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On the behavior of deuterium in ultrathin SiO₂ films upon thermal annealing

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Following the observation of the large isotopic effect in D₂ passivated gate dielectrics [J. Lyding, K. Hess, and I. C. Kizilyalli, *Appl. Phys. Lett.* **68**, 2526 (1996)], we studied the behavior of deuterium in ultrathin SiO₂ films by nuclear reaction analysis techniques. Accurate concentrations of deuterium in the films, deuterium depth distributions, and deuterium removal from the film upon thermal annealing in vacuum have been examined. For D₂ passivated films, we found rather high concentrations of deuterium near the SiO₂/Si interface, well above both the solubility of deuterium in silica and the maximum concentration of electrically active defects at the interface. Our results suggest a complex multistep mechanism of thermally activated deuterium removal from the film, which probably consists of D detrapping, diffusion, and desorption steps. © 1998 American Institute of Physics. [S0003-6951(98)03004-6]

Recent time-dependent degradation studies¹ of deuterated gate (5.5 nm) oxides have inspired a new wave of interest to the problem²⁻⁷ of hydrogen (and its isotope deuterium) in the SiO₂/Si system. In particular, it was shown that the buildup of interface traps upon irradiation is significantly retarded in deuterium-passivated samples, and that transistor lifetime improvements (due to reduced hot-electron degradation effects) by factors of 10–50 can be achieved.¹ Subsequently, these results were reproduced by Devine *et al.* who showed that the lifetime for a 10% reduction in the transconductance is enhanced by ~10 times for devices annealed in D₂ as compared to H₂.⁸ Several models have been suggested to account for this giant isotopic effect, although the behavior of deuterium in ultrathin oxides and its role in improving the properties of metal–oxide–semiconductor (MOS) devices are still not well understood.^{1,9}

Due to its chemical similarity to hydrogen and very low background level in processing environments, it is very convenient to use deuterium as a “marker” to elucidate basic chemical and physical properties of hydrogen in SiO₂ films. Previous secondary ion mass spectroscopy^{5,6,10,11} and nuclear reaction analysis (NRA) experiments^{3,12-15} made use of this fact to investigate various aspects of hydrogen in relatively thick (>100 nm) oxide films. Ultrathin (sub-10 nm) films of interest for near-future generation of MOS devices are much less studied. In this letter, we use a highly sensitive and selective nuclear reaction analysis technique^{3,12,14,16} to study deuterium in ultrathin (5.5 nm) SiO₂ films, specifically: (i)

accurate concentrations of deuterium in the films; (ii) thermal behavior of deuterium in the oxides upon vacuum annealing; (iii) activation energies associated with deuterium removal from the film; and (iv) deuterium depth distributions. In addition to the above mentioned giant isotopic effect,¹ one more practical aspect of this study follows from the fact that oxidation/annealing in H₂(D₂) is not the final (high-temperature) processing step and it is important, therefore, to understand the response of H(D) in the film to subsequent thermal treatments.

Ultrathin (5.5 nm) gate oxides were grown on 6 in. Si (100) wafers in a vertical furnace in dry O₂ at 850 °C. The oxidation step was followed by annealing in D₂ (diluted to 10% in an N₂ buffer gas, total pressure 1 atm) at 450 °C for 45 min. The wafers were then cut into pieces, transferred (in air) to another furnace, and annealed in vacuum (2 × 10⁻⁷ mbar) in the temperature range of 350–600 °C. Characteristic time of temperature ramp-up (cool-down) to (from) 400–600 °C was on the order of 5 min. The concentration of deuterium was measured (with an accuracy of ~5%) by the D(³He,*p*)⁴He reaction at 700 keV, calibrated against a deuterated silicon nitride reference sample containing 1.55 × 10¹⁷ D/cm², as described in detail elsewhere.^{12,14} The sensitivity of this method is on the order of 10¹² D/cm². Since hydrogen (deuterium) solubility in crystalline silicon is very low,⁵ we consider all measured deuterium to be located in the oxide film. This was directly confirmed by depth-profiling via HF-etch back. An oxide etching rate of about 0.2 nm/s was determined from the decay of the total amount of oxygen in the film, measured by the ¹⁶O(D,*p*)¹⁷O reaction

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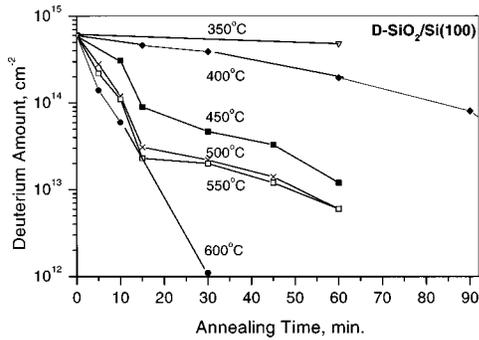


FIG. 1. Total amount of deuterium left in the SiO₂ films after vacuum anneal at different temperatures. Solid lines are a guide only.

at 730 keV, with a 13 μm mylar foil in front of the detector to stop deuterons, alpha particles, and low energy protons. The depth resolution of the HF etch depth profiling is estimated to be about 1 nm.

