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Hydrogen blistering of silicon: Effect of implantation temperature, isotope dependence, and key role of dynamic annealing

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Blistering of (001) Cz–Si crystals (>1 Ω cm), by either protium (H) or deuterium (D) ions of 5 keV energy, was studied as a function of the sample temperature during implantation in the range of 150–450 K. It was found that the blistering dose thresholds decreased with temperature, and very dramatically so in the case of D ions, revealing new aspects of the *giant isotope effect*. An optimal implantation temperature for ion cutting was found around 100 °C, where the required dose is reduced and the isotope effect is minimized. The results are interpreted in terms of models of the interaction of implanted hydrogen with radiation defects, and they show that dynamic annealing is incomparably more efficient in promoting blistering than purely thermal annealing. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2818105]

Hydrogen ion blistering of silicon, discovered by Ligeon and Guivarc'h,[1] is at the origin of the invention by Bruel[2] of the ingenious microelectronic process of ion cutting and layer transfer. Most of the numerous investigations of the last decade on these topics have been carried out by implantation of H ions (a few 10^{16} H/cm^2) at room temperature (RT), followed by annealing at several hundreds of °C.[3] Blistering can also be obtained without any high temperature annealing by implantation at RT of a very high H dose (>10^{17} H/cm^2).[3] However, the effect of implanting at other than RT has, as yet, not been studied systematically, although an interesting fact has been found: implantation at cryogenic temperature tends to make blistering more difficult,[4] whereas high temperature implantation makes it easier.[5,6] By "easy" ("difficult") we mean that lower (higher) ion doses or post-anneal temperatures are required. These facts hint at the role of the dynamic annealing taking place during the implantation process because blistering results from a complex sequence of interactions between the implanted H atoms and the defects created by irradiation.[3] A more systematic investigation of the effect of implantation temperature is thus necessary to pin down the role of dynamic annealing. Moreover, such a study may have practical consequences since the implantation temperature could be used to fine tune the ion-cutting process for particular applications, to make it more compatible, for instance, with some other steps in the chain of processes used in microelectronic/photonic fabrication.

Another control parameter has also been found to be of interest for blistering and ion cutting, namely, the hydrogen isotope being used. Indeed, deuterium implantation (at RT) has revealed a giant isotope effect.[7] This effect, again, showed the importance of dynamic annealing[8] and it is related to the fact that D irradiation typically generates 2.5–3 times as many primary point defects as H ions, depending on ion energy. In the present work, the blistering threshold doses for low energy (5 keV) ions are studied as a function of isotope and implantation temperature between 150 and 450 K. It is found that the surface morphology varies dramatically with both variables. The results demonstrate that the dynamic annealing taking place during implantation, which is strongly affected by the implantation temperature, is incomparably more efficient in promoting blistering than any purely thermal annealing performed after implantation.

Cz-grown *n*-doped (001) Si wafers (resistivity >1 Ω cm) were cleaved into 1 cm^2 pieces and inserted in an ion implanter having a base pressure <10^{-7} mbar. H_2^+ and D_2^+ ions with 10 keV energy were implanted to various doses ranging from 1×10^{16} to 1×10^{17} atom/cm^2 (all doses will be quoted in numbers of atoms, not ions, and the implantation energy assumed to be 5 keV/atom). The mean scanned current was ≈1 μA, resulting in no sample heating. Different samples were implanted at temperatures of 150, 300, 375, and 450 K (±5 K), as measured by a thermocouple inserted in the target holder right behind the target. The cryogenic samples were cooled by fixing them at the tip of an electrically insulated copper rod whose other end was dipped in liquid nitrogen outside the vacuum chamber. The high temperature samples were heated by radiation from the back (so as not to interfere with the ion current measurement). Afterward, the samples were cut again into four pieces and a subset subjected to rapid thermal annealing for 30 s at 850 °C under a nitrogen flow. The surface morphology of the samples was observed before and after annealing by atomic force microscopy (AFM) using a Nanoscope IIIa from Digital Instruments. Statistical analysis of the images was performed using the WSXM software package.[9]

Each AFM micrograph was analyzed to calculate the percentage of the total area that was blistered, defined as the percentage that was above the base level given by the AFM software. These numbers cannot be considered highly accurate but they agree with estimates based on visual inspection of the AFM pictures (actual pictures of the blisters, with submicron diameters at 5 keV, have been shown in our previous papers, e.g., Ref. 7). Some craters of exploded blisters are also present at higher doses, and they are included in the

