Evidence for solid-phase migration of Si atoms in laser-irradiated, Si^+-implanted SiO_2

1989 J. Phys.: Condens. Matter 1 5521

(http://iopscience.iop.org/0953-8984/1/32/022)

J. Phys.: Condens. Matter 1 (1989) 5521–5525. Printed in the UK

LETTER TO THE EDITOR

Evidence for solid-phase migration of Si atoms in laser-irradiated, Si^+-implanted SiO_2

Tsutomu Shimizu, Tetsuo Fujita and Noriaki Itoh
Department of Physics, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku,
Nagoya 464-01, Japan

Received 31 May 1989

Abstract. We measured ESR spectra of Si^+-implanted SiO_2 before and after laser irradiation, which causes re-emission of Si atoms. It is found that no change is induced in the concentration of the E_1-centres even after most implanted Si atoms are depleted. The results indicate that the energy absorbed in Si embedded in SiO_2 is not intransferred significantly to the SiO_2 lattice and that the re-emission is caused by migration of Si atoms in the solid phase of SiO_2.

Materials modification by laser irradiation is a topic of current technological interest. Most studies employ laser photons of above-gap energies and hence photons are absorbed homogeneously by surface layers causing melting (see for example, [1]). On the other hand, the response of materials to laser photons of sub-band energy has been shown to be the cause of laser damage [2, 3] but the microscopic processes are not yet understood.

It has been reported [4] that irradiation of Si^+-implanted SiO_2 with a laser pulse of energy greater than 0.2 J cm^{-2} induces a shift of the Si distribution in SiO_2 towards the surface, and induces re-emission if the intensity of the laser pulse is strong enough. It was found that a laser pulse of 1 J cm^{-2} removes a substantial proportion of implanted Si atoms [4]. The phenomena were ascribed to thermal diffusion, the diffusion being due to the temperature gradient. It is not yet known whether the re-emission occurs through diffusion of Si atoms in the molten layer or in the solid phase. Since the thermal stability of the E_1-centres generated by ion-implantation is known, measurements of laser-induced annealing of the E_1-centres produced by implantation are considered to give information on the temperature of the part of the specimen through which Si atoms passed before re-emission.

The purpose of this Letter is to report studies of the effects of laser irradiation and isochronal annealing on the defects in Si^+-implanted SiO_2. It is shown that no change was induced in the concentration of the E_1-centres (singly ionised oxygen vacancies) by laser irradiation, indicating that the parts of the specimens from which Si atoms are re-emitted, are not molten.

Suprasil fused quartz specimens of $10 \times 3 \times 1$ mm^3 were used in the present experiments. 150 keV Si^+ atoms were implanted into specimens at a current of 300 μA to fluences of 2×10^{17} and 5×10^{17} ions cm^{-2} at room temperature. Si^+-implanted SiO_2 specimens were further irradiated with laser pulses in air or heated to temperatures between 200 and 500 °C in a vacuum. Laser pulses of wavelength 308 nm with a pulse

0953-8984/89/325521 + 05 $02.50

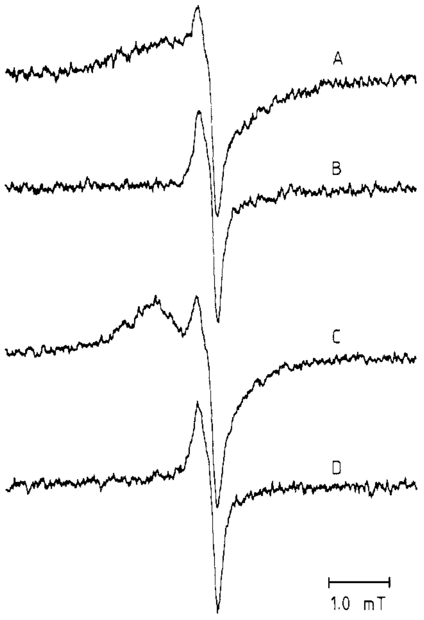

Figure 1. ESR spectra of Si^+-implanted SiO_2 to fluences of 2×10^{17} (curves A and B) and 5×10^{17} ions cm^{-2} (curves C and D) at an energy of 150 keV as-implanted (curves A and C) and after irradiation (curves B and D) with laser pulse of 1.2 J cm^{-2}.

duration of 20 ns were generated using a XeCl excimer laser and isochronal annealing was carried out using an electric oven.