Deuterium-annealed samples exhibit a surprisingly high concentration in the film, 6×10^{14} D/cm² (see Fig. 1 at $t = 0$), about three orders of magnitude higher than the “physical” solubility of molecular hydrogen (deuterium) in bulk silica in this temperature range,^{17,18} $3\text{--}4 \times 10^{17}$ at/cm³ (which corresponds to $\sim 2 \times 10^{11}$ at/cm² for a 5.5 nm film). The observed amount of D is also much higher than the “intrinsic” level of dangling bonds at the nonpassivated SiO₂/Si interface, $\sim 1 \times 10^{13}$ cm⁻², as measured by electron paramagnetic resonance (EPR) for the Si (111) substrate.¹⁹ One should, however, mention that other ion-beam studies have shown that the concentration of hydrogen/deuterium at the interface of thicker (95 nm) silicon oxide films can be as high as 10^{15} at/cm², also well above the solubility limit.¹⁵

Figure 1 shows the decay of the deuterium content in the film during vacuum anneal. One can see that the amount of D drops below the sensitivity limit (10^{12} D/cm²) after annealing at 600 °C for 30 min, consistent with previous studies on deuterium removal from thicker films³ and thermal desorption experiments on deuterium absorbed on clean silicon surfaces.²⁰ At lower temperatures ($T < 400$ °C), the decay is much slower. In the intermediate temperature range, the decay law becomes more complicated. A fast decay mode is observed at short annealing times (< 15 min), which is followed by a regime of slower decay. There is a break in the decay curves (plotted in a semilogarithmic coordinates) at $t \sim 15$ min, suggesting a complex (multistep and possibly multipath) behavior of D removal upon vacuum anneal. Each step is characterized by its decay law with a characteristic time constants [$\tau(T) = \tau_0 \exp(E_a/T)$], such that the overall decay mechanism could be described as $C_D(t) = C_1(0) \times \exp[-t/\tau_1(T)] + C_2(0) \exp[-t/\tau_2(T)] + \dots$

The time constant (τ_1) for the fast decay mode (determined from the least-squares fit of the slope of the straight lines in Fig. 1 at $t < 15$ min) is shown as a function of the inverse temperature in Fig. 2. This Arrhenius plot allows one to obtain apparent activation energies (E_a), associated with deuterium removal from the film upon annealing. They are ~ 0.35 eV for $T > 450$ °C, and ~ 1.2 eV for lower temperatures. Again, these results imply a multistep removal mechanism: At lower temperatures, the process with the higher activation energy is rate limiting, whereas the process with

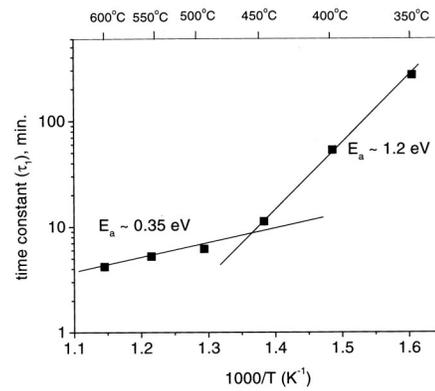


FIG. 2. Time constant (τ_1) of the fast ($t < 15$ min) stage of deuterium removal from the films as a function of inverse temperature.

the lower activation energy governs D removal at higher temperatures.

The depth distributions of deuterium in the initial deuterated oxide ($t = 0$ in Fig. 1) and at an intermediate step of vacuum anneal (450 °C for 30 min) are shown in Fig. 3. The initial deuterated film has 6×10^{14} D/cm² located closer to the SiO₂/Si interface. This result is complementary to recent observations by Devine *et al.*⁸ who showed by charge pumping techniques that the improved properties of deuterated oxides can be attributed to interface state passivation by deuterium. After vacuum anneal, the distribution is quite different: (i) the total amount of the isotope decreases by more than one order of magnitude, a result of D removal from the film; and (ii) the distribution exhibits two peaks—one near the interface and a new one near the surface of the oxide. For this set of particular annealing conditions (450 °C, 30 min), the deuterium is almost equally distributed in the two regions: 2.6×10^{13} D/cm² near the outer oxide surface and 2×10^{13} D/cm² near the interface. Deuterium fixation near the surface implies the existence of either specific bounded configurations of D near/at the surface (such as, for example

