Vacancy-type defects created by single-shot and chain ion implantation of silicon

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Abstract. Vacancy-type defects created by single-energy implantation of Czochralski-grown single-crystal silicon by 4 MeV silicon ions at doses of 10¹² and 10¹³ cm⁻² have been compared with those created by an energy chain of implants of 0.4, 0.9, 1.5, 2.2 and 4 MeV ions, each at one-fifth of the single-energy dose. Measurements were taken for as-implanted samples and after annealing to temperatures up to 600 °C. In contrast to the expectation that a more uniform depth distribution of interstitials and vacancies would lead to a more efficient recombination and consequently fewer surviving vacancies, vacancy-related damage survived in the chain-implanted samples to higher temperatures, before almost complete annealing at 600 °C. It is therefore concluded that it is the absolute initial monovacancy concentration, rather than any initial separation of vacancy- and interstitial-rich regions, that determines the probability of survival as divacancies, and that there exists a threshold divacancy concentration of 1–2 × 10¹⁸ cm⁻³ for clustering at 400–500 °C.

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1. Introduction

Vacancy engineering is an established method in front-end device processing, used for example to limit dopant diffusion, getter impurities and separate wafers [1–3]. A common way of introducing or ‘implanting’ vacancy-type defects is by ion implantation [4] in which ions of predetermined energy are implanted into a semiconductor target and create vacancies and interstitials (Frenkel pairs) along their path as they slow down. MeV silicon ions in silicon have a relatively narrow depth profile centred a few μm beneath the surface with a width of a few hundreds of nm; the vacancies (and recoil interstitials) they produce have a somewhat broader but nevertheless peaked depth profile, centred 100–200 nm below the ion range with a tail extending to the surface. The ion and vacancy profiles at the moment of implantation (i.e. before any post-implant diffusion or recombination) can be simulated using the standard code SRIM [5].

Monovacancies and Si interstitials are mobile below room temperature; it is therefore often assumed that the 5–10% of vacancies that survive room-temperature implantation are predominantly those which have encountered another vacancy to form divacancies, which are immobile at room temperature, rather than migrated to sinks or recombined with mobile interstitials. This rather simplistic model is complicated in the case of wafers doped with impurities (in which vacancy–dopant complexes may form) and in samples which have received a relatively large implantation dose in which complex defect structures may form prior to the eventual amorphization of the silicon substrate.

In order to investigate the dependence of vacancy survival on the depth profile of vacancy and interstitial defects, silicon has been implanted with (a) 4 MeV Si\(^+\) ions and (b) Si\(^+\) ions of five different energies, each with one-fifth of the dose of the single implant, so that in the latter case the interstitial and vacancy depth profiles extend more uniformly from the surface to the maximum ion range, and the surviving vacancy-type defects studied in the as-implanted samples and after annealing at a range of temperatures. The co-implant will henceforth be referred to as a ‘chain implant’ and the single mono-energetic implant as a ‘single-shot’.

A well-established method for probing the formation, evolution and annealing of vacancy-type defects in ion-implanted semiconductors is by variable-energy positron annihilation spectroscopy (VEPAS) [6]. Positrons implanted into a sample with energy \(E\) (in keV) penetrate silicon to depths described by a Gaussian derivative profile with a mean depth \(\sim 17E^{1.6}\) nm. They then diffuse at thermal energies for 100–200 ps before being annihilated by an electron with the emission of two gamma photons. The momentum of the annihilating pair, essentially provided by the electron, leads to Doppler shifts in the energies of the two photons above and below their zero-momentum value of 511 keV and a Doppler broadening of the annihilation.
line. If a diffusing positron encounters a neutral or negatively charged vacancy it is trapped in the defect site with a probability described by the specific trapping rate for the defect. The annihilation gamma energy spectrum is measured in VEPAS by a high-purity germanium detector; the Doppler-broadened linewidth is characterized by the single number parameter $S$ (for Sharpness), which is the fraction of the peaked annihilation line between two energies chosen symmetrically about the peak centroid. $S$ is not an absolute parameter, but the limits of the central region of the annihilation line are conventionally chosen so that $S \sim 0.5$, and then $S$ is usually normalized to the value measured for effectively defect-free silicon (i.e. $S/S_{Si}$). $S$ for bulk silicon is therefore equal to unity. However, the average momentum of electrons encountered by a positron trapped in vacancy defects is lower than that in bulk silicon, the extent of the Doppler broadening is decreased, the measured annihilation line is narrower, and $S$ is greater than 1. Because of the sensitivity of $S$ to annihilation of lower-momentum electrons it is sometimes referred to as the ‘lower-momentum fraction’.

