Raman-scattering elucidation of the giant isotope effect in hydrogen-ion blistering of silicon

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In this work, we investigate the origin of a giant isotope effect discovered in the blistering of hydrogen-ion-implanted and annealed silicon. Si(001) samples were implanted or coimplanted with 5 keV of H and/or D ions to total fluences of $2 \times 10^{16}$ and $6 \times 10^{16}$ ion/cm$^2$. The lower fluence is sufficient for blistering by pure H, but the higher one is required for the maximum blister coverage whenever D is involved. On these samples, we carried out Raman-scattering investigations of the evolution of Si-H/D complexes upon a stepwise thermal annealing from 200 to 550 °C. We have identified the critical chemical transformations characterizing the hydrogen-deuterium-induced blistering of silicon. The puzzling dependence on ion mass appears to be mainly connected with the nature of the radiation damage. We have found that H is more efficient in “preparing the ground” for blistering by nucleating platelets parallel to the surface, essentially due to its ability to agglomerate in the multihydride monovacancy complexes that evolve into hydrogenated extended internal surfaces. By contrast, D is preferentially trapped in the surprisingly stable monodeuteride multivacancies. © 2004 American Institute of Physics. [DOI: 10.1063/1.1794571]

I. INTRODUCTION

The transfer and bonding of thin silicon layers to silicon or to a different material has a wide spectrum of actual or potential applications in the production of microelectronic, photonic, and microelectromechanical devices. In recent years, the “ion-cut” process has emerged as an inventive approach by which to accomplish such heterogeneous materials integration. The ion-cut process consists of wafer bonding followed by a thermally induced splitting of a thin layer (<1 μm) from one of the wafers that had previously been ion implanted. The process utilizes the phenomenon of blistering due to the various gas ions, most commonly hydrogen, as an atomic scalpel that cuts through the wafer. The most successful application of the ion cut to date has been the production of a silicon-on-insulator (SOI). This process, commercially referred to as a Smart Cut™, has now superseded earlier technologies such as separation by implantation of oxygen, based on the high-dose implantation of oxygen and bond-and-etchback silicon-on-insulator. In Smart-Cut, the thermal growth of the oxide together with the wafer bonding ensure the high quality and uniformity of the buried oxide. The energy of the impinging ions determines their penetration depth and thus the transferred layer thickness. Furthermore, ion cutting opens up other exciting materials synthesis opportunities for the electronics industry such as silicon on glass, germanium, silicon carbide, diamond thin films, and even three-dimensional devices.

Although the ion-cut process is now widely used, several aspects of the microscopic mechanisms of ion cutting are little understood. Figure 1 illustrates, very schematically, the scenario leading to the blistering on free surfaces or else to the subsurface cleaving in the case of the vertically constrained surfaces. After the hydrogen implantation, H atoms attach to the Si dangling bonds created by the irradiation damage, thus forming Si–H complexes. Upon thermal annealing, a series of transformations in the Si–H bonding configuration is initiated, culminating in the formation of planar microcavities bounded by the internal surfaces. These transformations were first studied in detail by Weldon et al. and will be revisited in this paper. The microcavities fill with H$_2$ molecules by the desorption from these surfaces resulting in the buildup of internal pressure. They then grow by crack propagation and coalescence, a process that can easily “run away,” causing surface blistering of an unconstrained silicon or a complete cleaving and layer transfer for silicon wafers joined to a supporting wafer.

Since blistering is a sign of potential cleavage, our group is focusing on the study of the blistering of silicon induced by low-keV hydrogen ions and also by deuterium ions. The low-keV ions are used in order to obtain ever thinner (<100 nm) ion-split layers. The deuterium work is motivated by the increasing interest in this isotope in microelectronics—this will become apparent in this paper and has been suggested by others also. This low-keV work has revealed fascinating new phenomena; a remarkable difference in the behavior of the H and D isotopes was discovered. This is manifested by the widely dissimilar dependences on the ion fluences required for blistering. With H ions, a room-temperature (RT) implantation of $2 \times 10^{16}$ H/cm$^2$ followed by a thermal annealing up to ~500 °C leads to the appearance of abundant blisters covering 60% of the surface. This ion fluence corre-
sponds to \( \sim 5 \) at. % peak H concentration. Higher fluences produce less blistering, which practically disappears at a fluence of \( 4 \times 10^{16} \) H/cm\(^2\) (this other surprising effect will not be discussed here). In contrast, with the D ions, the threshold fluence is \( 3.5 \times 10^{16} \) D/cm\(^2\) and the maximum in the blistered area is not reached below a fluence of \( 6 \times 10^{16} \) D/cm\(^2\), corresponding to \( \sim 13 \) at. % peak D concentration. Disappearance occurs for \( \sim 9 \times 10^{16} \) D/cm\(^2\). Inasmuch as Si–H chemistry was shown\(^7\) to play a major role in the blistering, this dependence on ion mass is puzzling.

