Effects of Carbon on Dynamic Annealing and on Electrical Activation of Dopants in Silicon Substrate

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The effect of C on the implantation damage accumulation in Si crystal and on the electrical activation of dopants was investigated, using RBS-channeling technique, sheet resistivity and Hall measurements. The damage profiles in Si implanted with $^{12}C^+$ or $^{11}B^+$ at 50 keV to the same doses and dose rate were compared. It was found that the damage accumulates at a noticeably higher rate during $^{12}C^+$ implantation than in the case of $^{11}B^+$, especially for doses $> 2\times10^{15}$ cm^{-2}. It is shown that the dynamic annealing is strongly reduced in regions doped with C. In addition, the influence of C on the electrical activation of the co-implanted dopant is discussed for the case of B and Bi. A model considering an interaction between C and Si self-interstitial (Si_I) atoms during implantation and the subsequent thermal annealing is proposed to explain the enhanced implantation damage accumulation and the activation behavior of B in samples co-implanted with C.

I. Introduction

Carbon is an isoelectronic element in Si substrate. It is normally incorporated during Czochralski or float zone crystal growth in concentration respectively of 1 - 8 ppma and 0.1 - 5 ppma. Several phenomena that take place during thermal treatments of Si wafers have been found to be influenced by the presence of C. For example, C is known to affect the oxygen precipitation[1] and the formation of the new donors[2] in CZ Si crystals. Wong et al.[3] demonstrated that Au contamination can be gettered in a layer implanted with $^{12}C^+$. Liefting et al.[4] showed (i) that the annealing of a C implantation does not result in dislocation generation even for a $^{12}C^+$ dose 100 times above that required for $^{11}B^+$ and (ii) that C can prevent dislocation formation of co-implanted B ions. Recently, Nishikawa et al.[5] demonstrated that the transient enhanced diffusion of B can be reduced by $^{12}C^+$ co-implantation. Furthermore, the formation of the end of range dislocation band during the solid phase cpitaxial rcgrowth of amorphized Si can be eliminated by a $^{12}C^+$ co-implantation[6].

The above referred publications strongly suggest that C interacts with point defects during thermal annealing. Since point defects generated in the collision cascades are mobile at room temperature one can expect that they interact with C atoms during the implantation process. Furthermore, because the electrical activation is affected by interactions between dopant atom and point defects it may be influenced by a $^{12}C^+$ implantation. This statement is discussed in the present publication, comparing the activation in Si samples single $^{11}B^+$ or $^{209}Bi^+$ and dually implanted ($^{11}B^+ + {}^{12}C^+$) or ($^{209}Bi^+ + {}^{12}C^+$).

It is well known that ion implantation introduces radiation damage which may be detrimental to the electronic device performance. Partial annealing of the damage occurs concomitantly with the implantation process and this phenomenon is called dynamic annealing. The dynamic annealing is known to be more pronounced for light mass ion implantation, low dose rate

and in heated substrate.

In the present investigation the as-implant damage concentration in $^{12}C^+$ implanted Si is compared with that by $^{11}B^+$. Since the masses of these ions are nearly equal, similar collision cascade properties and primary defect production rates are expected to occur when their energy and dose rate are identical. However, in contrast to this prediction, the actual damage profiles due to $^{11}B^+$ and $^{12}C^+$ implants at an energy of 50 keV, performed to the same doses, differ significantly particularly for doses in excess to 1 x 10^{15} cm^{-2}. For example, the damage concentration level after $^{12}C^+$ implantation to a dose 4 x 10^{15} cm^{-2} results about ten times higher than that of $^{11}B^+$. This seems to indicate that the dynamic annealing is strongly influenced by the chemical behaviour of C in Si.

II. Experimental details

The study of damage accumulation by $^{11}B^+$ and $^{12}C^+$ implantation was performed using n-type Si samples of (100) orientation and resistivity of 4-11 Ω.cm. All the implantations were performed at an energy of 50 keV, at a dose rate of 0.4 $\mu A/cm^2$ with $^{11}B^+$ to the doses of 1 and 4 x 10^{15} cm^{-2} or $^{12}C^+$ to doses ranging from 2 x 10^{14} to 5 x 10^{15} cm^{-2}. In order to minimize channeling effects the samples were tilted by 7° with respect to the beam incidence direction. The as-implanted damage profiles were analysed by Rutherford backscattering spectrometry (RBS) with a 760 keV He^{++} beam aligned with the < 100 > crystal direction. The overall energy resolution of the RBS analysis was of 14 keV. The as-implanted damage were obtained using an iterative procedure to calculate the dechanneling background[7].