Electron-spin resonance (ESR) spectra of specimens before and after laser irradiation and isochronal annealing were measured at room temperature using an X-band spectrometer (JEOL, JES-FE1XG) with a modulation frequency of 100 kHz and a microwave power of 5 μW. The low microwave power was used to avoid power saturation. It has been shown that the E_1-centres are generated at a concentration of about 10^{19} cm^{-3}.

In our previous experiments [4] we employed implantation energies of 50 keV and 180 keV at a fluence of 5×10^{17} ions cm^{-2} and showed that the general trends, including the absolute value of the laser fluences that induce the shift of the Si-atom distribution and re-emission, were not appreciably dependent on the energy of implantation or on the ion fluence. In the present experiments, 150-keV Si^+ were implanted to fluences of 2×10^{17} and 5×10^{17} ions cm^2.

ESR spectra were obtained for Si^+-implanted specimens before and after irradiation with a laser pulse of fluence 1.2 J cm^{-2}. Figure 1 shows the results for the specimens implanted to fluences of 2×10^{17} and 5×10^{17} ions cm^{-2}. It is clear that the spectra before irradiation are composed of at least two components: the sharp line has been ascribed to the E_1-centres and the broad line to the a-centres [5] (defects in amorphous Si). It is also clear that the broad component is eliminated after irradiation with a laser pulse of fluence 1.2 J cm^{-2}. Although it is not shown in the figure, the intensity of the broad component is found to be diminished by irradiation with a laser pulse of fluence above 0.3 J cm^{-2}. These results are consistent with the assignment that the a-centres are defects in amorphous Si, since we found that only the shift in the distribution takes place at 0.3 J cm^{-2} and that almost complete re-emission is induced at 1.2 J cm^{-2}. From figure 1, it is clear that almost no change is induced by laser irradiation in the concentration of the E_1-centres.

In order to investigate the thermal stability of the ESR centres in the Si^+-implanted specimens with two different fluences, isochronal annealing measurements were carried

