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Defect-related diffusion of hydrogen in silicon

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Abstract

Hydrogen-related effects in silicon with radiation defects are discussed in the present report. The first effect is the defect-related out-diffusion of hydrogen from an implanted layer. The second one is the saturation with hydrogen of some layers in neutron-irradiated silicon, during its boiling in pure water.

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Keywords: Defects; Hydrogen; Diffusion; Silicon

1. Introduction

Due to the high activity of the hydrogen atoms in silicon (i.e. the creation of shallow and deep centers, hydrogen complexing with different defects and impurities, the passivation effect) this impurity has attracted considerable attention during the last years [1]. Hydrogen can penetrate into silicon during crystal growth and in effect of different chemical and heat treatments since its diffusion coefficient is large enough even at low temperatures [2]. It is well known that the hydrogen diffusion is strongly dependent on interaction with defects and impurities in silicon [3]. Two hydrogen-related effects are considered in the present report. The first one is out-diffusion of the hydrogen from an implanted layer during annealing at moderate temperatures. The second effect is the penetration of hydrogen into neutron-irradiated silicon during boiling in pure water. Hydrogen accumulation in the near-surface layers of silicon and native oxide leads to visible photoluminescence from such structures.

2. Experimental

Czochralski grown silicon samples with the 1 1 1 and 1 0 0 orientations were used in this investigation. The oxygen concentration obtained from IR absorption measurements was $7\text{–}9 \times 10^{17}\,\text{cm}^{-3}$. Some samples were implanted with H_2^+ (energy of 120 keV and fluence of $6 \times 10^{16}\,\text{H/cm}^2$). The ion beam contained 94–96% of H_2^+ ions (projected

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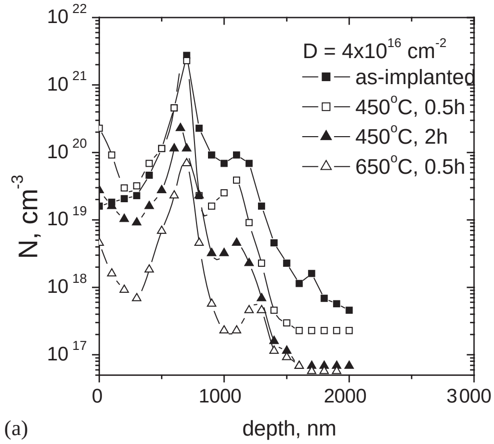
range, $R_{p1} = 500\,\text{nm}$) and 4–6% of H^+ ions ($R_{p2} = 950\,\text{nm}$) with the same energy. Two different regimes of implantation were used. The first regime provides higher ion current (110 μA) than the second one (70 μA). The samples were annealed at 450–650°C for 0.5–10 h. Other samples were irradiated with fast neutrons at fluences of 5×10^{16} and $1 \times 10^{17}\,\text{cm}^{-2}$. The irradiated and initial reference samples were boiled in pure water for 5–10 h. Secondary ion mass spectroscopy (SIMS), photoluminescence (PL), high-resolution X-ray diffraction (HRXRD), and capacity–voltage (CV) measurements were used for sample characterization. SIMS measurements were performed with a Cameca IMS 6F instrument using 14 keV cesium ions beam for detection of hydrogen. A pulsed N_2 laser ($\lambda = 337\,\text{nm}$) with a pulse duration of 7 ns and a peak power density of $4\,\text{kW}\,\text{cm}^{-2}$ was used for PL excitation. The PL signal was detected by a cooled S-20 photomultiplier operating in the photon counting mode. The PL measurements were conducted at room temperature. The structural characterization of the samples was carried out using a high-resolution MRD Philips diffractometer applying the double-crystal (DCD optic) and the triple-axis (TAD optic) configurations. The instrument was equipped with a four-crystal Ge 220 monochromator and a two-reflection Ge 220 analyzer. CuK_α radiation was used to measure the 1 1 1 and 4 4 4 reflections. High frequency (1 MHz) CV measurements were performed using a mercury probe with a mercury probe with a probe square of $3.7 \times 10^{-4}\,\text{cm}^2$.