The thermal-desorption spectrometry performed during the annealing of the samples implanted with H or D or mixtures thereof showed that H\(_2\) generally desorbed at a lower temperature (\( \Delta T \sim 25 \) °C) than HD, and HD at a similarly lower temperature than D\(_2\), an indication of a higher—but hardly giant—stability for D (or D\(_2\)) compared to H (or H\(_2\)).\(^8\) We therefore undertook a Raman-scattering investigation of Si–H/D bond evolution upon annealing. Local-mode vibrational frequencies give information about the chemical bonding of H/D and the number of H/D atoms involved in the defect complexes. We have identified the critical chemical transformations that occur before the blister appearance or their failure to occur resulting in no blistering. It appears that the origin of the H/D discrepancies lies in the physics of radiation damage, i.e., in the differences in the amounts and nature of the defects caused by the D versus H implantation.

II. EXPERIMENT

Blistering after hydrogen implantation and subsequent annealing was investigated for \( n \)-type CZ-grown Si(001) substrates with a resistivity of 1–10 Ω cm. The 5 keV H\(^+\) or D\(^+\) ions were implanted at total fluences of \( 2 \times 10^{16} \) and \( 6 \times 10^{16} \) ion/cm\(^2\) at room temperature. The samples did not significantly heat up during the implantation because the beam power is only \( \sim 10 \) mW cm\(^{-2}\). To investigate the temperature evolution of Si–H interactions, the Raman scattering spectroscopy (RSS) analyses were accomplished with a Renishaw 3000 Raman system having a resolution of 2 cm\(^{-1}\). The excitation was supplied by an Ar-ion laser (514.5 nm and 25 mW) at a normal incidence. The laser light was focused on the sample surface through a 50\( \times \) objective lens, the diameter of the focused laser spot was about 3 \( \mu \)m. The scattered light was collected at RT by a charge coupled device detector (collection time: 500 s and averaging factor: 4). For comparison, all spectra were normalized to the maximum of the optical Si phonon line at \( \sim 520 \) cm\(^{-1}\) and the background luminescence was subtracted from the data. The annealing protocol was the following: The samples were subjected to a linear ramp of 20 °C/min up to a target temperature, e.g., 200 °C, cooled to RT for measurement, and then ramped up again to a higher temperature, and so on until 550 °C. In the end, the surface topography of the samples was observed by atomic force microscopy (AFM) in contact mode with a Digital Instruments Nanoscope IIIa on at least five different spots. The morphology was quantified and statistically analyzed using the WS\( \times \)M program.\(^1\)

III. RESULTS

A. Protium data

With the protium, the maximum blister coverage occurs for a fluence of \( 2 \times 10^{16} \) H/cm\(^2\). Figure 2(a) shows an AFM micrograph of the surface after a sequence of anneals up to 550 °C. The single-step RTA gives essentially identical results.\(^8\) Figure 3(a) shows the Si–H stretch mode region of the RSS spectrum of the as-implanted sample (thick line). Previous infrared absorption measurements suggest the existence of at least 20 discrete modes,\(^12\) superimposed on a dominant broadband.\(^7\) The precise assignment of some specific features is still disputed, but there is a general consensus that discrete modes are associated with the isolated point defect complexes. Table I shows the assignments of RSS spectral features to the hydrogen-related centers and it also gives the specific references\(^7,13–19\) on which these assignments are based. We note that the Si–H stretch frequency increases with the number of hydrogen atoms in the vacancy. Some complexes present more than one vibration mode; for instance, V\(_{H} \) with \( T_d \) (cubic) symmetry has four modes, three of them are degenerate (2208 cm\(^{-1}\)) and the fourth
(2234 cm$^{-1}$) is infrared inactive but visible in the Raman scattering. The main features at RT [Fig. 3(a)] are the low-frequency (LF) broadband (delimited by LF $<2050$ cm$^{-1}$), believed to be due to the monohydride-terminatated multivacancies ($V_nH_m$ and $m\leq n$) located in the most highly disordered regions of the crystal and a few narrower peaks, the main ones at 2025 cm$^{-1}$ (divacancies $V_2H$ or $V_2H_2$), $\sim$2125 cm$^{-1}$ [perturbed mode Si(100):H involving H atoms adsorbed on (001) internal surfaces] and 2182 cm$^{-1}$ ($VH_3$ and/or $V_2H_4$). The bending modes (550–820 cm$^{-1}$) contain complementary information and their existence was seen in the data, but they could not be used in the present conditions of a relatively low dose at low energy because of the large background due to the Si phonon band. Finally, a definite, albeit weak and noisy signal was found in the region around 3820 cm$^{-1}$, showing the presence of H$_2$ molecules after the implantation.

