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S. Fatima, J. Wong-Leung, J. Fitz Gerald, and C. Jagadish

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Effect of ion mass on the evolution of extended defects during annealing of MeV ion-implanted $p$-type Si

S. Fatima, a) J. Wong-Leung, J. Fitz Gerald, b) and C. Jagadish c)
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

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Evolution of extended defects during annealing of MeV ion-implanted $p$-type Si has been characterized using deep level transient spectroscopy and transmission electron microscopy. The $p$-type Si was implanted with Si, Ge, and Sn ions with varying energies and doses from $5 \times 10^{12}$ to $1 \times 10^{14}$ cm$^{-2}$ then annealed at 800 °C for 15 min. For all implanted species, the critical dose for transformation from point to extended defects has been determined. The type of extended defects formed depends upon the mass of the implanted species even though the dose was adjusted to create a similar damage distribution for all implanted species. © 1999 American Institute of Physics.

Ion implantation is widely used in Si industry for microelectronic device fabrication. Implantation is followed by high temperature annealing to remove the implantation-induced disorder in the lattice. During post-implant annealing, transient enhanced diffusion (TED) of dopants and formation of extended defects have been reported.1-3 Despite several years of research, the knowledge about the evolution of extended defects and their role in dopant diffusion is still limited.

In ion-implanted Si, point defects and defect-impurity complexes4 form in the low dose regime ($10^7$–$10^9$ cm$^{-2}$). On the other hand, high dose implants result in the formation of amorphous layers which undergo upon annealing solid phase epitaxy, leaving a band of dislocation loops at the amorphous/crystalline interface.5 In the medium dose regime (which is widely used for device fabrication), annealing results in the formation of [311] defects. We reported a correlation between electrically active defects and structural defects in $p$-type Si implanted with MeV Si ions and annealed at 800 °C.6

In this letter, we report the influence of ion mass on the extended defect evolution during annealing in $p$-type Si implanted with MeV Si, Ge, and Sn ions. Deep level transient spectroscopy (DLTS) and transmission electron microscopy (TEM) measurements were used to characterize electrically active and structural defects.

Czochralski (Cz) $p$-type Si(100) boron doped with a resistivity of 6–8 Ω cm, is implanted with 4 MeV Si, 6.5 MeV Ge, and 8.5 MeV Sn ions at room temperature. The concentration of interstitial oxygen atoms [O$_i$] atoms varied between $\sim 1.7 \times 10^{18}$ and $\sim 7 \times 10^{17}$ cm$^{-3}$, while the concentration of substitutional carbon [C$_s$] was below $2 \times 10^{16}$ cm$^{-3}$. The ion energies have been adjusted to create a similar projected range of around 2.8 μm for all three ion species. Dopant and surface effects can be ruled out in our case as only group IV elements are implanted and implant depths are identical in all three cases. According to FASTRIM7,8 calculations, the peak concentration of vacancies for Ge and Sn is about a factor of 2.7 and 4, respectively, more than for a same dose Si implant. Hence, the doses are scaled down, according to these factors for direct comparison with Si. Irradiation was carried out using the NEC 1.7 MV Tandem accelerator at Australian National University. The Si substrate was tilted 7° off axis with respect to the incoming ions to minimise channeling. After implantation, the samples were all annealed at 800 °C for 15 min in a conventional quartz furnace under Ar ambient. All the samples were then chemically cleaned, including a final dip in diluted HF to remove any surface oxide. Immediately after cleaning, Schottky barrier diodes were fabricated by evaporation of Ti onto the samples. Eight DLTS spectra with rate windows between (100 ms)$^{-1}$ and (12,800 ms)$^{-1}$ were simultaneously recorded during one single temperature scan from 77 to 300 K. A lock-in type weighting function was applied to extract the DLTS signal from the transients recorded. Cross-sectional samples were prepared using mechanical polishing, dimpling and ion beam thinning. TEM was carried out using a Philips 430 instrument operated at 300 kV.