For the investigation of the electrical activation of B and Bi Van der Pauw devices[8] were prepared. The central area of the devices were implanted with $^{11}B^+$ or $^{209}Bi^+$ to the dose of 5 x 10^{14} cm^{-2} and at an energy of 50 keV or 150 keV, respectively. In the $^{11}B^+$ implanted samples $^{12}C^+$ was co-implanted with doses in the range from 5 x 10^{13} to 5 x 10^{15} cm^{-2} at an energy of 55 keV. In the case of $^{209}Bi^+$ implanted samples the $^{12}C^+$ co-implantation was performed to a dose of 2 x 10^{15} cm^{-2} at 20 keV. Subsequently, both the single and dually implanted samples were annealed in nitrogen atmosphere.

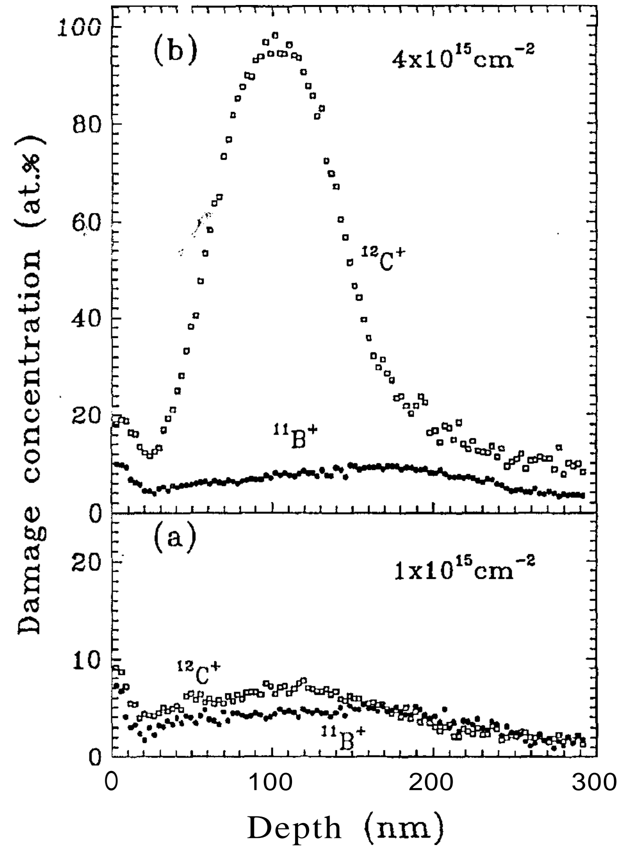

Figure 1: Depth profiles of the damage created by $^{11}B^+$ and $^{12}C^+$ implanted Si at RT with energy of 50 keV and doses of 1×10^{15} cm^{-2} (a) and 4×10^{15} cm^{-2} (b).

The Van der Pauw devices were electrically characterized by sheet resistivity and Hall measurements.

III. Dynamic annealing in C implanted Si

Fig. 1 presents the damage depth profiles in samples implanted with $^{11}B^+$ or $^{12}C^+$ to the doses of 1×10^{15} cm^{-2} [Fig. 1(a)] and 4 x 10^{15} cm^{-2} [Fig. 1(b)]. For the lower dose the damage profile due to the $^{11}B^+$ and $^{12}C^+$ implantations are almost similar, with concentration level at the profile peak of 5% and 7%, respectively. The increasing of the $^{11}B^+$ dose by a factor of four resulted in a increase of a factor of two in the accumulated damage. However, for the case of $^{12}C^+$ the same increasing of the dose leaded to a fourteen times increase of the damage concentration level at the profile peak.

The accumulated damage by $^{12}C^+$ implantation at 50 keV was studied for doses ranging from 2×10^{14} to 5×10^{15} cm^{-2}. The accumulated damage is considered here as the integral of the damage concentration

