RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 2 15 JULY 1987-I

Hydrogen-implantation-induced damage in silicon

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(Received 9 December 1986)

Distributions of H atoms, displaced Si atoms, and vacancy-type defects in Si(100) produced by the room-temperature implantation of 1×10^{16} 35-keV H^+ ions per cm^2 have been measured by ion- and slow-positron-beam techniques. Three different damage regions were observed. The damage distributions do not correlate with the deposited-energy distribution. A threshold energy of 2.0 ± 0.5 keV for primary Si recoils is needed for the production of a permanent vacancy-type damage region, i.e., an energy spike is needed for damage formation.

Ion-bombardment-induced damage in crystalline silicon (*c*-Si) has been studied extensively (e.g., Refs. 1–6 and references therein). However, due to the several implantation variables (temperature, flux, fluence, ion mass, and energy) the mechanisms by which a cascade of atomic displacements results in a damage, and ultimately an amorphous zone, are controversial.[7–9]

In this Rapid Communication, we present new results on the damage induced by the room-temperature H implantation of *c*-Si. The results show that (i) there are three different damage regions, (ii) the damage distributions do not correlate with the deposited-energy distribution, i.e., an average density of the deposited energy cannot be used to explain the damage formation, and (iii) the formation of vacancy-type defects provides a threshold energy.

In the study we combined the distribution measurements of vacancy-type defects by slow positrons with those of H atoms and displaced Si atoms (Si_D) by ion-beam techniques. The samples were prepared at the University of Helsinki isotope separator by implanting 1×10^{16} 35-keV H^+ ions per cm^2 into *n*-type Si(100) slices at room temperature. The incident H^+ beam was normal to the (100) face with an intensity of 0.4 $\mu A/cm^2$. To ensure the lateral homogeneity of the samples, the beam was raster scanned.

The recovery of different defects was studied by using 60-min isochronal annealings. For the evolution of H and Si_D concentration profiles the annealings were done in a quartz-tube furnance in a low-pressure (<50 μPa) dry argon atmosphere in the temperature range 500–1000 K. In the slow-positron measurements the annealings from 300 to 1200 K were performed *in situ* in ultra-high vacuum (UHV).

The depth profiling of implanted H atoms was carried out by the nuclear resonance broadening (NRB) technique using a $^{15}N^{2+}$ beam from the University of Helsinki EGP-10-II tandem accelerator in conjunction with the 6.385-MeV resonance of the $^1H(^{15}N,\alpha\gamma)^{12}C$ reaction.[10] In the determination of the depth scale, the commonly adopted stopping power of 300 eV/10^{15} atom cm^{-2} was used.[11,12]

The Si_D distributions were measured by Rutherford backscattering (RBS) and channeling with 2.0-MeV $^4He^+$ ions from the University of Helsinki 2.5-MV Van de Graaff accelerator. Backscattered particles were analyzed with a Si(Li) detector located at 167° with respect to the incident beam and at a distance of 8 cm from the target. The samples were mounted on a goniometer and the beam was aligned with respect to the ⟨100⟩ axis. The number of Si_D atoms was determined following the conventional procedure.[13] The stopping power from Ref. 14 with the 10% reduction for the impinging channeled $^4He^+$ ions yielded the depth scale compatible with that obtained with the ^{15}N stopping; for the coupling of H and Si_D distributions, see below.

The depth distributions of vacancy-type defects were measured using the slow-positron beam at the Helsinki University of Technology.[15] The sample was mounted in an UHV chamber with a pressure of about 10 nPa. The Doppler-broadened annihilation line-shape parameter[16] S was measured as a function of incident positron beam energy E (0–25 keV) both in the H^+-irradiated and unirradiated areas of the same specimen. Vacancy distributions associated with the H^+ bombardment were obtained from fitting the difference data $\Delta S(E)=S_{irr}(E)-S_{unirr}(E)$ to the positron diffusion-annihilation equation.[17,18] The positron diffusion in the unirradiated part was well characterized with a freely diffusive positron state.[19] The values $S_{surface}=0.410$ and $S_{bulk}=0.433$ were measured at $E=0.1$ and 30 keV, respectively. The latter describes annihilations far behind the damaged region in the sample. A value $S_{defect}=0.440$ describing positron annihilation at H-irradiation-induced defects was adopted. We observed in the fitting that a change in S_{defect} causes a change in the total number of defects but not in the shape of the defect distributions. A value of 10^{14} s^{-1} was used for the specific trapping rate of vacancies in Si.[20] The mean depth and total area of the extracted vacancy-type defect profiles have a statistical uncertainty of about 15%.