DLTS measurements on the samples implanted with 4 MeV Si ions to doses in the range of $2 \times 10^{13}$–$1 \times 10^{14}$ cm$^{-2}$ and annealed are shown in Fig. 1(a). For a dose of $2 \times 10^{13}$ cm$^{-2}$, the DLTS spectrum shows a sharp peak, having an activation energy of $E_v + (0.28 \pm 0.01)$ eV, with a capture cross section of $\sim 2.7 \times 10^{-16}$ cm$^2$. Increasing the ion fluence to $4 \times 10^{13}$ cm$^{-2}$ results in broad features appearing on the low and high temperature shoulders of this peak. These broad features in DLTS spectra have been attributed to the presence of extended defects.9,10 With a further increase in the dose to $1 \times 10^{14}$ cm$^{-2}$, the amplitude of both the broad features and the sharp peak increases. We note that in all cases, the peak at $E_v + (0.28 \pm 0.01)$ eV was sharp and characteristic of point defects. Indeed, hole capture kinetics of this level showed exponential dependence, hence excluding the formation of large electrically active point defect clusters or extended defects. In order to identify the nature of the
interstitials involved in the level at $E_v + (0.28 \pm 0.01)$ eV, implantation was carried out in Cz, Fz, and epitaxial $p$-type Si with similar boron concentrations ($\leq 2 \times 10^{15}$ cm$^{-3}$). In Fz $p$-Si, $[O_i]$ and $[C_s]$ concentrations were less than $5 \times 10^{14}$ cm$^{-3}$ and in epitaxial Si they are $\leq 10^{13}$ cm$^{-3}$. No systematic variation in the amplitude of this DLTS peak with varying $O_i$ and $C_s$ concentrations was observed. This makes it very difficult to identify the nature of interstitials involved in this defect. In addition to the level at $E_v + (0.28 \pm 0.01)$ eV, an additional level at $E_v + (0.44 \pm 0.01)$ eV with a capture cross section of $\sim 9.5 \times 10^{-15}$ cm$^2$ emerges for doses $\geq 4 \times 10^{13}$ cm$^{-2}$.

Similarly, in Ge-implanted samples, a dose of $7 \times 10^{13}$ cm$^{-2}$ shows a sharp peak in the DLTS spectra with $E_v + (0.28 \pm 0.01)$ eV. Increasing the ion fluence to $2 \times 10^{13}$ and $4 \times 10^{13}$ cm$^{-2}$ results in the appearance of the broad features shown in Fig. 1(b) with their amplitude increasing with increasing dose. With Sn implantation, for doses $\leq 1 \times 10^{13}$ cm$^{-2}$, DLTS spectra showed sharp peaks, as shown in Fig. 1(c). Increasing the dose to $3 \times 10^{13}$ cm$^{-2}$, produces broad features in the DLTS spectra. For a fixed implantation dose ($1 \times 10^{14}$ cm$^{-2}$) in Si-implanted samples, prolonged annealings at 800 °C led to the reduction in the broad features in the DLTS spectra. Similar reductions in (111) defect density was also observed in TEM studies suggesting that broad features in DLTS spectra are a signature of the presence of extended defects. Hence, from the DLTS spectra it is evident that, irrespective of the mass of the implanted species, a critical dose has been established below which only point defects (sharp peak) are found and above which some extended defects (broad features) are indicated.

TEM examination of the Si-implanted samples did not show any extended defect formation for doses $\leq 2 \times 10^{13}$ cm$^{-2}$. Higher Si implant doses resulted in the formation of rod-like (111) defects. Figure 2(a) is a typical micrograph of the Si-implanted sample to a dose of 1

FIG. 1. DLTS spectra [window (3200) ms$^{-1}$] of various doses below and above the transition from point to extended defects after (a) 4 MeV Si, (b) 6.5 MeV Ge, and (c) 8.5 MeV Sn ion implanted and thermal annealing at 800 °C, 15 min, in to $p$-type Si. Bias voltage-12 V, pulse amplitude 11.5, pulse width 50 ms.