3. Results and discussion

The depth distributions of hydrogen obtained by SIMS, for the as-implanted and annealed samples for both implantation regimes, are given in Fig. 1a and b. The integral amount of hydrogen in these samples is presented in Fig. 2. The decrease in hydrogen concentration due to out-diffusion is clearly seen to depend on implantation regime. The diffusion coefficient of hydrogen is so large that all the released hydrogen atoms are removed from the implanted area without the spreading of hydrogen profiles. The distribution of



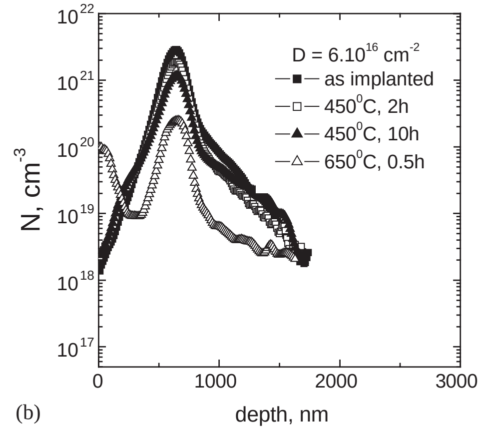


Fig. 1. Depth distribution of hydrogen atoms in silicon implanted with hydrogen ions, before and after annealing at temperatures 450°C and 650°C for 0.5–10 h. Ion currents during implantation were 110 μA (a) and 70 μA (b).

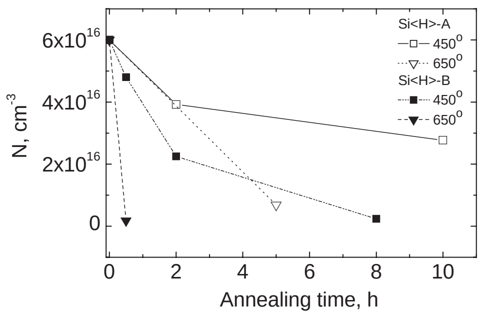


Fig. 2. Integral amount of hydrogen in implanted silicon as a function of annealing time at temperatures 450°C and 650°C for samples implanted with the ion currents 110 μA (Si⟨H⟩-A) and 70 μA (Si⟨H⟩-B).

hydrogen atoms bound in different complexes with radiation defects are seen in Figs. 1 and 2. The higher ion current leads to higher temperature of crystal during implantation. As a result different defects are formed in the samples and the same annealing regime leads to release of different amounts of hydrogen. Thus, the amount of hydrogen presented in the sample is determined primarily by the type of the residual hydrogen-contained defects in the crystal.

Let us consider the results of hydrogen penetration into neutron-irradiated silicon during boiling in pure water. The depth distributions of hydrogen are shown in Fig. 3 for the samples irradiated with different hydrogen doses and boiled in pure water for different times. SIMS did not detect penetration of hydrogen into the non-irradiated silicon. Much higher concentration of hydrogen was found in the neutron-irradiated silicon. The interaction of the hydrogen with defects in silicon crystal is seen to be a complicated function of the neutron fluence: the increase in neutron fluence does not lead to an increase in the hydrogen concentration and the penetration depth. Oxygen accumulation in the layer enriched with hydrogen was found for the sample subjected to irradiation with the highest neutron dose. An estimation of the effective diffusion coefficient of hydrogen was made basing on the results presented in Fig. 3: It was equal to $D^* = 2 \times 10^{-15}\,\mathrm{cm^2/s}$ for the temperature 100°C in silicon irradiated with a dose of $5 \times 10^{16}\,\mathrm{cm^{-2}}$. This value was obtained for the case of diffusion from a limited source, which provide the best fit with the experimental profile.

Saturation of the near-surface layers of silicon with hydrogen leads to visible photoluminescence from such structures (Fig. 4). This effect is related to the oxide grown on the silicon surface during boiling. An increase in the time of boiling leads to an increase in the PL intensity. If the initially present oxide is removed in HF solution, PL was not observed. Then the native oxide grown on the surface of silicon incorporates again hydrogen atoms and demonstrates similar PL spectra.

Fig. 5 presents the CV characteristics for non-irradiated samples boiled in water. The type of

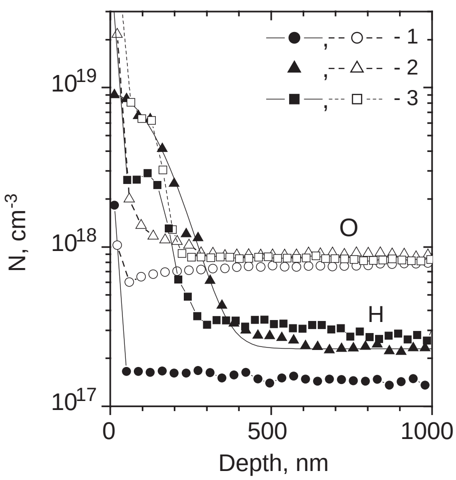


Fig. 3. Hydrogen and oxygen profiles obtained from SIMS measurements for samples irradiated by neutrons with fluences $5 \times 10^{16}\,\mathrm{cm^{-2}}$ (1,2) and $1 \times 10^{17}\,\mathrm{cm^{-2}}$ (3) and boiled in pure water for 1 h (1), 10 h (2) and 16 h (3).