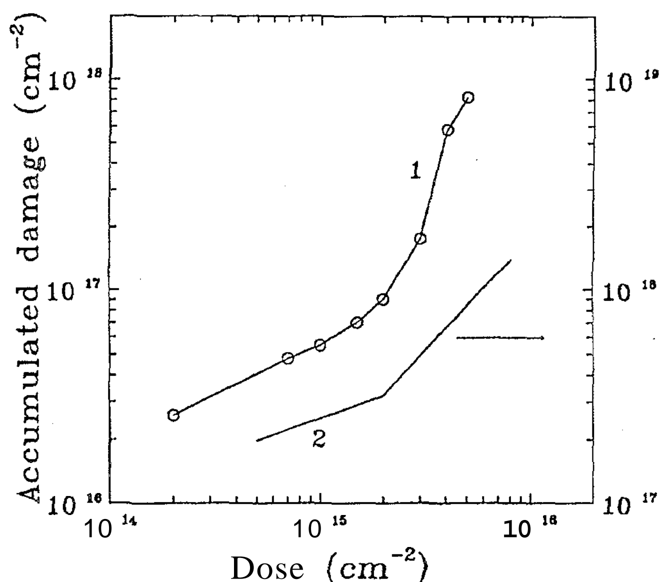

Figure 2: Accumulated damage as function of the implanted $^{12}C^+$ dose at 50 keV (curve 1) and at 200 keV according to Eisen and Welch[9] (curve 2).

depth profile. Fig. 2 compares the accumulated damage versus the implanted $^{12}C^+$ dose from the present work with those extracted from the paper by Eisen and Welch[9] regarding a 200 keV $^{12}C^+$ implanted at a dose rate of 0.6 $\mu A/cm^2$.

It is interesting to note that for doses < 2 x 10^{15} cm^{-2} independently of the energy the accumulated damage increases with the square root of the dose (Φ). For the dose range > 2 x 10^{15} cm^{-2} while the data of Eisen and Welch[9] indicate that the accumulated damage dependents linearly with Φ, our data vary with Φ^n (2 < n < 3).

The enhanced damage accumulation for $^{12}C^+$ doses above 2 x 10^{15} cm^{-2} can be explained considering that the dynamic annealing becomes strongly reduced when C concentration in the Si sample exceeds $\approx$ 2 x 10^{20} cm^{-3} (the concentration at the profile peak for a $^{12}C^+$ implantationat 50 keV and dose of 3×10^{15} cm^{-2}). Such enhancement of damage accumulation was not observed by Eisen and Welch[9], probably because for their implanted doses at energy of 200 keV the C concentrations are below 2×10^{20} cm^{-3}.

The effect of the C doping on the damage accumulation is demonstrated by a separate experiment in which C was firstly implanted at 50 keV to a dose of 4 x 10^{15} cm^{-2} with the substrate heated to 200 °C to enhance

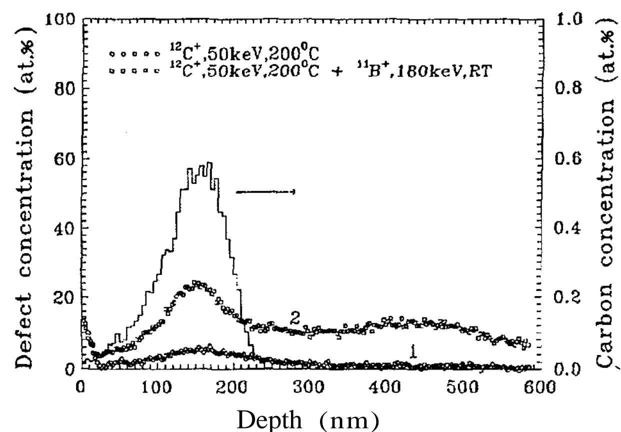

Figure 3: Damage concentration depth profiles in a Si sample implanted with 4×10^{15} cm^{-2} of 50 keV $^{12}C^+$ at 200 °C (curve 1) followed by 180 keV $^{11}B^+$ at RT (curve 2). The histogram represents the estimated C atom concentration profile at 50 keV according to TRIM code simulation[10].

the dynamic annealing. The as-implanted damage profile due to this $^{12}C^+$ high temperature implantation is presented in curve 1 of Fig. 3, which shows that the maximum damage concentration is below the 10 % level. The histogram in Fig. 3 represents the calculated C atom concentration profile at 50 keV according to the TRIM[10] code simulation. Subsequently, $^{11}B^+$ was implanted at room temperature to a dose of 4×10^{15} cm^{-2} and energy of 180 keV. The estimated damage profile peak for this $^{11}B^+$ implantation is at the depth of 0.45 μm, which is far deeper than the C concentration profile. The final damage profile is shown in curve 2 of Fig. 3. The damage profile presents a peak located at the depth of 0.15 μm which corresponds closely to the depth of the C concentration maximum. This result shows that whenever carbon is present in Si at concentration above 2 x 10^{20} cm^{-3}, there is a clear tendency to build up of damage accumulation, decreasing the dynamic annealing during implantation.