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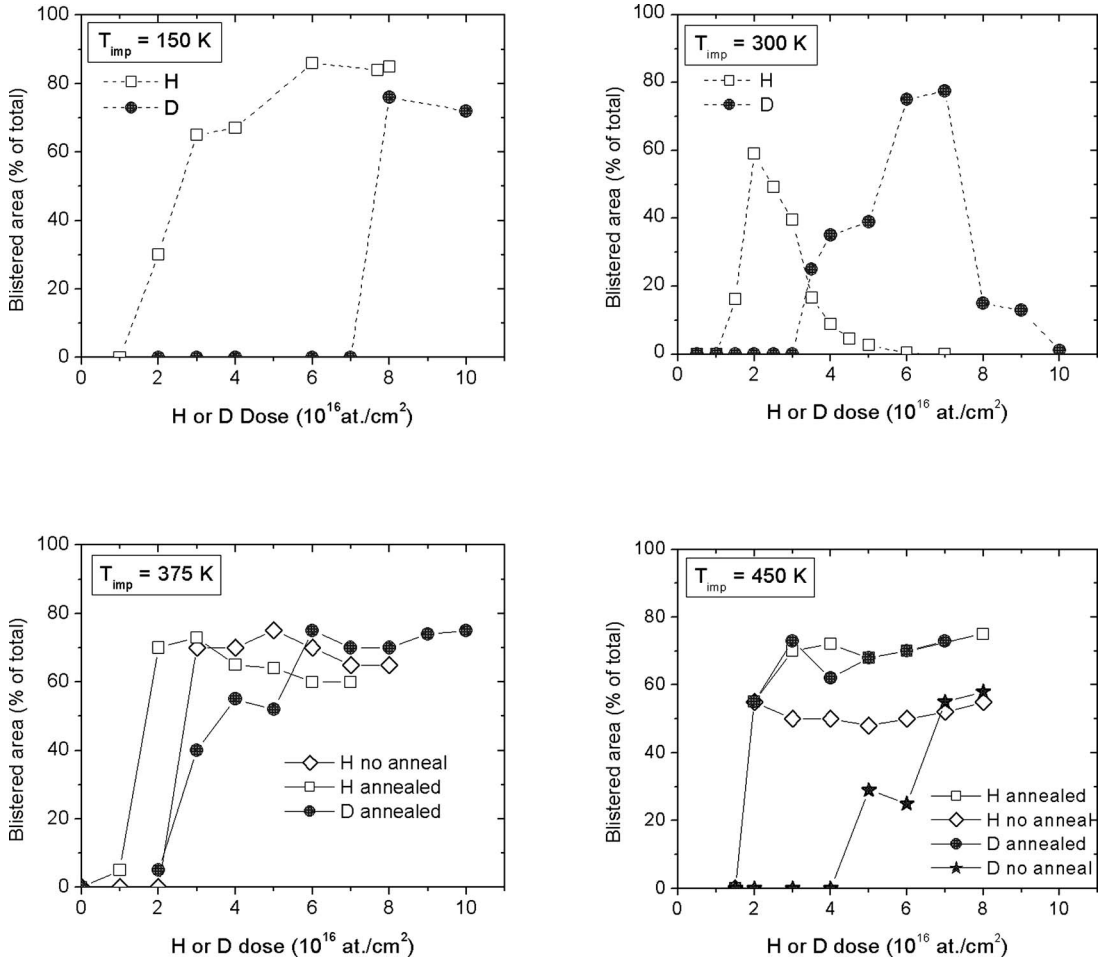

FIG. 1. Blistered area as a function of dose for samples implanted with H or D at 5 keV. The implantation temperatures of 150, 300, 375, and 450 K are indicated in the respective panels. At 150 and 300 K, only some postannealed samples blistered; at 375 and 450 K, some samples blistered upon implantation without postanneal.

count of the blistered area. The whole set of results is summarized in Fig. 1, where the implantation temperature T_{imp} is indicated in each panel. Starting with the lowest temperature, the top left panel shows the blistered area for the samples that were implanted with H or D ions at 150 K, removed from the implanter (and thus brought to RT), and annealed at high temperature. While the protium data are unsurprising, those for deuterium show a threshold dose four times higher than for H. This is the manifestation of the giant isotope effect discovered earlier at RT,[7] and it is even more pronounced for cryogenic implantation.