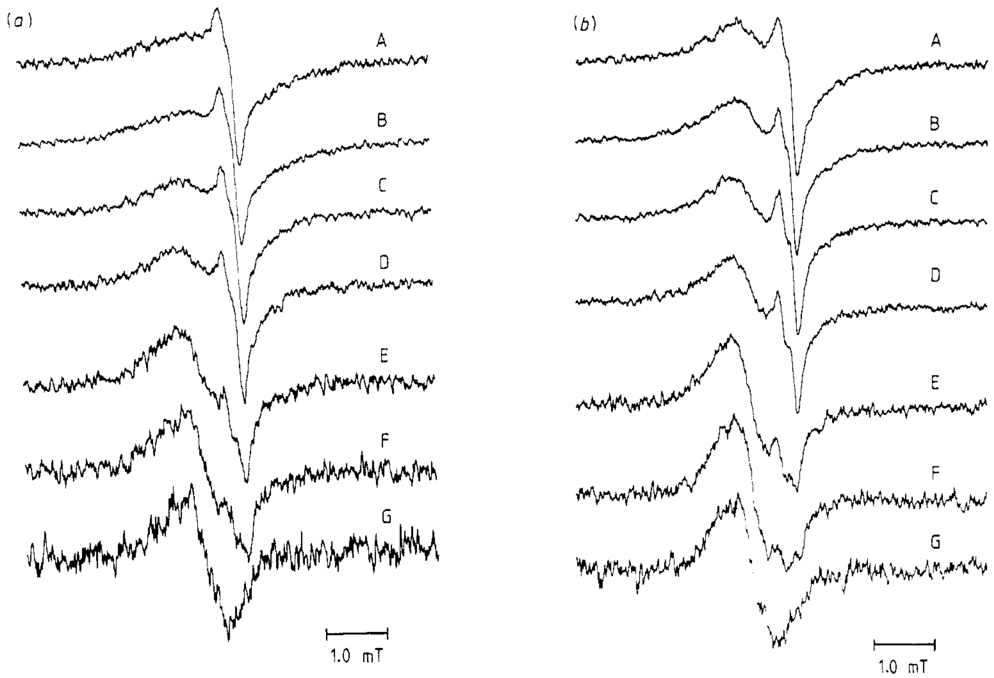

Figure 2. ESR spectra of Si^+-implanted SiO_2 to fluences of (*a*) 2×10^{17} and (*b*) 5×10^{17} ions cm^{-2} at an energy of 150 keV. Curve A, as-implanted; curves B–G, after isochronal annealing for 30 min at various temperatures. Curve B, 200 °C; curve C, 300 °C; curve D, 350 °C; curve E, 400 °C; curve F, 450 °C; curve G, 500 °C.

out in a vacuum for 30 min. The results for the two implantation fluences are shown in figure 2. The figures show the ESR spectra before and after isochronal annealing at several temperatures. It is clear that the E_1-centres are unstable above about 500 °C. These isochronal annealing data are identical with those for γ-ray irradiation [6]. The activation energy for annealing of the E_1-centres has been obtained to be around 1.35 eV [7].

It has been generally accepted that the distribution of the implanted ions is peaked at the end of the range and that of the defects is peaked nearer to the surface [8]. In our previous experiments [4] we showed that the Si distribution after implantation at an energy of 180 keV to a fluence of 5×10^{17} ions cm^{-2} peaks at about 200 nm from the surface and that the peak concentration is about 40%, and the concentration near the surface is less than 5%. The concentration of the a-centres generated by Si^+-implantation depends strongly on the ion fluence, as can be seen from figure 2. It has been shown [5] that almost no a-centres, the presence of which indicates formation of Si precipitates, were observed at a fluence of 1×10^{17} ions cm^{-2}. Thus it is likely that Si precipitates exist only near the peak of the Si distribution and that both dispersed Si (probably in the form of SiO_x) and defects, including the E_1-centres at a concentration of $2 \times 10^{19} cm^{-3}$ as previously obtained [5], are distributed between the peak and the surface. Now photons are absorbed only by the Si precipitates and dispersed Si atoms. The results of the present and previous experiments show that: (i) when the laser fluence is high enough, the Si atoms are re-emitted without inducing any effects on the E_1-centres and (ii) when the laser fluence is not sufficiently high, the distribution of the Si atoms is pushed toward the surface, again without influencing the E_1-centres.

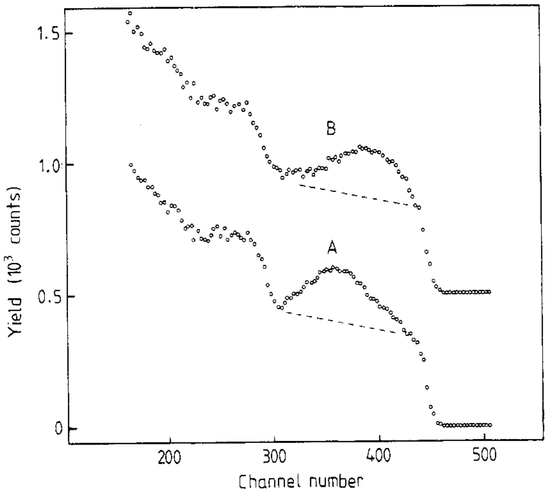

Figure 3. Rutherford backscattering spectra (RBS) of Si^+-implanted SiO_2 to a fluence of 5×10^{17} ions cm^{-2} at an energy of 180 keV. Data A, as-implanted; data B, after irradiation with a laser pulse of 0.58 J cm^{-2}. The broken lines are RBS of non-implanted SiO_2.

The absence of any influence on the E_1-centre concentration indicates that the SiO_2 layers, through which re-emitted Si atoms passed, were not molten. (Here, molten means that the part of the solid in question is in the liquid phase over a time period of the inverse of the lattice characteristic frequency and hence defects are considered to be transformed to other forms and/or to be substantially annihilated.) Thus we conclude that the migration of Si atoms occurs without formation of a molten SiO_2 phase. As reported in the previous paper [4], the Si distribution is shifted without changing the total amount of Si atoms appreciably for a low fluence laser pulse. In figure 3, we present the original RBS (Rutherford backscattering) spectra, from which the results in the previous paper were derived, in order to show that the Si distribution does indeed shift. In view of these experimental results, we can exclude the possibility that the implanted Si atoms form a channel, through which Si atoms diffuse to the surface.

