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Direct experimental evidence for monosilane formation after proton or deuteron implantation of crystalline silicon

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We report the first experimental data on monosilane formation after proton or deuteron implantation of crystalline silicon. No mixed silane frequencies nor any changes of the shapes of the observed bands are noticed in the region between 300 and 2300 cm^{-1} after successive proton and deuteron irradiation. These results imply a random substitution of implanted hydrogen or deuteron atoms in the crystalline lattice.

The vibrational properties of hydrogen in silicon have been the subject of considerable study (for a comprehensive review see the recent paper by Cardona[1]). The major conclusion, supported by the work of various workers,[1] is that multisilanes are present in hydrogenated amorphous silicon, as well as after proton irradiation of the crystalline material. Although, in principle, it is possible to form these silanes (i.e., disilane and trisilane), up until now there has been no direct experimental evidence that they are formed during deposition or irradiation. The simple heuristic argument that there is not enough hydrogen to form multisilane molecules, especially after irradiation, is silently dismissed (see the references given in the paper by Cardona[1]). In this paper, we would like to present measurements which, in our opinion, suggest that hydrogen is bounded within damaged regions as monosilane only. The basic idea of our experiment is to implant not only protons but also deuterons into the same sample and observe the localized vibrational mode (LVM) frequencies and the intensities of the (hypothethically possible) mixed silanes, e.g., SiHD. Similar experiments were performed with deuterated and hydrogenated amorphous silicon,[2] but the experimental conditions in these studies did not permit the observation of mixed LVM's. On the other hand, the technique developed by one of the authors,[3] allows us to observe all the possible vibrations of silane molecules in crystalline silicon (i.e., stretching and wagging or rocking) with good accuracy. The method is very sensitive and enables a precise estimate of oscillator strengths of the different LVM's to be made.[4]

Taking into account the similarity between the vibrations of gaseous deuterated silanes (see Ref. 2), i.e., SiH_2D_2, $SiHD_3$, and SiD_4 and the LVM's of hypothetical disilanes existing in the crystal after implantation, one should expect dramatic changes in the shape of the bending-modes band (600–900 cm^{-1}). Some bending vibrations have entirely new positions for the mixed silane ($SiHD_3$) as compared with $SiHD_2D_2$ and SiD_4. In the stretching-mode band one expects a decrease of the relative intensity by a factor of 2 in the mixed implanted sample, which should be reflected in the shape of the high-frequency shoulders of this band. We are thus searching for changes in the relative intensities (as compared with the samples implanted solely with protons or deuterons) proportional to the relative abundance of the disilane.

We have used B-doped silicon monocrystals with an initial resistivity of about 100 $\Omega\,cm$, which contained less than 10^{16} cm^{-3} oxygen and carbon atoms. The samples were cut in the (111) plane and polished mechanically and chemically to a thickness of about 1.85 mm, with matching pairs of samples being used for differential absorption measurements (for a detailed description of this technique and the apparatus used, see Ref. 3).

The samples were implanted with the protons and deuterons in the Warsaw van de Graaff accelerator LECH. Since the maximum energy of the deuterons was 2 MeV, we had to determine the energy of protons which would give a similar total range in order to obtain the same region of high silane concentration. Using the tables in Ref. 5, we have found the total range of 2-MeV deuterons in silicon of about 32 μm. It is known from experiments[6] that the total proton range in silicon of 32 μm corresponds to an energy of about 1.6 MeV (see also Ref. 5). In the present study we used a mean proton or deuteron current of about 1 $\mu A/cm^2$ and implantation times of about 20 h; hence we get the total dose of about 5.6×10^{17} $ions/cm^2$. Taking into account the range straggling for 1.6-MeV protons in silicon of about 5 μm (Ref. 7), and assuming a similar range straggling for 2-MeV deuterons, we get hydrogen or deuterium concentrations of about 2.5-at.%. This concentration is typical of amorphous silicon.[1] It is interesting to note that the concentration of the introduced divacancies for deuterons is twice as large as it is for protons (the latter being about 2×10^{16} cm^{-2} according to the scaling of Stein, Vook, and Borders[8]). This result shows that our irradiations were carried out correctly. We estimate that, since the samples were water cooled (through the heat sink) during implantation, the temperature was kept below 50 °C.