By measuring $S(E)$ one can therefore gain semi-quantitative information on the type, concentration and depth profile of vacancy defects in ion-implanted silicon. One can study the formation of vacancy–impurity complexes [7], the evolution of vacancy-type defect structures from divacancies to clusters [8–10] and the energetics of vacancy migration [11].

2. Experimental details

Low-doped (p-type, $<10^{15}$ cm$^{-3}$ boron) Czochralski-grown single-crystal Si was implanted with 4 MeV Si$^+$ ions at the University of Surrey Ion Beam Centre at doses of $10^{12}$ and $10^{13}$ cm$^{-2}$. Chain implants were performed with Si$^+$ ions of energies 0.4, 0.9, 1.5, 2.2 and 4 MeV, each with one-fifth of the dose of the single-shot implant so that the total numbers of implanted ions were the same in both cases.

VEPAS was performed using the magnetic-transport slow positron beam system at the University of Bath [12]. Positrons of energies $E$, with an energy spread of $\sim 1.5$ eV, are implanted into the samples for $E = 0.5$–30 keV (in 0.5 keV steps up to 5 keV, 1 keV steps to 10 keV and 2 keV steps up to 30 keV). Ex-situ annealing was carried out on all samples at 50 °C intervals between 100 and 500 °C, and at 600 °C, and $S(E)$ measured at room temperature after each annealing—40 sets of measurements in all. On occasion $S$ was not measured at every value of $E$ as this was not necessary to observe the essential features of the $S(E)$ curves.

3. Results and discussion

Figure 1 shows simulations using the standard code SRIM [5] for the single-shot implant at $10^{13}$ cm$^{-2}$ and the associated chain implants. In both cases an estimate of the absolute divacancy distributions for each implant has been arrived at by (a) assuming that the final and initial vacancy depth profiles are similar, the latter being given by SRIM, and (b) by fixing the concentrations at half ion range to be those given by the formula developed by Coleman et al [13], which accounts for post-implantation defect recombination. Assumption (a) was shown to be reasonable by high-resolution VEPAS vacancy depth profiling measurements [14]. A similar procedure was followed to simulate the vacancy damage created by the lower-dose implants, and the result was so similar in depth dependence to figure 1 that it is not shown here. Procedure (b) was checked and shown to be consistent with the measured $S$ parameters, via a calculation of the trapped positron fraction and using 1.035 for the $S$ value of the divacancy;
Figure 1. Depth profiles of implanted Si\(^+\) ions (dose 10\(^{13}\) cm\(^{-2}\)) and divacancies remaining at room temperature, simulated by SRIM [5], for both chain and single-shot implants. The divacancy distribution is assumed to be similar to the initial (time zero) monovacancy distribution, and the absolute concentrations are derived using the expression linking divacancy concentration at half-ion range with ion dose derived in [12]. In the case of the chain implants this procedure was followed for each implant energy and the resulting distributions summed.

The recoil ion distribution is very similar to that of vacancies, and their total numbers are assumed to be equal. Therefore, the implanted ion distribution shown in figure 1 represents that of the excess interstitials, and their mean separation from divacancies is significantly greater than between the recoils and the divacancies. On the basis that vacancies are always relatively close to recoil interstitials, and somewhat farther from the implanted Si ions, it is not clear whether the overall average separation between interstitials and vacancies is significantly different after chain and single-shot implants; hence this experimental study.

The results for \(S(E)\) for samples implanted with a total of 10\(^{12}\) and 10\(^{13}\) ions cm\(^{-2}\) are shown in figure 2. Three curves are shown for each sample; the data for annealing temperatures
Figure 2. $S(E)$ for high- and low-dose, chain and single-shot implants. The data shown represent those taken after annealing at temperatures between 20–350, 400–500 and 600 °C.

up to 350 °C were similar, and so are grouped, as are those for 400–500 °C; finally, the data after complete annealing at 600 °C are shown. These last data exhibit $S(E)$ characteristic of unimplanted Si, rising smoothly from the surface $S$ to bulk $S$ (unity).

Focusing on the results for the higher-dose samples in figure 2, one sees that $S(E)$ for the as-implanted sample and for annealing temperatures up to 350 °C shows a somewhat larger response to divacancies for the chain-implanted sample over a wider range of incident positron energies (and thus depths below the surface), becoming similar to the single-shot response only at $E \sim 20$ keV when the divacancy concentration for the single-shot-implanted sample becomes significant (see figure 1). Above 20 keV, $S$ decreases towards the Si substrate value of 1 as a greater fraction of the increasingly broad positron implantation depth profile (width~mean depth) extends beyond the defected region.