IV. Influence of C on dopant activation

The electrical measurements in Van der Pauw devices demonstrated that besides being an isoelectronic element in Si matrix C can strongly affect the activation behavior of co-implanted $^{11}B^+$ or $^{209}Bi^+$.

The effect of C on the electrical activation of B was discussed in a previous publication[11]. Fig. 4 presents the main results from this paper. There are two main components associated to the $^{12}C^+$ implantation which

influence the activation of B: (i) the associated implantation damage and (ii) the C concentration level in the B doped layer. When the $^{12}C^+$ dose is below 1×10^{14} cm^{-2} both the implantation damage and C concentration are not enough to affect noticeably the activation of B [see curve (a) of Fig. 4]. For $^{12}C^+$ doses in excess to 5×10^{14} cm^{-2} the C doping becomes the most relevant factor for the changes in the activation of B [curves (b) and (c)]. In addition, the damage associated to the $^{12}C^+$ implantation to a heavy dose improves the electrical activation of B [curve (c)]. When the implantation damage of the $^{12}C^+$ implantation is annealed prior to the $^{11}B^+$ implantation, the major role in the activation behavior of B should be played by the C doping level [curve (d)]. Then, the most prominent result is the complete suppression of the reverse annealing.

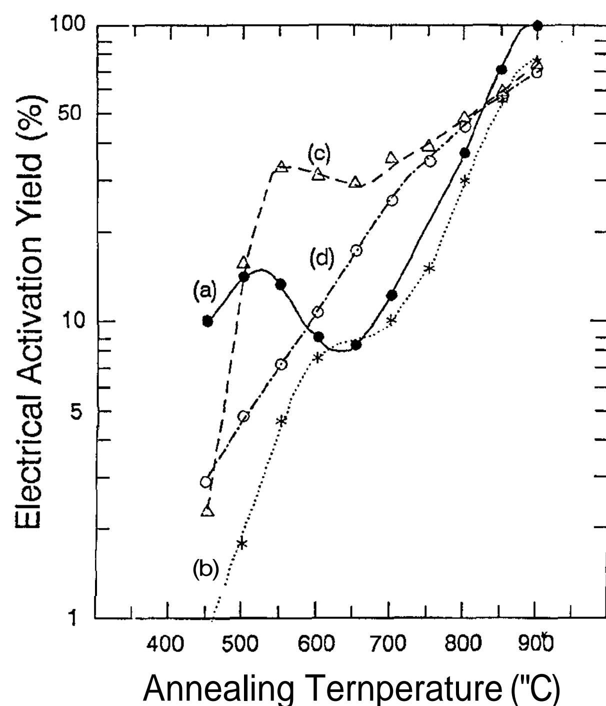

Figure 4: Electrical activation yield after isochronal annealing for 30 min of samples implanted only with $^{11}B^+$ (5×10^{14} cm^{-2} at 50 keV) [curve (a)] or dually implanted with $^{11}B^+$ (5×10^{14} cm^{-2} at 50 keV) and $^{12}C^+$ to the dose of 5×10^{13} cm^{-2} [curve (a)], 5×10^{14} cm^{-2} [curve (b)] or 5×10^{15} cm^{-2} [curve (c)]. Curve (d) shows the electrical activation yield of samples implanted with $^{12}C^+$ to a dose of 5×10^{15} cm–2 and annealed at 900 °C for 30 min prior to the $^{11}B^+$ implantation. All the $^{12}C^+$ implantations were performed at energy of 55 keV.

The electrical activation of Bi implanted silicon by rapid thermal annealing (RTA) was also addressed previously[12]. It was found that approximately 95 % of the Bi dose is substitutional and 90 % electrically active after annealing performed at 600 °C for times longer than 1 min. The electrical activation yield (EAY) of Bi after RTA at temperatures $\geq$ 700 °C is observed to decrease with the increasing of the temperature and time of the annealing process. Angular scan measurements carried out on annealed samples revealed that the electrically inactive concentration of Bi correlates with the concentration of Bi atoms located slightly displaced from the crystal rows. The displaced Bi atoms should be associated with the formation of electrically inactive Bi-vacancy defect complexes.

Table I. The sheet resistivity (R,) and electrical activation yield (EAY) for the silicon samples, implanted with $^{209}Bi^+$, energy 150 keV, dose 5 x 10^{14} cm^{-2} and co-implanted with $^{12}C^+$, energy 20 keV, RTA annealed with the following temperature (T) and time durations (t) are shown.