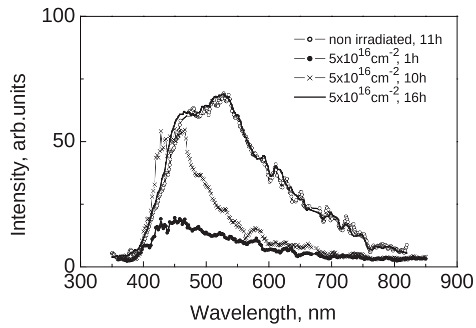


Fig. 4. Spectra of PL intensity for initial and neutron-irradiated samples boiled in pure water. Time of boiling and neutron dose are given in the figure.

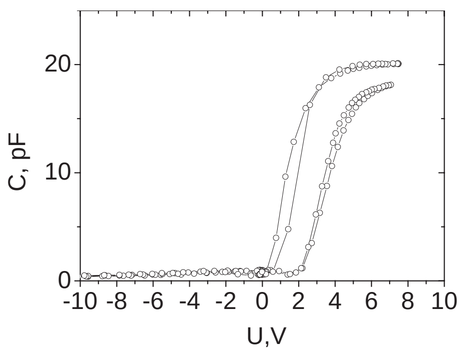


Fig. 5. CV characteristics for non-irradiated samples boiled in water for 16 h. The different curves correspond to different points on the sample surface.

hysteresis which is seen in the CV characteristics is most likely connected with the recharging of traps located in silicon near the Si/SiO_2 interface. The density of this traps calculated from float band voltages is $8 \times 10^{11}\,cm^{-2}$. We have suggested that presence of hydrogen in high concentration in native oxide and Si/SiO_2 interface provides the visible PL from the silicon samples.

Modulation of the capacitance for irradiated samples was not observed due to high irradiation fluence and to large compensation of the material by the radiation defects. Nevertheless, we have to assume that silicon oxide on the surface of the irradiated samples is similar to the oxide for non-irradiated samples. At least, the PL spectra for the irradiated and initial samples are very similar.

Comparing rocking curves obtained in the DCD and TAD optics for the 1 1 1 and 4 4 4 reflections it has been found that the differences of diffuse scattering intensities between the neutron irradiated and initial samples are larger for the 1 1 1 reflection than for the 4 4 4 one (Fig. 6). It means that the defects responsible for X-ray diffuse scattering are very close to the sample surface (because the X-ray penetration depth for the 4 4 4 reflection is larger than that for the 1 1 1 one). In effect of pre-radiation (before boiling) of the Si sample, the diffuse scattering was enhanced. Possibly, this effect is related to diffusion of hydrogen/oxygen to the near-surface areas with creation of some O-, H-related complexes, promoted by the presence of irradiation-induced defects. Neutron irradiation is introduced the large defect complexes both interstitial and vacancy related types in silicon. A number of novel electrically active H-related complexes with defects and passivation of the well-known radiation defects were observed in implanted and electron-irradiated silicon [4,5]. Formation of the O–H and/ or O–H_2 complexes is also known at low-temperature annealing (50–70°C) [6,7]. X-ray and CV results can be considered as an evidence that the near-surface area in neutron-irradiated sample is directly disturbed and, jointly with SIMS results (more hydrogen + oxygen detected) suggest the creation of defect complexes of above mentioned or similar kinds.

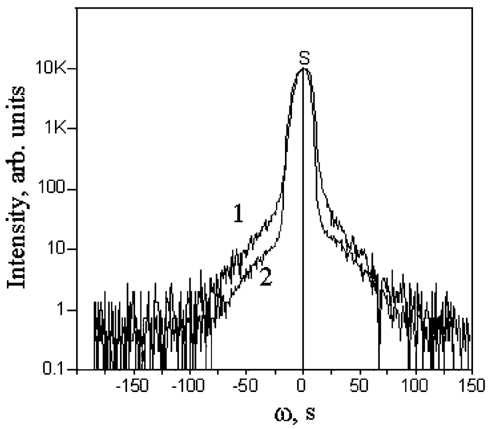


Fig. 6. X-ray rocking curves obtained in TAD optic for 4 4 4 reflection from silicon irradiated with maximal dose of neutrons and boiled for 10 h in pure water (1) and from as-grown (initial) silicon (2).

4. Conclusions

Out-diffusion of hydrogen from the hydrogen implanted layer in silicon is found to be dependent on the type of hydrogen-contained radiation defects formed during H_2^+ implantation. Saturation of the near-surface layer (of ~400 nm thickness) with hydrogen (up to $10^{19}\,cm^{-3}$) was observed after boiling of the samples irradiated by fast neutrons in pure water. Visible photoluminescence connected with the hydrogen-enriched native oxide on the surface of silicon saturated with hydrogen was demonstrated.

Acknowledgements

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