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ABSTRACT

Rutherford backscattering and channelling analysis of high-dose, room-temperature, ion-implanted germanium has revealed an anomalous near-surface yield deficit. Implant dose and species dependencies and the effect of annealing have been examined. A marked loss of implanted impurity was also

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(Continued)

noted. The yield deficit is attributed to the absorption of oxygen and other light mass contaminants into a highly porous implanted layer upon exposure to air. Loss of implant species is attributed to enhanced sputtering effects. Anomalous yield deficits have been observed in heavily implanted silicon, but the effect is not as pronounced as in germanium.

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ANNEALING; BACKSCATTERING; GERMANIUM; IMPURITIES; ION CHANNELING; ION IMPLANTATION; OXYGEN; PHYSICAL RADIATION EFFECTS; RUTHERFORD SCATTERING; SILICON; SPUTTERING; TEMPERATURE DEPENDENCE

CONTENTS

1. INTRODUCTION

Ion implantation is an important technique in the semiconductor industry for doping Si and GaAs. Consequently, the associated damage and its subsequent removal have been relatively well characterised in these semiconductors [Mayer et al. 1970]. By contrast Ge, being of lesser technological importance, has not been as extensively studied. However, recent investigations [Appleton et al. 1982; Wilson 1982] have shown that room-temperature implantation into Ge can result in near-surface structural modifications which differ markedly from that typically observed in Si and GaAs.

In particular, the Rutherford backscattering (RBS) and channelling spectra from ion-implanted Ge exhibit a large near-surface yield deficit which is correlated with an anomalously high incorporation of light mass impurities into room-temperature implanted Ge [Appleton et al. 1982]. These light impurities are absorbed into the surface after implantation, upon exposure to air. Implantation and analysis without breaking vacuum showed no near-surface yield deficit or impurity incorporation. Furthermore, channelling analyses revealed that the yield deficit persists over the depth of the implantation damage, and transmission electron microscopy (TEM) investigations showed that the near-surface region is comprised of a highly porous, amorphous and part-crystalline layer. Wilson [1982], using scanning electron microscopy (SEM), showed a porous surface structure produced by self-implantation of Ge. However, although some RBS examinations were made, neither yield deficit nor uptake of impurities was observed, in contrast to the findings of Appleton et al. [1982]. Furthermore, the latter workers also found that the anomalous yield deficit in Ge was temperature-dependent, not being present at liquid nitrogen temperatures and being much reduced at 275°C.

In this report detailed investigations of RBS yield deficits in ion-implanted Ge and Si are described. In particular, the dose and species dependence of anomalous yield deficits, loss of implant species and the annealing behaviour have been studied for room-temperature, ion-implanted Ge. The results have been published in abbreviated form elsewhere [Lawson et al. 1983]. Since Ge is the lightest ion so f⁻ to have produced an anomalous yield deficit [Appleton et al. 1982; Lawson et al. 1983], there is a need to demonstrate the effect with very low mass ions; consequently, a preliminary experiment is reported in which He ions were implanted into Ge.

Anomalous yield deficits in Si have not previously been reported. In this study, we have examined RBS spectra from heavily implanted Si to compare them with those obtained from Ge and, in particular, to search for anomalous behaviour.

2. EXPERIMENTAL

2.1 General

The spectra and results presented here are derived from 2.0 MeV He^+ RBS and channelling techniques using 170° and grazing-exit-angle geometries [Williams 1978] for optimum mass and depth resolution respectively. The 3 MeV Van de Graaff accelerator at Lucas Heights was used in all cases.

2.2 Germanium

Bismuth, thallium, antimony and indium were implanted into (100) p-Ge (5×10^{11} cm^{-2}) at doses in the range 5×10^{14} to 1×10^{16} cm^{-2}. The implantations were performed at room temperature with the Ge samples offset by $\sim$ 7° to ensure no channelling effects. Current densities during implantation were typically 0.1 $\mu A\ cm^{-2}$, which is insufficient to raise the surface temperature significantly [Dearnaley 1978]. The implant energies were chosen to provide similar range distributions. For example, 90 keV implants of Bi and Tl, and 70 keV implants of In and Sb have projected ranges R_p of $\sim$ 23 nm and standard deviations ΔR_p of $\sim$ 9 nm [Gibbons et al. 1975]. Values of R_p and ΔR_p are included in Table 1.