The top right panel of Fig. 1 displays the similar data obtained for RT implantation. Both minimum blistering doses are decreased, compared with 150 K, especially for D. However, instead of a sharp threshold, for D we observe a gradual increase of the blistered area with increasing dose. Note also the disappearance of blisters at high dose. The evidence is that the stress is released by swelling of the implanted layer rather than by splitting in that case.[10] However, we do not believe that it represents a fundamentally new phenomenon because if another wafer is bonded on top of the implanted wafer and the annealing performed, splitting (ion cutting) does take place at the depth of implantation.[11]

For 375 K implantation (bottom left), the minimum D dose has again decreased considerably and the increase with dose is still gradual. Blisters do not disappear at high dose anymore, for doses up to 8×10^{16} H/cm^2 and 1×10^{17} D/cm^2, respectively. In addition, for H doses of 3×10^{16} H/cm^2 or more, the samples blister upon implantation, without the need for annealing. For RT implantations, this occurs only for a dose of $\approx2\times10^{17}$ H/cm^2.[10]

At T_{imp}=450 K (bottom right), the H-implanted samples come out blistered without annealing for doses of 2×10^{16} H/cm^2 and more. The threshold for D blistering is also 2×10^{16} D/cm^2, but it requires annealing. Finally, D-implanted samples can also blister without annealing, provided that the dose is $\geqslant5\times10^{16}$ D/cm^2.

Thus, with increasing implantation temperature, we observe three qualitatively different regimes: at the lowest temperatures, a regime of truly giant isotope effect, at more moderate temperatures, a regime of high dose blister disappearance, and at somewhat higher temperatures, blistering at low dose without the need for an annealing. Ion cutting, based on the two-step process (implantation+anneal) thus has a rather narrow favorable operational window, namely, 300–375 K, at least at the low keV energies investigated here. The most striking observation is that no amount of purely thermal annealing (TA) can duplicate the effects of dynamic annealing (DA) and that, interestingly, DA is enor-

mously efficient in promoting blistering: an increase of ~100 K in T_{imp} causes blisters to appear at low dose without further annealing, and a 200 K increase makes the isotope effect practically disappear.

At the fundamental level, the two questions are then the following. (1) By what mechanism does DA so efficiently induce the evolution toward blistering? (2) How is that related to the isotope effect? The essential ingredient for blister nucleation is the formation of H (or D) passivated (001) platelets[12,13] parallel to the surface. Their formation appears to depend on the presence of an in-plane compressive stress and an out-of-plane tensile strain, favoring the separation of (001) planes,[14] and their stability requires readily available hydrogen to passivate the dangling bonds.[15] One is then led to assume that DA, compared with TA, favors either a higher strain, or a higher H mobility, or both. Regarding the strain, Lee *et al.*[16] found that its peak level was almost twice higher when H was implanted at RT than when it was implanted at 130 K and let to warm up to RT; this demonstrates that DA indeed is particularly powerful in producing those structures that cause the strain, although the nature of those structures is not yet clearly established. Regarding the availability of H (or D) at the right time near an incipient platelet, DA is expected to accelerate H atomic diffusion through radiation-enhanced diffusion (RED). Note that the self-interstitial mobility is also expected to be enhanced by DA. The isotope effect, for its part, has been semiquantitatively explained,[8] at least at RT, in terms of random migration and reactions between the three species, vacancies (V), self-interstitials (I), and atomic H. The much higher density of defects under D bombardment, compared with H, indeed results in more defect clustering instead of the D-V reactions necessary for platelet nucleation.

The temperature dependences found here provide important insights into the blistering mechanism. First, since cryogenic implantation necessarily leaves many more defects, especially of the interstitial type, than high temperature implantation, and since this results in lower strain[16] (and more difficult blistering), it does mean that the strain is not caused by defect clusters but by hydrogen-related complexes, as postulated by Cerofolini *et al.*[17] This is consistent with the isotope effect since D implantation produces around ~2.8 times as many primary defects as H implantation.[18] Second, as noted, the evolution toward blistering ensues from a sequence of DA and TA, the relative contribution of each varying with T_{imp}: relatively unimportant at low T_{imp}, DA becomes the only one necessary at sufficiently high T_{imp} (e.g., 375 K for 3×10^{16} H/cm^2). Therefore, the isotope effect is overwhelmingly important when TA dominates but almost negligible when DA dominates. Since the distinguishing character of DA is RED, the facts suggest that the particular combination of enhancements in V, I, and H(D) diffusivities resulting from RED here favors H-V encounters over defect clustering.

In conclusion, the threshold doses for blistering of silicon by H and D ions of low keV energies ($R_p < 100$ nm) decrease rapidly at increasing implantation temperature; the effect is especially dramatic for deuterium. Around 100 °C, the conditions appear optimal for ion cutting: the required dose is below 2×10^{16} H/cm^2, without causing premature blistering during implantation, and the isotope effect is minimized. The results demonstrate that dynamic annealing is incomparably more efficient in promoting blistering than purely thermal postannealing. When the role of dynamic annealing is enhanced by higher temperature implantation, the isotope effect weakens. The likely explanation is the classic enhancement in atomic diffusivities (RED) during irradiation, which here appears to favor the formation of hydrogen-vacancy complexes, with a strong in-plane compressive stress rather than defect clustering.

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