

Comment on "Reduction of hot electron degradation in metal oxide semiconductor transistors by deuterium processing" [Appl. Phys. Lett. 68, 2526 (1996)]

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Lyding *et al.*¹ have recently reported significant improvements in the lifetime of metal oxide semiconductor (MOS) transistors due to incorporation of deuterium (D), rather than hydrogen (H), at the Si/SiO₂ interface. This remarkable achievement indicates that the Si–D bond is more resistant to hot-electron excitation than the Si–H bond. Lyding *et al.* pointed out that the phenomenon is probably analogous to the observed reduction in desorption of deuterium versus hydrogen from hydrogenated Si(100):H surfaces using the scanning tunneling microscope (STM).² In this comment, we propose a specific pathway for the dissociation of Si–H and Si–D bonds, providing a natural explanation for the difference in dissociation rates.

Shen *et al.*³ have proposed that the low-voltage STM-induced desorption of Si–H bonds from Si(100) proceeds via a multiple-vibrational excitation by tunneling electrons. Electrons excite Si–H vibrational transitions with a rate proportional to the tunneling current. The extent to which vibrational energy can be stored in the bond depends on the lifetime, i.e., on the rate at which energy is lost by coupling to phonons. Because the lifetime of H on Si is long,⁴ efficient vibrational excitation is expected. In the quantitative analysis of Ref. 3, it was assumed that the vibrational energy is deposited in the *stretch* mode of the Si–H bond, which has a frequency around 2100 cm^{−1}. The same assumption is usually implicitly made in discussions of dissociation of Si–H bonds.

Our main purpose here is to point out that both the vibrational lifetime and carrier-enhanced dissociation mechanisms are most likely controlled by the Si–H *bending* modes. The vibrational frequency of the bending mode for Si–H is around 650 cm^{−1}, and the estimated frequency for Si–D is around 460 cm^{−1}. This value is close to the frequency of bulk TO phonon states at the X point (463 cm^{−1}).⁵ We therefore expect the coupling of the Si–D bending mode to the Si bulk phonons to result in an efficient channel for de-excitation. While it is quite possible to reach a highly excited vibrational state in the case of Si–H, this will be more difficult for Si–D. Deuterium should therefore be much more resistant to STM-induced desorption and hot-electron induced dissociation, due to the relaxation of energy through the bending mode.

Furthermore, the bending mode provides a likely pathway for dissociation in the presence of carriers. We have previously investigated this pathway for Si–H bonds in a small void in crystalline Si, using first-principles density-functional-pseudopotential calculations.^{6,7} Two conclusions of that investigation have direct consequences for the vibrational excitation mechanism: (a) In the bulk, the bending-mode pathway for dissociation of a single Si–H involves an intermediate metastable state with the H atom located in a bond-center site adjacent to the dangling bond (from which H has been removed). The activation barrier to reach this intermediate state is 1.5 eV, which is 1 eV lower than the energy difference between the Si–H bond and an isolated interstitial H. In this intermediate state, the system has electrically active levels in the band gap; upon capture of a carrier, the charge state of the hydrogen can change and subsequent dissociation will proceed with no additional barrier. (b) Even before this intermediate metastable state is reached, levels are introduced into the band gap. When the displacement of H from its equilibrium position reaches about 0.8 Å, gap levels emerge from the conduction and the valence band. Again, capture of carriers in a gap level results in immediate dissociation.

We conclude that the bending-mode excitation pathway proposed here is attractive because of the potential for carrier-enhanced dissociation. The overlap of the Si–D bending mode frequency with Si bulk phonons provides a natural explanation for its reduced dissociation rate compared to Si–H.

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