Figures 3(b)–3(j) display the evolution of the Raman spectra after each step in the annealing. We note that the Si–H complexes are fairly stable up to 200$^\circ$C. After annealing up to 300$^\circ$C, we see a general attenuation of the LF broadband and a depletion around 2050 cm$^{-1}$, maybe connected with H$_{BC}$ in the H$_3^*$ mode, whereas this LF region shows more and more structure. Upon annealing up to $\sim$335$^\circ$C and above, the reduction is more pronounced for the monohydride multivacancy complexes (LF broadband) and accompanied by stability or possibly growth in the higher frequency (HF>$2050$ cm$^{-1}$) peaks associated with the multiply hydrogenated monovacancies (VH$_n$). At around 370$^\circ$C, in particular, one can detect the 2208 and especially 2120 cm$^{-1}$, labeled Si(100):H, believed to be due to the various stretch modes of H bound to the internal (100) surfaces; these modes are perturbed from their nominal frequencies on clean surfaces by the roughness of the internal surfaces or the proximity to other defects. Note that the unperturbed modes (2060–2100 cm$^{-1}$, Table I) are also non-negligibly populated at 470–500$^\circ$C. The previous infrared spectroscopy work attributes a crucial role to the feature at $\sim$2120 cm$^{-1}$ in the blistering and ion-cutting processes. There is both a net loss of bound hydrogen and agglomeration of the remaining trapped hydrogen at the existing vacancies and internal surfaces. The blistering develops simultaneously. This is essentially the same scenario as that observed at a higher implantation energy by Weldon et al., if we disregard some details due to the use of a different technique (IR absorption versus Raman scattering) and different photon beam and detection geometries.

The main effect is a drastic transformation of the HF modes, with some H loss, especially by the desorption from the LF complexes; we therefore display in Fig. 4(a) the evolution of the normalized integrated Raman intensities of the LF ($<2050$ cm$^{-1}$) and HF ($>2050$ cm$^{-1}$) regions as a function of the annealing temperature. Unfortunately, we could not obtain meaningful fits of the LF region in terms of discrete modes superimposed on a broadband. In the present case however, the broadband seems to be so dominant that the LF integral basically represents the broadband. This graph illustrates the particularly large loss of LF broadband above 200$^\circ$C and the relative stability of the HF modes between 300 and 435$^\circ$C, accompanied by the emergence of sharp spectral features (Fig. 3). This result constitutes direct evidence of the implication of VH$_n$ complexes in the nucleation and the growth of extended planar defects leading to the surface blistering. It has been proposed that the H$_2$ molecule is the vehicle for H transfer from the HF broadband structures to the HF modes or from the smaller to the larger planar defects; however, in our data, the weak H$_2$ signal disappears above 300$^\circ$C. This fact is consistent with both the LF mode depletion of Fig. 4 and the very significant loss of H$_2$ by desorption starting as low as 200$^\circ$C.