In order to interpret our experiment, precise knowledge of the depth of the damaged region within the crystal, where the implanted ions are retained, is crucial. Hence, we have employed three different methods to measure this depth. When the samples were implanted with the same energies during preliminary tests to the dose of 10^{18} $ions/cm^2$, we could see interference fringes in the spectrum. From the distances between these fringes we have calculated the depth of the damaged region to be 33 and 32 μm for proton and deuteron implantation, respectively. Fast thermal annealing leads to the bursting of the heavily proton-

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implanted layer (see Ref. 9 for a description of this effect). In our samples we have measured the thickness of the layer in which such a bursting took place to be between 27 and 33 μm for both types of implantation. Moreover, we have made a 2° bevel which has shown (under an optical microscope) a homogeneously damaged region for the doubly implanted sample. These experiments confirm our hypothesis that 1.6-MeV protons and 2-MeV deuterons produce the majority of the defects at the ends of their tracks. The maximum depth of the damaged region is about 32 μm from the crystal surface, whereas the width of this region is about 5 μm. Hence, one can suppose that in the doubly implanted sample both protons and deuterons are stopped and bound within the same layer. As the final experimental confirmation of the validity of our method, we have implanted one sample to a dose of 3.75×10^{17}-cm^2–2-MeV deuterium ions and later with the same doses of 1.25×10^{17}-cm^{-2} hydrogen ions with three slightly different energies: 1.55, 1.60, and 1.65 MeV, respectively. The results obtained were the same as for the double implantation case.

Figure 1 shows our experimental data for proton, deuteron, and mixed implantation. We note the presence of silicon one-phonon vibration TO modes at about 480 cm^{-1}. These bands were induced by irradiation because the defects break the lattice symmetry.[10] All the other bands observed are attributed to implanted hydrogen and deuterium. We have used the frequencies of LVM's of hydrogen (comparable with those obtained in an earlier work[3]) to calculate the expected positions of the deuterium LVM's, with the reduced masses of hydrogen and deuterium in silicon being about 0.973 and 1.880 amu, respectively. The square root of the ratio of these masses gives a value of about 1.39, whereas the experimentally observed shift of the frequencies is about 1.375 (see also Ref. 11, where a similar effect is described). The difference of about 1% can be easily explained by the anharmonicity of the LVM's of SiH and SiD defects. The calculated frequencies are shown in the middle of Fig. 1; they give a perfect fit to the observed spectrum. The oscillator strengths of the vibrational transitions in the case of deuterium resemble those obtained for hydrogen defects in c-Si (see Table I and Ref. 4). The doubly implanted sample exhibits slightly weaker hydrogen absorption, which we explain by the higher defect concentration and/or partial dehydrogenation during subsequent deuterium implantation.

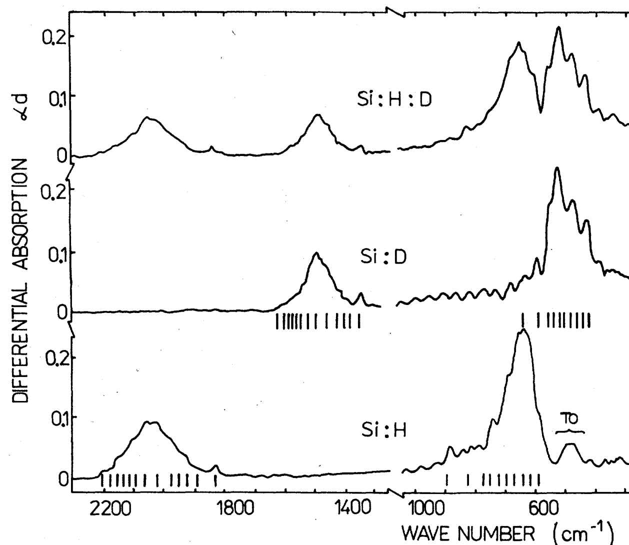

FIG. 1. Absorption spectra of proton, deuteron, and mixed implanted crystalline silicon (doses of 5.6×10^{17} ions/cm^2), measured at about 300 K. The silicon one-phonon TO modes are marked.

Our main experimental result is that the spectrum for the mixed hydrogen- and deuterium-implanted sample is a simple sum of the corresponding spectra for single hydrogen- and for deuterium-implanted samples. Since we have not seen any changes of the shapes of the observed bands in the whole range of wave numbers examined (from 300 up to 2300 cm^{-1}), we claim that the main configuration in which hydrogen is retained in the crystalline lattice after irradiation is monosilane. We estimate that the upper limit of the con-

TABLE I. Experimental intensities and estimated oscillator strengths of the dominant absorption bands for proton, deuteron, and mixed implanted silicon.

LVM type	LVM's positions (cm^{-1})	Intensities of the bands I^a	Estimated oscillator strengths $f_0{}^b$
	Hydrogen		
Stretching	1800–2210	0.009	0.2
Wagging-rocking	500–800	0.048	0.4
	Deuterium		
Stretching	1300–1650	0.0075	0.25
Wagging-rocking	350–570	0.044[c]	0.45
	Hydrogen-deuterium		
Stretching	1800–2210	0.006	0.15
Stretching	1300–1650	0.006	0.2
Wagging-rocking	550–800	0.036	0.3
Wagging-rocking	350–550	0.04[c]	0.45

[a] $I=\int_{\text{band}}(\alpha d/\omega)\,d\omega$.

[b] For the method of calculation see Refs. 1 and 4.