The extracted vacancy-defect distributions are displayed in Fig. 1, the *H*-concentration distributions in Fig. 2, and the Si_D distributions in Fig. 3. The inset of Fig. 1 illustrates the experimental and fitted annihilation

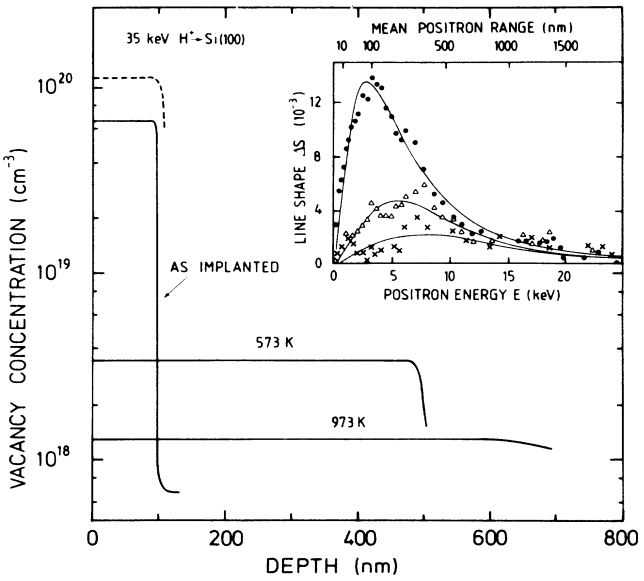

FIG. 1. Distributions of vacancy-type defects after annealing at different temperatures. The simulated vacancy distribution is displayed by the dashed line. The inset shows the Doppler broadened annihilation line-shape data ΔS vs positron energy (closed circles: as implanted, triangles: 573 K, crosses: 973 K). The solid lines are the fits corresponding to the vacancy profiles.

line-shape data ΔS *versus* the positron energy. Note that the distribution of the vacancy-type defects in the as-implanted sample is confined to the region 0–100 nm, but the distributions of Si_D and H atoms to the region 250–600 nm. The annealing behavior of H and Si_D atoms shows in agreement with earlier studies[21] that these distributions are coupled together.

The room-temperature irradiation of *c*-Si with neutrons[20] or ^{16}O (Refs. 22 and 23), ^{11}B, ^{64}Zn, and ^{121}Sb ions (Ref. 24) is known to yield the formation of divacancies as predominant vacancy defects. Divacancies are known to become mobile at 470–610 K.[2,20,25] We observed the abrupt annealing of vacancy-type defects from the region of 0–100 nm at 570 K. In the temperature range 570–900 K, no change in the vacancy distribution is observed. Above 900 K, a continuous loss of vacancies leads to a defect-free state at 1200 K.

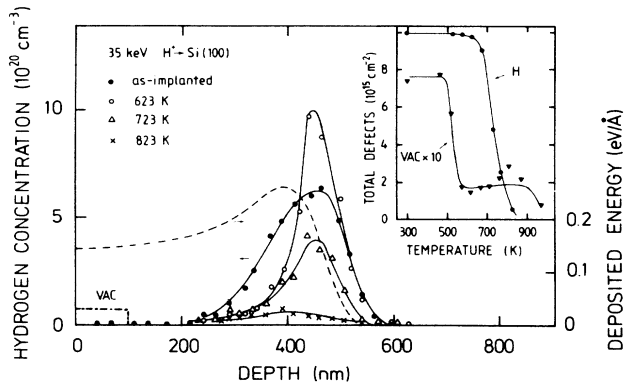

FIG. 2. Hydrogen distribution at different temperatures. The solid line through the measured points of the as-implanted sample is the computer simulation of the range profile. The dashed line shows the corresponding distribution of the deposited energy due to the nuclear stopping. The solid lines corresponding to the annealed profiles are drawn to guide the eye. The dot-dashed line shows the distribution of vacancy-type defects in the as-implanted sample. The inset shows the amounts of retained H and total number of vacancies vs annealing temperature.

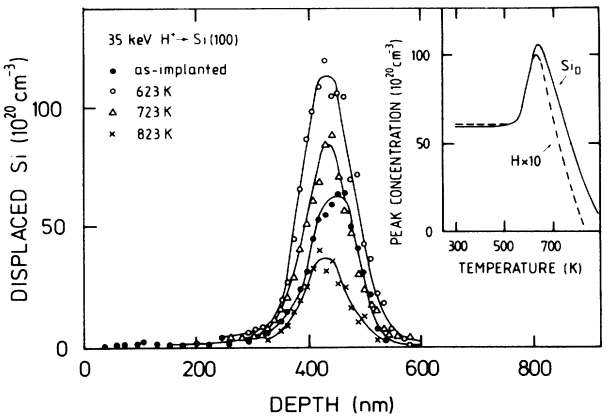

FIG. 3. The annealing behavior of displaced Si atoms in H implanted *c*-Si. The distributions of Si_D atoms were obtained in the comparisons with the amount of Si atoms observed in the random spectrum. In the inset the maximum concentration of the displaced Si atoms (solid line) is compared with the maximum H concentration (dashed line).