B. Deuterium data

Now we compare with D implantation at the same fluence, $2\times10^{16}$ D/cm$^2$, for which there is no blistering [Fig. 2(b)]. In Fig. 3(a), we show the Si–D (thin line) stretch mode region of the RSS spectrum of the as-implanted sample. The main features are shifted down in frequency, as expected, by a factor of $\sim$1.39 (square root of reduced mass). Deuterium is overwhelmingly trapped in the monodeuteride multivacancy complexes (LF modes <1490 cm$^{-1}$). The LF modes...
are dominated by the 1403 plus 1472.5 and 1453 cm\(^{-1}\) peaks, respectively, associated with the \(V_2 \text{D}/V_2 \text{D}_2\) and \(D^+_B\) complexes. The obvious difference between the Si–D and Si–H complexes at RT is the strength of these discrete LF modes, the relative weakness of the LF broadband, and the paucity of HF modes with the deuterium. The evolution of the normalized integrated Raman intensities as a function of the annealing temperature [Fig. 4(b)] shows a dull scenario. The LF as well as the HF modes progressively disappear. The difference between the Si–D and Si–H spectra and their temperature evolution can be appreciated in Fig. 3. Weak to start with, the Si–D HF modes are never intense enough to trigger blistering. The Si(100):D peak only emerges at 500 °C, apparently too late.

However, D blistering does take place at the higher fluence, e.g., \(6 \times 10^{16}\) D/cm\(^2\) [see Fig. 2(c)]. The first indication

![Fig. 3](image-url)
TABLE I. Identification of Si–H/D local vibration modes.

<table>
<thead>
<tr>
<th>$k$ (cm$^{-1}$)</th>
<th>Si–H Modes</th>
<th>Si–D Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Identification</td>
<td>Identification</td>
</tr>
<tr>
<td>Broadband</td>
<td>Monohydride-terminated multivacancies in highly defective regions (Ref. 7)</td>
<td>Monodeuteride-terminated multivacancies in highly defective regions</td>
</tr>
<tr>
<td>1900–2050</td>
<td>$V_2$H or $V_2$H$_2$ (Ref. 7)</td>
<td>1403 $V_2$D or $V_2$D$_2$</td>
</tr>
<tr>
<td>1930</td>
<td>4th harmonic, Si–Si optical phonon (Ref. 14)</td>
<td>1428.6–1445.6 $ID_2$</td>
</tr>
<tr>
<td>1960</td>
<td>$ID_2$ (Ref. 7)</td>
<td>1506 DV$_{2}$D (110)</td>
</tr>
<tr>
<td>1980–2000</td>
<td>$V_H$ or $V_H$$_2$ (Ref. 7) and $VH$ (Ref. 16)</td>
<td>1472.5 $V_2$D or $V_2$D$_2$</td>
</tr>
<tr>
<td>1990–2010</td>
<td>$H_2^-$ or $H_2^-_{ac}$ (Ref. 15)</td>
<td>1496 $D^-_{2c}$</td>
</tr>
<tr>
<td>2000</td>
<td>$H^-_{ac}$ (Ref. 7)</td>
<td>1472.5 $V_2$D or $V_2$D$_2$</td>
</tr>
<tr>
<td>2025</td>
<td>$V_H$ or $V_H$$_2$ (Ref. 7) and $VH$ (Ref. 16)</td>
<td>1490.5 $D^-_{2}$</td>
</tr>
</tbody>
</table>

FIG. 3. (Continued.)
as to the cause of the appearance of blistering at the higher fluence can be seen in Fig. 4(c), which shows the temperature evolution of the normalized integrated Raman intensities at the higher fluence. One notes that the contribution of HF modes is definitely higher than for $2 \times 10^{16} \text{D/cm}^2$ (though still not quite dominant). A possible explanation could be that the amount of damage starts to saturate at the higher fluence, so that the ion/vacancy ratio is higher, hence more multideuterides. Moreover, contrary to the low fluence, no significant loss of the Si–D complexes is detected below 335 °C. The percentage of HF modes that is reached around this temperature is even higher than for H [Fig. 4(a)] and the D blister volume is roughly twice that of the H blisters.\(^8\) One may surmise that it is due to the high D atom density (>10%), which somehow forces the generation of multideuterides.

Figure 5 shows a comparison between the temperature evolutions of the Raman spectra obtained with $2 \times 10^{16}$ and $6 \times 10^{16} \text{D/cm}^2$, respectively. At the lowest fluence (thin line), after annealing up to 300 °C, one can observe a strong attenuation of the LF modes, which seems to affect about equally the broadband and the discrete peaks. The vibration modes at 1555, 1587, and 1621 cm\(^{-1}\), associated with the $\text{VD}_2$, $\text{VD}_3/\text{V}_2\text{D}_6$, and $\text{VD}_4$ multideuteride monovacancy complexes, respectively, appear enhanced relative to the as-implanted spectrum. The growth of the $\text{VD}_3/\text{V}_2\text{D}_6$ and $\text{VD}_4$ complexes may be explained by the retrapping into the existing vacancies of the deuterium released from the multideuteride multivacancy centers. This behavior is accelerated after annealing at 400 °C. Nevertheless, the HF mode intensity remains too weak to trigger the blistering. Contrary to the H (Fig. 3), which is completely detrapped after annealing at 550 °C, some D are still present at this temperature, bound in good part to the self-interstitial as ID\(_2\).