The most significant difference between the positron response to the two samples in figure 2 can be seen in the raw data after annealing to temperatures between 400 and 500 °C. While $S(E)$
for the chain-implanted sample stays high (except at the lowest $E$, when the somewhat lower surviving divacancy concentration leads to enhanced positron diffusion to the surface, which has a lower characteristic $S$), the response for the single-shot sample is considerably lower for $E < 20$ keV. After annealing at 600 °C, essentially all of VEPAS response to vacancy damage has been removed in all samples.

The data for the lower-dose samples show the same significant difference between chain- and single-shot-implanted samples at annealing temperatures below 350°C; all of the measurable response is annealed away at higher temperatures.

It is important to note that the ion doses used in this study were chosen so as not to produce vacancy concentrations high enough to trap all implanted positrons (i.e. to lead to saturation trapping), either before or after annealing, as this would severely complicate data interpretation.

The deduction that there is a higher surviving concentration of divacancies at depths below 2 µm in the chain-implanted sample before annealing—rather than, say, a tendency to form small vacancy clusters with a higher characteristic $S$ value—is supported by considering figure 1. The initial monovacancy concentrations in the 0–2 µm region are never more than $\sim50\%$ of the peak, and are not high enough to trap all implanted positrons. Many years of VEPAS studies of Si have indicated that under these circumstances, monovacancies formed in these concentrations at the moment of implantation at room temperature either migrate to sinks, recombine with interstitials or form divacancies and become immobile, the last being only a few per cent of the initial number.

The data for the single-shot-implanted samples bear resemblance to those of Coleman et al [9] in which the persistence of VEPAS response at the vacancy peak was explained by the formation of small clusters $V_n$, with $n \sim 3–4$, with consequently lower mobility and higher annealing temperatures (divacancy annealing is reported to occur at 290–350°C [15]). The significant reduction in the response at shallower depths corresponds to simple annealing of $V_2$. It was noted in [9] that vacancy evolution mechanisms depend to some extent on annealing methods and history, and some apparent differences between VEPAS and other techniques were discussed by the authors of that paper. For the chain-implanted samples we can therefore postulate that the higher absolute divacancy concentrations at shallower depths (i.e. from the surface to $\sim2$ µm) compared to the single-shot-implanted samples (figure 1) mean that on annealing at least some of the $V_2$ agglomerate to form small clusters which survive to higher temperatures.

Fits of the raw data using the standard code VEPFIT [16], requiring self-consistency between fitted positron diffusion lengths and $S$ parameters, support this model. The expressions linking defect concentrations with fitted $S$ (or diffusion length) values were given in [9]. For example, fitting $S(E)$ for the higher-dose chain-implanted sample (top graph, figure 2) yields a mean divacancy concentration of $3 \times 10^{18}$ cm$^{-3}$ in the first 1.5 µm below the surface in the as-implanted sample, in broad agreement with the estimated value shown in figure 1, whereas after annealing at temperatures between 400 and 500 °C the fit is consistent with the formation of small vacancy clusters $V_n$ (with $n \sim 4$) in the same depth range, with a mean concentration of $10^{17}$ cm$^{-3}$, implying that about 7% of the divacancies agglomerated into tetravacancies after annealing. In contrast, the mean divacancy concentration in the top 1.5 µm of the higher-dose single-shot-implanted sample is $\sim8 \times 10^{17}$ cm$^{-3}$ (again consistent with figure 1), but after annealing at 400–500 °C no defect signature is detectable by VEPAS.
4. Conclusion

The results of this study imply that (a) monovacancies survive (in divacancies) more readily in chain-implanted samples than single-shot-implanted samples, and (b) there is a threshold concentration for divacancy clustering at 400–500 °C of between 1 and $2 \times 10^{18}$ cm$^{-3}$. The key to these observations appears to lie in the lack of, or at best minimal, influence of interstitial silicon atoms, either from the implanted ions or from those recoiling during implantation. This may be explained by the relative lack of movement of any surviving interstitials at the temperatures employed in this study. The VEPAS measurements of [11] showed that the migration energy for silicon interstitials was about five times smaller than for monovacancies ($\sim 0.1$ eV), and therefore it is likely that at room temperature all interstitials have migrated to sinks, recombined with vacancies, or formed immobile clusters—playing no further significant role in the vacancy evolution seen here.

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