C^+ dose	T	t	R,	EAY
[cm^{-2}]	[°C]	[s]	[Ω/□]	[%]
0	900	60	389	40
2×10^{15}	900	60	890	22
0	900	300	610	22
2×10^{15}	900	300	3840	1.5

In a limited number of experiments single $^{209}Bi^+$ and dually $^{209}Bi^+$ and $^{12}C^+$ implanted samples were submitted to RTA at the temperature of 900 °C for 60 and 300 s. The electrical measurements shown in Table 1 indicate that the $^{12}C^+$ co-implantation has a pronounced influence on the electrical deactivation of Bi. For example, after 300 s RTA, the EAY is reduced 15 times in the dually implanted sample compared to that of single implanted with Bi.

In order to explain this phenomenon one can suppose that the trapping of Si_I atoms by the co-implanted C leads to an increasing of the relative vacancy concentration and hence of the probability for vacancy-Bi complex formation.

V. Discussion and conclusions

All the effects associated to the C implantation presented above can be understood assuming an interaction between C and Si_I atoms during the implantation and the subsequent thermal annealing.

The enhanced damage accumulation during implantation in Si doped with high concentration of $C(> 2 \times 10^{20}$ cm^{-3}) can be explained assuming that C atoms capture Si_I atoms produced in the collision cascades. The accumulation of trapped Si_I atoms at the neighborhood of the C atoms would form complex defect precipitates in the Si matrix which are stable at room temperature. The abnormal enhanced damage accumulation in samples implanted with $^{12}C^+$ doses $> 2 \times 10^{15}$ cm^{-2} may be understood considering that the concentration of precipitates or their sizes increase with the implanted $^{12}C^+$ dose. This fact leads to an enhancement of probability for Si_I capturing and damage accumulation. Hence, a reduction of the dynamic annealing takes place.

The electrical activation of B in samples co-implanted with $^{12}C^+$ at doses lower, equal or higlier than that of $^{11}B^+$ was discussed. The implantation damage and the C concentration influence significantly the electrical activation behavior of B. In the case of Bi and C co-implanted Si an enhanced deactivation of Bi was observed after RTA. The trapping of Si_I atoms by the implanted C may lead to an increasing of the relative vacancy concentration and consequently strongly favoring the formation of electrically inactive vacancy-Bi complexes.

In summary, all the effects associated to the C implantation presented above can be explained assuming that C and Si_I atoms chemically interact during the implantation and the subsequent thermal annealing, forming stable point defect complexes.

Acknowledgments

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References

1. J. Wang and M. Kulkarni, ECS-Meeting, Extended Abstract No. 532 (Florida, 1980).
2. A. Kanamori and M. Kanamori, J. Appl. Phys. 50, 8095 (1979).
3. II. Wong, N.W. Cheung, K.M. Yu, P.K. Chu and J. Liu, in Ion Beam *Processing of* Aduanced *Electronic* Materials, edited by N.W. Cheung, A.D. Marwick and J.B. Roberto, (Materials Research Society, Pittsburg, 1989), vol.147, p. 97.
4. J.R. Liefting, J.S. Custer and F.W. Saris, in Phase *Formation* and *Modification* by Beam-Solid *Interactions*, edited by G.S. Was, L.E. Rehn and D.M. Follstaedt, (Materials Research Society, Pittsburg, 1992), vol. 235, p. 179.
5. S. Nishikawa, A. Tanaka and T. Yamaji, Appl. Phys. Lett. 60, 2270 (1992).
6. S. Nishikawa and T. Yamaji, Appl. Phys. Eett. **62,** 303 (1993).
7. F. II. Eisen, in *Channeling*, edited by D.V. Morgan (Wiley, New York, 1973) p.417.
8. L. J. Van der Pauw, Philips Res. Rep. 13, 1 (1958).
9. F. II. Eisen and B. Welch, in European *Conference* on Ion Implantation (Reading, U.K., 1970) p. 227.
10. J. F. Ziegler, J. P. Biersack and U. Littmark, in The Stopping and Ranges of *Ions in Solids* (Pergamon, New York, 1985).
11. J. P. de Souza and H. Boudinov, J. Appl. Phys. 74, 6599 (1993).
12. J. P. de Souza and P. F. P. Fichtner, J. Appl. Phys. 74, 119 (1993).