FIG. 2. Weak-beam micrographs showing the microstructure of the samples implanted with (a) Si, $1 \times 10^{14}$ cm$^{-2}$, (b) Ge, $4 \times 10^{13}$ cm$^{-2}$, (c) Sn, $3 \times 10^{13}$ cm$^{-2}$ all after annealing at 800 °C for 15 min. (Loops are marked with arrows.)
\( \times 10^{14} \text{ cm}^{-2} \). The rod-like defects are planar defects with a preferred elongation along (011) and with a dilation perpendicular to the \{311\} habit plane.\(^{11}\) For Ge- and Sn-implanted samples, the highest doses studied showed no visible defects by TEM were \( 7 \times 10^{12} \) and \( 1 \times 10^{13} \text{ cm}^{-2} \), respectively. For doses just above this threshold, TEM showed rod-like defects for both Sn- and Ge-implanted samples. Higher doses showed the formation of loops in addition to the \{311\} defects [Figs. 2(b) and 2(c)]. These loops are faulted and interstitial type with \{111\} habit plane and Burgers vector perpendicular to the habit plane. TEM is generally in agreement with DLTS except in two cases where the DLTS spectra did not reveal extended defects observed in low densities by TEM.

For each ion mass, a critical implantation dose exists for the extended defect formation after annealing at 800 °C for 15 min. This dose characterizes the onset of transformation from point to extended defects. DLTS studies in \( n \)-type Si using low doses (\( \approx 10^{10} \text{ cm}^{-2} \)) have shown the annihilation of vacancy type defects at 400 °C.\(^{12}\) Though our doses are much higher (a factor of 700–1000), persistence of point defects in \( p \)-type Si after high temperature annealing is surprising. Benton et al.\(^{10}\) have reported the presence of point defect clusters in Si involving interstitials, and produced with doses similar to ours after annealing at 680 °C. We conclude that such clusters are unstable at 800 °C and release interstitials.

The effects of the ion species were analyzed by scaling down the ion doses to Si. The results are summarized in Table I, clearly showing that the critical dose for extended defect formation is lower for heavier mass species, in closer agreement with the atomic displacement model.\(^{5}\) Similar trends have been noted previously by Kringlebaum et al.\(^ {13}\) from Si, Ge, and Sn implants in \( n \)-type Si. In contrast, the +1 model\(^ {14}\) cannot explain the formation of extended defects for Ge and Sn implants to doses of \( 2 \times 10^{13} \text{ cm}^{-2} \) and below. Recently, Herner et al.\(^ {15}\) measured the interstitial concentration bound by \{311\} defects in Si implanted with Pb-ions and reported a significant deviation from +1 model (+4.5 for Pb).

To the best of our knowledge, this is the first report in \( p \)-type Si where the trend in the critical dose can only be explained by the difference in the mass of the ion. This is consistent with the atomic displacement model where the damage distribution is taken into account.

Based on FASTRIM, a similar damage distribution for implantation with \( 1 \times 10^{14} \text{ Si cm}^{-2} \) is predicted for Ge and Sn implants of \( 4 \times 10^{13} \) and \( 3 \times 10^{13} \text{ cm}^{-2} \), respectively. In such samples, we found \{311\} defects to be universal but loops occurring only for the heavier mass species. Such dependence of the type of extended defects on the mass of the ion is not predicted from any existing models. MD simulations\(^ {16}\) have predicted the formation of dense disordered zones, ‘‘amorphous pockets’’ and few isolated defects from heavier mass ions. On the other hand, light ions mainly produce point defects and small disordered zones. Amorphous pockets recrystallize during annealing, injecting many point defects into the lattice. It is most likely that Ge and Sn implants in Si result in defect injection at high concentrations, which leads to loop formation.

In summary, using MeV Si, Ge, and Sn ion implantation in \( p \)-type Si and annealing at elevated temperature, a critical dose is identified below which point defects exist and above which extended defects are formed. In addition, the type of extended defects depends on the mass of the implanted species, with only \{311\} defects in Si implanted samples, but \{311\} defects plus \{111\} loops from equivalent doses of Ge and Sn.

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\(^{7}\) H. J. Hay, FASTRIM is a modified version of TRIM-90 which takes into account the multilayer target (interfaces) problems inherent with TRIM (unpublished).