From the arguments above, we conclude that migration of Si atoms induced by a laser pulse occurs in the solid phase. A laser pulse of 1 J cm^{-2}, which induces almost complete re-emission, gives energies of about 50 eV to each Si atom in average, if absorbed by 2×10^{17} ions cm^{-2} Si atoms. If the energy imparted to Si atoms is converted to heat SiO_2 lattice, the temperature rise was evaluated to be 2000 °C. Assuming that the annealing rate is given by $\nu = \nu_0 \exp(-E/kT)$, and using the value $\nu_0 = 10^{12}$ s^{-1} and $E = 1.35$ eV [7], we obtained the annealing rate at 2000 °C as being $\nu = 10^9$. Therefore if all energy absorbed by silicon atoms were imported into the SiO_2 lattice, the E_1-centres would have been annealed within the duration of a laser pulse of 20 ns. The heat will be stored longer than the duration of a laser pulse, because of the low thermal conductivity of the material. Thus it is likely that the energy imparted to Si atoms is not transferred efficiently to the SiO_2 lattice, but is partly carried away by emitted Si atoms. In fact we observed acoustic emission as well as photon emission when re-emission of Si atoms is induced. We also observed that the re-emission is highly oriented to the surface normal from the pattern of re-deposited silicon on a glass plate, and that, when a specimen was bombarded with a laser pulse, it was repelled in the rearward direction.

The energy imparted to each Si atom is too small for penetration through the SiO_2 layer to take place. We consider that the migration of Si atoms is assisted by thermal diffusion. Since the Si clusters are highly pressurised by photon absorption, Si atoms acquire momentum unidirectionally toward the surface. During migration through the

SiO_2 layer, a part of the energy possessed by Si atoms is imparted to the SiO_2 lattice, and because of the high Si concentration, the SiO_2 lattice is heated, but to a temperature which is not high enough to annihilate the E_1-centres. Because of this temperature rise the Si atoms are forced to diffuse thermally, whilst retaining an appreciable amount of energy. If the laser intensity is low and the energy is not sufficient for Si atoms to migrate to the surface, only a change in the Si distribution is observed. If the energy imparted to Si atoms is sufficiently high, ions are re-emitted keeping some amount of energy. Further studies of the velocity and angular distribution of emitted particles are in progress.

The authors are grateful to Dr Kouli Matsuda for carrying out ion implantation, and to Professor Hisatsugu Kashiwabara for the use of the ESR spectrometer. They also thank Hiroshi Matsuoka for assistance in constructing the experimental apparatus.

Note added in proof. Recently Miotello [9] explained our results in terms of migration of silicon in liquid phase but not in solid phase of SiO_2. Our present results, however, indicate otherwise. We consider that the results can be interpreted to be thermal diffusion and the diffusion constant of Si is νa^2, where ν is the lattice characteristic frequency and a is the lattice constant, as discussed in [4]. This assumption will be valid, since Si atoms are energised by absorbing photons and the energy is partially transferred to SiO_2 for heating, while Si atoms migrate through SiO_2.

References

[1] Appleton B R and Celler G K (ed.) 1982 *Laser and Electron-Beam Interactions with Solids* (Amsterdam: North Holland)
[2] Bloembergen N 1974 *IEEE J. Quantum Electron.* **QE-10** 375
[3] Smith W L 1978 *Opt. Eng.* **17** 489
[4] Shimizu T, Itoh N and Matsunami N 1988 *J. Appl. Phys.* **64** 3663
[5] Fujita T, Fukui M and Itoh N 1987 *Japan. J. Appl. Phys.* **26** L1967
Fujita T, Fukui M, Okada S, Shimizu T and Itoh N unpublished
[6] Griscom D L 1984 *Nucl. Instrum. Methods* B **1** 481
[7] Devine R A B 1984 *Nucl. Instrum. Methods* B **1** 378
[8] Biersack T P and Haggmark L G 1980 *Nucl. Instrum. Methods* **174** 257
[9] Miot A 1989 *J. Phys.: Condens. Matter* **1** 3363