At a low temperature, the spectra at the highest fluence (thick line in Fig. 5) are rather featureless, indicative of the high degree of damage. Their evolution shows that the attenuation of the broadband takes place at a much higher temperature compared to the low fluence case. In fact, a significant loss of Si–D centers occurs only after annealing up to 335 °C. After annealing up to 400 °C at the high fluence, the Si–D complexes display partly the same behavior as that at low fluence; however, the process of growth of the $\text{VD}_3/\text{V}_2\text{D}_6$ and $\text{VD}_4$ complexes associated with a loss of the multideuteride monovacancy modes is more pronounced than at the low fluence. Interestingly, the loss of $\text{VD}_4$ modes at 470 °C is accompanied by the growth of the discrete spectral feature at 1544 cm\(^{-1}\), identified with a monodeuteride mode of D trapped on the extended internal surfaces. Such a conversion mechanism is not observed in the low fluence RSS spectra, where the 1544 cm\(^{-1}\) mode shows no enhancement above 470 °C.

On the basis of the preceding observations, we conclude that the absence of D blistering at the low fluence is related to the following facts: First, it appears that blistering requires the LF broadband to be definitely much more intense than the LF discrete modes. This implies a minimum disorder in the lattice. Second, the LF modes must vanish or at least be strongly attenuated above 300–400 °C, contrary to the hydrogen LF modes that disappear; deuterium LF modes tend to evolve into the ID\(_2\). Third, the deuterium HF modes evolve qualitatively similar to the hydrogen HF modes, i.e., toward the $\text{VH}_3/\text{V}_2\text{H}_6$ or $\text{VD}_3/\text{V}_2\text{D}_6$ and Si(100):H or Si(100):D, but these modes are relatively weak and their evolution requires higher temperatures with the deuterium. The precise behavior of the Si–H/D complexes during annealing is more critical for the blistering than the raw amount of traps. But, in turn, this behavior is somehow conditioned
by the initial repartition between the broadband and the LF and HF defects.

C. Mixed implantation data

In order to study the Si–H and Si–D complexes in the same environment, successive H and D implantations, each at the same fluence, were carried out for the total fluences of $2 \times 10^{16}$ and $6 \times 10^{16}$ ion/cm$^2$. Blistering occurs only at the highest fluence (Fig. 6). Some of these blisters are completely exfoliated giving craters with a 95-nm depth. The blistering behavior under H and D coimplantation has a fluence dependence that is intermediate between those of H and D alone.$^{8,9}$ RSS measurements have been done after each step of thermal annealing. Figures 7 and 8 show the evolu-

FIG. 5. Temperature evolution of the Si–D stretch modes of D-implanted Si: (---) $6 \times 10^{16}$ D/cm$^2$; (-----) $2 \times 10^{16}$ D/cm$^2$. (a) as implanted at RT and (b)–(f) after annealing at 200, 300, 335, 370, 400, 435, 470, 500, and 550 °C, respectively.
tation of the normalized integrated Raman intensities of the LF, HF, and total Si–H/D as a function of the annealing temperature at the fluences of $2 \times 10^{16}$ and $6 \times 10^{16}$ ion/cm$^2$, respectively. At the lowest fluence (Fig. 7) and at RT, the trapped protium is equally distributed between the multihydride monovacancy and monohydride multivacancy complexes, practically exactly as in the case of a single H implantation [Fig. 4(a)], whereas deuterium is preferentially trapped in the monodeuteride multivacancy complexes, as in the case of a single D implantation [Fig. 4(b)]; it is as if each isotope was "blind" to the defects created by the other isotope. Another fact pointing in the same direction is that mixed HD molecules account for only $\sim 25\%$ of the total amount of desorbed molecules ($\mathrm{H}_2$, HD, and $\mathrm{D}_2$), whereas 50\% would be expected under the ideal mixing conditions.$^8$ (We checked that this is not due to the poor