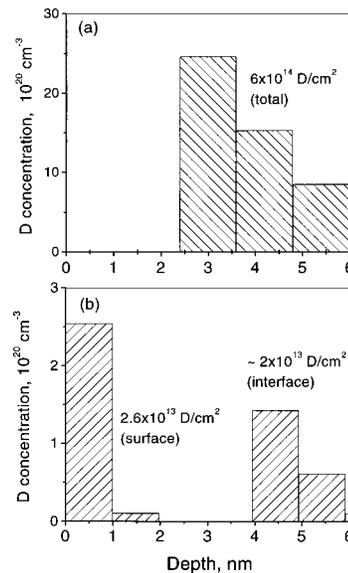


FIG. 3. Deuterium depth profiles (as a function of the distance from the outer oxide surface) for (a) the initial deuterated film before vacuum anneal and (b) after intermediate vacuum anneal at 450 °C for 30 min.

Si-OD and Si-D groups, some of them could be caused by H/D exchange at the surface) or/and an energy barrier for D to desorb into the vacuum. The thermally activated nature of deuterium desorption was indeed observed in thermal desorption experiments of deuterium on clean Si surfaces²⁰ and in D₂O grown films.²¹ One should note that, after this intermediate vacuum annealing, the amount of deuterium near the interface (2×10^{13} D/cm²) approaches the intrinsic level of the interface traps (1×10^{13} D/cm²)¹⁹ which may indicate that this relatively strongly bonded deuterium is responsible for the passivation of the interface defects.

The activation energy of 0.35 eV for the fast initial decay at $T > 450$ °C (Fig. 2) agrees with the activation energy of molecular deuterium (hydrogen) diffusion in silica of $E_d \sim 0.38$ eV.¹⁸ (Park *et al.* reported a different value of $E_d = 1.9$ eV for diffusion of implanted deuterium in “wet” oxides.⁵ One should, however, keep in mind that hydrogen/deuterium diffusivity in silica is very sensitive to the “dryness” of the oxide.⁷) As far as the value of 1.25 eV (Fig. 2) at $T < 450$ °C is concerned, at the moment, we cannot identify a known process involving D in SiO₂ with this activation energy. It is about half of the Si-D surface bond strength of 2.67 eV (Ref. 22) and the activation energy for dissociation of deuterium-passivated interface defects (P_b) of 2.56 eV,⁴ and higher than the activation energies of H₂O and OH diffusion in SiO₂, 0.86 and 0.8 eV, respectively.²³⁻²⁵ It may reflect the activation energy for deuterium desorption from the oxide surface or it may be indicative of the multiple dissociation, diffusion, and reaction steps that yield an apparent activation energy quite different from activation energies of the individual steps involved.

Based on our results (specifically: (i) high concentration of D in the film [Figs. 1 and 3(a)], (ii) D depth distributions (Fig. 3), (iii) multistep features observed in the t , and T dependences (Figs. 1 and 2)) one can speculate on D behavior in the following way. During D₂ annealing, deuterium both passivates the interface defects and incorporates in the near-interface oxide. Hydrogen (deuterium) passivation of the interface traps is fairly well understood.^{4,7,8,19,26,27} It is also known that protons can exist in the SiO₂ in several forms, such as hydroxyl and hydride groups, molecular hydrogen, etc. The high concentration of D near the interface may be caused (in addition to the dangling bond passivation) by deuterium bonding to other (electrically nonactive) defects in the structural transition region (including strain, suboxide states, etc.) near the interface.

Vacuum annealing results in fast (possibly diffusion-limited at high temperatures) removal of deuterium from the “bulk” near-interface oxide and slower depassivation of the interface defects. Based on the rate constant determined from the EPR measurements⁴ [$k_{\text{EPR}} = 9.8 \times 10^{11} \exp(-2.56 \text{ eV/kT}) \text{ s}^{-1}$] for depassivation of the dangling bonds in a deuterated (50 nm) oxide, one can estimate that the time constant [$\tau_{\text{EPR}}(T) = 1/k_{\text{EPR}}$] for D removal from the dangling bonds ranges from 5.5 min (at 600 °C) to 1.1×10^5 min (at 400 °C). The time constant deduced from our experiment (Fig. 2) is 4.2 min at 600 °C and 45 min at 400 °C. Comparison of the two time constants (from EPR⁴ and NRA, this work) suggests that, at low temperatures, deuterium atoms, passivating the interface traps, are relatively

stable and the deuterium is more favorably removed from other configurations in the near-interface oxide. As the temperatures increase, the rate of depassivation of the dangling bonds also becomes high, and as a result, fast decay of deuterium to below the detection limit is observed (Fig. 1).

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