[c] The absorption due to Si TO modes has been subtracted.

centration of multisilanes is 5% of the total bonded hydrogen. This estimate is based on the accuracy of the absorption measurement ($\Delta\alpha d = 0.005$). Only a very weak scissor mode[2] of possible SiH_2 is observed at about 890 cm^{-1} (for a deuterium-implanted sample at about 660 cm^{-1}). No lines typical of SiH_3 vibrations [910 and 860 cm^{-1} (Ref. 1)] are observed. In the doubly implanted sample, two small peaks are visible near 800 cm^{-1}. The intensity of the above-mentioned lines is at least 20 times smaller than those of the other lines observed in this frequency region; hence our 5% limit of hydrogen in multisilanes is also met here.

A similar estimate can be obtained from the simple statistical model of hydrogen atoms randomly placed in a crystal lattice. The radius of a "temperature spike"[3] in silicon during proton irradiation is about 9 Å; hence the probability of bonding of two hydrogens in the region of one spike to the same silicon atom is less than 0.04. In other words, our result means that hydrogen saturates the dangling bonds caused by the radiation damage introduced during implantation, and forms SiH molecules bound to the host lattice. This point of view supports the model of Paul,[12] who postulated four configurations with monosilanes in amorphous hydrogenated silicon, leading to higher bending vibrational frequencies.

The slightly different shape of the bending-mode bands for hydrogen- and deuterium-implanted samples can be explained by two facts. Keeping in mind the two-phonon silicon crystal absorption, we have to note that the resolution of our measurement in this specific region (between about 550 and 700 cm^{-1}) is the worst because of the absence of light transmitted through both samples (irradiated and reference). This also means that although our reference sample has been matched before the implantation, this can be spoiled by the thickening of the other sample after irradiation; we have added about 2 at.% of foreign atoms and many defects. We have already observed[9] that the surface of the heavily implanted sample is curved and bubbled. Even the smallest difference in thickness will introduce an artificial absorption line, corresponding to the maximum of the two-phonon absorption of crystalline silicon (610 cm^{-1}), which can overlap the three possible peaks observed for deuterium. With higher-energy implantations (see Ref. 3) this effect was not visible because of the much lower hydrogen concentrations involved. Hence, we have observed lines which are much better resolved (see, e.g., Ref. 4).

In order to obtain further confirmation of the validity of our model, we have made some thermal annealing experiments (isochronal as well as isothermal). No transition LVM frequencies were observed for the mixed proton- and deuteron-implanted sample, though, as has been the case in previous studies,[9,11] we have found some changes of the relative intensities of the LVM's. As reported previously,[9] during thermal annealing at 300 °C (20-min isochronal steps of 50 °C), the lines with the maximum at about 2000 cm^{-1} start disappearing, whereas the lines centered at around 2100 cm^{-1} persist up to 450 °C. The same effect is observed for the corresponding 1500- and 1550-cm^{-1} deuterium lines. We also observe a very weak absorption line corresponding to possible SiH_2 molecules (at 890 cm^{-1}), but, because of the above-mentioned thickening of the sample during thermal annealing (which eventually leads to the bursting of the implanted surface), we are unable to resolve any lines in the region between 600 and 700 cm^{-1}. Moreover, after the 450-°C step we observe interference fringes, because bursting starts at this temperature (the complete destruction of the sample happens at 500 °C, in agreement with the thermal evolution of hydrogen in amorphous silicon; see Ref. 1). The agglomeration of defects and hydrogen during annealing is another expected event (see, e.g., Ref. 4).

The observed shape of the broad stretching band, centered for *c*-Si:H at about 2000 cm^{-1} (at about 1500 cm^{-1} for *c*-Si:D), suggests that there are some monosilanes placed in different lattice environments (small changes of the basic frequency). The high internal stress in the crystal due to radiation damage could widen LVM lines as compared with the low hydrogen concentrations used in the previous studies (see Refs. 3 and 4). Since hydrogen or deuterium concentration in the present experiment far exceeds (by three or four orders of magnitude) the concentration of any impurity in the crystal, it is impossible to assign the various sub-bands to the different atomic clusters comprising other impurity atoms, as has been suggested for amorphous hydrogenated silicon by Lucovsky.[13] To check the possible influence of the lattice stress on the observed LVM's, we have implanted four additional samples to the same dose of 5.6×10^{17} cm^{-2} with 2-MeV protons. The three samples were cut in the (111), (110), and (100) planes, respectively, whereas the fourth was the polycrystalline one. No measurable effects (except a slight widening of the lines in the case of the polycrystalline sample) has been noticed, thus eliminating this explanation of the origin of the multiplicity of the lines in the observed spectra.

We believe that our interpretation of the experimental data obtained, i.e., the proposal that mainly monosilanes are present after irradiation (though their lattice environments differ), is consistent with all that is known about hydrogen is silicon, and simplifies the picture of hydrogen or deuterium defects in *c*-Si.

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