![Fig. 5. (Continued.)](image)

![Fig. 6. AFM images of Si(001) surfaces coimplanted with equal amounts of H and D at 5 keV and annealed up to 550 °C. (a) $2 \times 10^{16}$ atom/cm$^2$ and (b) $6 \times 10^{16}$ atom/cm$^2$. Note the different vertical scales.](image)

![Fig. 7. Dependence on temperature of the normalized integrated intensities of the LF and HF Si–H/D stretch modes of Si coimplanted with $2 \times 10^{16}$ (H+D)/cm$^2$.](image)
Fig. 8. Dependence on temperature of the normalized integrated intensities of the LF and HF Si–H/D stretch modes of Si coimplanted with $6 \times 10^{16}$ (H+D)/cm$^2$.

overlap between the H and D depth profiles by repeating with 4-keV D together with 5-keV H, which have practically the same range).

We note that H and D detrappings occur at the same rate after annealing up to 370 °C, the detrapped H comes from both the multihydride monovacancy and monohydride multivacancy complexes, whereas in this temperature range, the detrapped D comes essentially from the monodeuteride multivacancy complexes. Above 400 °C, Si–H/D bond breaking now does depend on the isotope mass and is more easily achieved for H than for D; this result is in agreement with the thermal-desorption spectrometry, which shows that the H$_2$ and D$_2$ desorption start at the same temperature, but that H$_2$ total desorption is reached at a lower temperature than D$_2$. In particular, we note that H is only released from the LF complexes and remains trapped in the HF complexes until a higher temperature. In contrast, D is progressively lost from the HF structures, but above 370 °C, it remains surprisingly stable in the LF structures.

At the higher fluence (Fig. 8), Si–H and Si–D complexes behave apparently similarly during the thermal annealing. At low temperature (below 335 °C), these complexes are much more stable than at the low fluence, but at the increasing annealing temperature, the Si–H/D bonds are broken. We note that D prefers LF structures, whereas H is equally trapped in the LF and HF structures. From Figs. 4, 7, and 8, we can generally conclude that the H or D repartition between the multihydride/deuteride monovacancy and monohydride/deuteride multivacancy complexes is not highly sensitive to the H or D fluences after the implantation, but that its evolution during annealing depends strongly on the total amount of gas and defects.

Figures 9 and 10 show the evolution during annealing of the RSS spectra obtained after the H and D coimplantation at $2 \times 10^{16}$ and $6 \times 10^{16}$ ion/cm$^2$, respectively. One can also detect a narrow peak at 1555 cm$^{-1}$ corresponding to the Si–Si third harmonic and/or to the VD$_2$ complex. In parallel, hydrogen forms mainly the V$_3$/V$_2$/H$_2$ (2025 cm$^{-1}$) and H$_2$C (2050 cm$^{-1}$) complexes and a strong broadband. Also, a fraction of H is trapped in the V$_4$/V$_2$/H$_6$ (2182 cm$^{-1}$) complexes. Annealing up to 400 °C induces the collapse of the monohydride multivacancy complexes (1900–2050 cm$^{-1}$), and the remaining H is in a good part trapped in the V$_3$/V$_2$/H$_6$ complexes and a small fraction in the fully passivated vacancy (VH$_4$) complex. At the same temperature, we detect only a moderate loss of monodeuteride multivacancy complexes and the appearance of VD$_3$/V$_2$/D$_6$ (1587 cm$^{-1}$) centers, which grow further after annealing at 470 °C. The VD$_2$ or the Si–Si third harmonic is still dominant and becomes shoulder by a small peak (1544 cm$^{-1}$) associated with D on the (100) internal surfaces. The appearance of the extended internal surfaces is more pronounced in the case of hydrogen, whereas the LF deuterium modes are more stable at a high temperature. Up to 500 °C, the disappearance of the VH$_4$ structure is associated with the growth of Si(100):H. The same behavior is observed in the case of a single H implantation but at a slightly lower temperature (470 °C). The too low concentration of hydrogen must be the reason for the blister absence for coimplanted samples at $2 \times 10^{16}$ion/cm$^2$.

