Si–H bond will lie in between these two values. Soft breakdown does not occur in the D_2-treated device under the current stress as large as -3 A/cm^2. This indicates the lifetime of an excited Si–D bond is shorter than 5×10^{-7} s. The excited Si–D bond indeed has a shorter lifetime than that of an excited Si–H bond by the calculation of Foley *et al.*,[14] and the calculated lifetime of excited Si–D bonds is 2×10^{-10} s.

In conclusion, the desorption of Si–H/D bonds are monitored by the occurrence of soft breakdown on NMOS diodes under constant current stress. If the bias voltage exceeds -4 V (the electron energy is $\sim$3 eV), both the hydrogen and deuterium atoms will emit over the barrier directly by direct electron excitation. Under high current stress condition (high carrier impact rate) at low gate voltage, the Si–H bond may be broken via multiple vibrational excitation. However, the isotope effect is observed for D_2-treated NMOS due to the vibration frequency resonance between Si–D bending mode and transverse optical phonon states. The Si–D bond will decay rapidly after excitation by the injected electrons. The speculative mechanisms of excitation are schematically illustrated in Fig. 5. High-energy electrons can directly excite both hydrogen and deuterium over the barrier [Fig. 5(a)]. Low-energy electrons with high impact rate can desorb the Si–H bond by multiple vibrational excitation, but can rarely desorb the Si–D bond due to the shorter lifetime of the Si–D bond [Fig. 5(b)].

This work is supported by National Science Council, Taiwan, R.O.C. (Contract No. 89-2218-E-002-017 and No. 89-2218-E-002-012) and Yen Tjing-Ling Foundation.

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