The number of observed Si displacements (Fig. 3) does not correlate with the deposited-energy distribution (for the computer simulation of the distribution, see below and Fig. 2). According to the modified Kinchin-Pease model,[26,27] the number of Si_D atoms should be about 5×10^{21} Si_D atoms/cm^3, calculated for the fluence 10^{16} H^+ ions/cm^2, the deposited energy 0.25 eV/Å, and the threshold displacement energy 20–30 eV for creating a permanent Frenkel pair.[28–30]

In the region at about 390 nm where the peak of the deposited-energy distribution overlaps the H distribution also a rapid loss of H starts at 570 K. In this region, only isolated Frenkel pairs are produced during the implantation. The association of vacancies with SiH centers has previously been postulated by Stein.[31] However, the change of the H profile at 570 K and the increased positron trapping between 100 and 400 nm, show that the migration of H is now related to the migration of the divacancies.

As illustrated in the inset of Fig. 2, the total amount of retained H stays constant during the annealings between 300 and 650 K. The mobile H is trapped in the region of maximum H concentration, presumably by the H-induced dislocation loops.[2] The evolution of the maximum H and Si_D concentrations around the modal H range at 450 nm, shows that the defect due to one H atom corresponds effectively to about 10 Si_D atoms (inset of Fig. 3). Therefore, the number of Si_D atoms is associated with the H concentration in the lattice, rather than with the damage

due to the deposited energy. The increase of the ratio 10:1 of Si_D to H atoms above 650 K, is explained by the fact that the damage is removed by the solid-phase epitaxial growth at temperatures 800–900 K (Ref. 32) after the loss of H at 650–850 K.

By comparing Figs. 2 and 3, we observe that the Si_D distributions have a constant width, similar to that of the H distributions above 570 K. This fact indicates that in the region of the deposited energy peak of the as-implanted sample, the vacancies associated with SiH centers strongly reduce the number of Si_D atoms, which would otherwise be produced by the presence of H impurities. This mechanism can be expected to affect the ion-beam-induced epitaxial crystallization of Si.[33]

We have performed computer simulations[34] to further understand the damage production during the H implantation. In the simulation, the structure and orientation of the *c*-Si sample during the measurements were taken into account. The range distribution of dominantly channeled H^+ ions was reproduced to be in agreement with that measured by NRB. Thus, the deposited energy distribution shown in Fig. 2 is compatible with the experimental situation. The collision cascades were calculated using the binary collision approximation.[34] In the first part of the range, the damage is partly produced in the form of energetic spikes; the energies of primary recoiling Si atoms are up to 4.6 keV. Near the end of the range, i.e., in the peak region of the deposited energy distribution where the energies of primary recoils are below 1 keV, isolated Frenkel pairs are produced. Note that during the slowing down of ions heavier than H, collisions lead dominantly to the formation of spikes and the mechanisms associated to the spike model[7] or the critical-damage-density model[8,9] cannot be separated experimentally.

The experimentally obtained region of the vacancy-type defects in the as-implanted sample was reproduced adapting a threshold energy of 2.0 ± 0.5 keV for the primary recoiling Si atoms. The error limits are mainly due to the uncertainty in the width of the experimental vacancy-defect distribution. This value corresponds to the energy needed to produce enough damage to survive the dynamic and room-temperature annealing. The concentration shown in Fig. 1 was obtained by using a cutoff energy 25 eV (Refs. 28–30) for the recoiling Si atoms to create a permanent Frenkel pair.

The concept of the threshold energy explains the failure to produce amorphous Si in a high-fluence 1-MeV e^- irradiation below 10 K.[35] The energies of primary recoiling Si atoms ($\lesssim 150$ eV) did not exceed a threshold value. At 10 K, the threshold energy for the production of permanent damage is apparently between 150 and 2.0 keV. A somewhat similar threshold-energy concept has previously been proposed by Stein and co-workers[22–24] on the basis of B, O, Zn, and Sb implantations of *c*-Si. They explained the results by assuming that an energy of 1.5 ± 0.5 keV per unit volume is needed to form a divacancy. Thus they assumed that the critical-damage-density model is valid. The essential point of the present work is that by a suitable choice of the implanted ion and its energy, we can show that a critical threshold energy is needed and that a stable divacancy is created only if a large enough disorder is produced locally, i.e., in an energy spike.

The present results show that there are three different regions of damage which survive the dynamic and room-temperature annealing. By focusing attention on the distribution of the deposited energy only, the damage accumulation in H-implanted *c*-Si cannot be predicted realistically.[6]

In conclusion, we have combined the distribution measurements of H and Si_D atoms with those of vacancy-type defects in H-implanted *c*-Si. The results show for the first time that there are three different damage regions which do not correlate with the deposited energy distribution. Furthermore, a threshold energy of 2.0 ± 0.5 keV is needed for primary Si recoils for the production of a vacancy-type damage region.

This work has been supported by the Academy of Finland.

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