Indeed, at a higher fluence (Fig. 10), H undergoes roughly the same transformations except that the conversion of VH$_4$ complexes to the hydrogenated internal surfaces occurs at a lower temperature (below 470 °C), and these structures grow rapidly at an increasing temperature, hence blistering. The results are different for D: no VD$_4$ complexes are detectable in the Si–D RSS spectra. While the peak due to the deuterated internal surfaces can indeed be observed above 435 °C, its appearance may be explained by a partial conversion of the V$_3$/V$_2$/D$_6$ complexes, because their intensity decreases and the total amount of D trapped in the HF modes does not change significantly (Fig. 8). Comparing the Si–D RSS spectra measured for the different fluences of deuterium-implanted singly or with hydrogen, we note that the agglomeration of deuterium on the extended internal surfaces is easily achieved for the high concentration of deuterium and defects, whereas at a low D concentration, the VD$_2$ (or the Si–Si third harmonic) and ID$_2$ appear to be the favored complexes. In the case of hydrogen, the concentrations of H or defects do not influence the distribution of hydrogen in the different multihydride monovacancy complexes.

The contrast H and D behaviors were confirmed by the coimplantation of H or D with helium; H and He coimplantation is known to cause blistering at a reduced dose. We have found that blistering can be obtained by the implantation of a H fluence as low as $0.7 \times 10^{16}$ He/cm$^2$, in samples already implanted with an even smaller He fluence of $0.25 \times 10^{16}$ He/cm$^2$, whereas He itself does not cause blistering except for an extremely high fluence of $\sim 15 \times 10^{16}$ He/cm$^2$. This result shows that $0.7 \times 10^{16}$ He/cm$^2$ is enough to “prepare the ground” for blistering by nucleating platelets parallel to the surface, which the inert helium can fill and pressurize by a purely physical process. On the contrary, D and He coimplantation at the same fluences induce no blis.
tering whatsoever. (These experiments will be reported in detail elsewhere.)

IV. DISCUSSION AND CONCLUSION

We have identified a number of critical chemical transformations associated with the hydrogen- or deuterium-induced blistering of silicon. The puzzling dependence on ion mass is connected with the differences in the amounts and nature of defects caused by the D versus H implantation. In addition, as seen in particular in the case of the coimplantation, there are qualitative differences in the ways in which H and D interact with defects, even defects previously created by another implant, and the way the complexes evolve during thermal annealing. H is more efficient in promoting

![Graphs showing temperature evolution of Si–H/D stretch modes of Si coimplanted with 2×10^{15} (H+D)/cm².](image-url)
the blistering by nucleating platelets parallel to the surface, essentially due to its tendency to agglomerate under annealing in the multihydride monovacancy complexes, which are the precursors of hydrogenated extended internal surfaces. However, D is preferentially trapped in a highly stable low-frequency discrete modes, which are useless for the blister growth. We wish to emphasize that the interest in deuterium is not only academic; its use is increasingly envisaged for microelectronics applications. For instance, Lyding et al.\textsuperscript{22} have discovered how D is vastly superior to H for the passivation of the Si–SiO\textsubscript{2} interface. Also, as proposed by Gösele,\textsuperscript{23} the fact that D blistering occurs at a somewhat higher temperature than the H surface desorption, it can be an asset for the wafer bonding and layer transfer.

A first factor contributing to the isotope effect is the higher number of primary defects per incident ion for D in comparison with H; this is illustrated quantitatively by the SRIM\textsuperscript{10} computations shown in Table II. Experimental\textsuperscript{25} and theoretical\textsuperscript{23} work has indeed established an energy deposition threshold of \( \sim 12\, \text{eV/atom} \) for Si amorphization. However, one cannot but notice that the implantation of \( 2 \times 10^{16} \, \text{H/cm}^2 \) gives less damage than required for amorphization, whereas the energy deposition by the same fluence of D ions is definitely above the threshold. As we have checked, Si that has been deliberately preamorphized by the self-ion implantation is indeed immune to H blistering. However, the isotope effect cannot be a question of amorphization because a higher D fluence (6 \times 10^{16} \, \text{D/cm}^2) gives blisters, although a high fluence produces more amorphization than a low fluence. A second remark is that, according to the simple Lindhard-Scharff-Schiott (LSS) collision theory,\textsuperscript{26} the average distance between vacancies for D (\( \sim 1.7 \) interatomic distance) is about 30\% shorter than for H; the probability of producing divacancies is thus higher for D. It is well known that the single vacancy is mobile in the Si whereas the divacancy is stable.\textsuperscript{27} A similar conclusion can also be drawn using the LSS theory and the Kinchin-Pease model.\textsuperscript{28} The average Si recoil energy for H is \( \sim 20\, \text{eV} \), below the \( 2E_d \) threshold for divacancy production, whereas it is \( \sim 30\, \text{eV} \) for D, i.e., just around the threshold. We believe that this is a major point and that it favors the LF multivacancy monodeuteride defects over the HF monovacancy multideuteride defects, as observed.

The observed interplay between the \( \text{VH}_3/\text{V}_2\text{H}_6 \), \( \text{VH}_4 \) and Si(100):H (or their D counterparts) is compatible with some theoretical scenarios of Reboredo et al.\textsuperscript{19} or Zhang et al.\textsuperscript{29} for the nucleation and growth of (100) H platelets in silicon. They involve the reactions of free hydrogen with \( \text{VH}_4 \) and \( \text{V}_2\text{H}_6 \) complexes that lead to agglomeration into...
larger defects in (100) planes, larger defects that are the embryos of extended H-decorated internal surfaces. It is unfortunate, however, that we cannot identify a Raman signature for these larger planar defects that are intermediate between the small individual H-passivated vacancies or divacancies and the extended platelets. They may have a broad spectrum that simply contributes to the “HF broadband;” or else, their lifetime is so short that they are unobservable—maybe not surprising because blistering is a runaway phenomenon.

At this point, it is enlightening to discuss the related work of hydrogen isotopic substitution in silicon. First, let us dispose of the strong isotope effects found in the vibrational excitation of the H/D–Si bonds by the fast electrons. These bear no relation to our observations because they have been shown to be strictly nonthermal effects. Indeed, in the thermal adsorption/desorption of H and D on clean Si sur-

![Graphs showing temperature evolution of Si–H/D stretch modes of Si coimplanted with $6 \times 10^{16} (\text{H}+\text{D})/\text{cm}^2$.](http://jcp.aip.org/jcp/copyright.jsp)
faces, it is established that there is no anomalous isotope effect.\textsuperscript{32} Similarly, Heyman et al.\textsuperscript{14} found a remarkable similarity between the H and D infrared absorption spectra of the remote-plasma-hydrogenated (deuterated) crystalline silicon. The same conclusion also applies to the hydrogenated (deuterated) amorphous silicon.\textsuperscript{33} On the other hand, effects very similar to ours are found in the work of Budde et al.\textsuperscript{12} on the hydrogen-defect complexes formed by a very low fluence H/D implantation of silicon at a MeV energy. This confirms our hypothesis that the isotope effect is connected with the ion implantation—in spite of the fact that, under a MeV irradiation, the ion energy loss is totally dominated by the inelastic processes (electron excitation and ionization), whereas at our low energy, elastic collisions are also important. Moreover, as found by Fukata et al.,\textsuperscript{17} a neutron irradiation of hydrogenated (deuterated) silicon also results in strong isotopic differences, whereby some local vibration modes change in relative intensity or even disappear upon an isotope substitution. This last result is particularly instructive because the nature and the amount of the neutron-induced primary damage is of course the same with both isotopes. This, together with our experiment of coimplantation, lead to the striking notion that H and D interact differently with the same primary defects, whether they have been produced by a previous implant (coimplant) or by a postirradiation (neutrons). One can then conclude that H and D present similar vibration modes when trapped in an undamaged silicon or when adsorbed on a clean silicon, but that they behave very differently in the presence of a radiation damage.

It would be of great interest to see our conclusions verified by the state-of-the-art computations of the trapping of H and D in Si.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Isotope & Displacement density (dpa) & Peak energy deposition (eV/atom) \\
\hline
Hydrogen & 0.08 & 8 \\
Deuterium & 0.20 & 20 \\
\hline
\end{tabular}
\caption{SRIM (Ref. 10) computations of the peak dpa and energy deposition into recoils by $2 \times 10^{16}$ 5-keV H or D ions per cm$^2$ in Si.}
\end{table}

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10 As computed by the binary collision code SRIM, see J. F. Ziegler and J. P. Biersack, www.srim.org.
11 Nanotec Electronica, C/Padilla 1, 28006 Madrid (Spain), http://www.nanotec.es.
23 U. Gösele (private communication).