A dose of 1.3×10^{17} He^+ cm^{-2} was implanted at 2.0 MeV into (100) Ge with the Van de Graaff accelerator. Current density was $\sim$ 3.5 $\mu A\ cm^{-2}$ and range distribution parameters were $\sim$ 5.7 μm and $\sim$ 0.33 μm for R_p and ΔR_p respectively. The samples were exposed to air at several stages during the implantation.

2.3 Silicon

Elevated temperature implants were chosen since no anomalous yield deficits have been reported at room temperature, and because the temperature dependence of the Ge data suggests that higher temperatures may be more suitable for observing the effect in Si. Antimony and arsenic were implanted into (100) and (111) Si for substrate temperatures in the range 150 to 450°C. Doses were 2 x 10^{15} cm^{-2} at 80 keV for Sb and 2 x 10^{16} cm^{-2} at 40 keV for Sb and As. The current density was typically 0.1 to 1.0 μA cm^{-2}. Implantation details and projected range parameters are given in Table 2.

3. RESULTS

On examination of the implanted Ge by RBS, a distinct yield deficit was noted from the near-surface region. The series of spectra shown in Figure 1 illustrate the dose dependence of the effect for 90 keV Tl implantation into (100) Ge. The yield deficit clearly increases with increasing dose. Moreover, it is a maximum at the surface and decreases with depth over the extent of the implantation damage, as indicated by the channelled spectra. If the near-surface is assumed to be amorphous and have a density close to that of crystalline Ge, the 'amorphous' layer of the spectrum in Figure 1c is about 70 to 80 nm thick, or roughly three to four times the R_p for 90 keV Tl. However, the depth scale has not been given in Figure 1 since, as is illustrated below, considerable variation in the structure, composition and density of the implanted layer can result in drastic changes to the depth scale. The dose dependence of the yield deficit was observed with all implant species. Furthermore, after implantation the samples had an unusual black appearance following exposure to air.

The random spectra from virgin Ge show a small near-surface peak followed by a deeper region of lower yield. This results from oscillations in yield when close to a planar channelling direction. Difficulty is sometimes experienced in obtaining the ideal random spectrum from fixed angular settings with the present goniometer, but this does not affect any of the results or conclusions.

Another feature is the apparent loss of Tl with increasing dose (see Figures 1b and 1c). This effect is characterised in Table 1, where implanted and measured doses (from 170° spectra) are listed for the most heavily implanted samples. A striking loss of implant material is observed for the highest dose of all species.

The magnitude of the yield deficit is anomalously large since it cannot be explained by the addition of implanted species into the near-surface structure of the Ge. The magnitudes of 'implant-impurity-induced' yield deficits are discussed in Section 4. The yield deficits from room-temperature implanted Ge are dominated by the anomalous uptake of light impurities into the porous surface structure.

Figure 2 shows RBS spectra which illustrate that the yield deficit is not significantly dependent on the implanted species. Similar doses of In and Bi result in a similar magnitude and distribution. The Bi channelled spectrum is shown in line form as it was necessary to normalise it in terms of both yield and depth. Channelling runs could not be taken at exactly the same scattering geometry for the Bi- and In-implanted samples, hence the depth scale and yield of one or other spectrum had to be normalised for accurate comparison.

Preliminary annealing measurements were carried out to ascertain the effect of the anomalous near-surface structure on damage removal. Figure 3 shows that furnace annealing at 350°C for 30 min, then 400°C for 30 min, does not significantly reduce the magnitude and distribution of the yield deficit. This annealing sequence should be sufficient to recrystallise the amorphous Ge completely [Lau et al. 1980]. The damage layer has recrystallised epitaxially but only over approximately half its thickness. Considerable residual damage is present in the near-surface region. Indeed, the channelling spectra following the 350 and 400°C anneals were identical, indicating dramatic inhibition of the epitaxial growth process in the surface region which corresponded to the anomalous yield deficit.

The anomalous deficit was sought in He-implanted Ge. Figure 4 shows spectra obtained after implanting 1.3×10^{17} He cm^{-2} at 2.0 MeV into (100) Ge. No deficit is observed, the random spectrum being unchanged by the implantation. However, in comparison with virgin Ge, the channelled spectrum shows a considerable increase in the minimum yield (χ_{min}) as a function of depth in the sample.

Silicon samples implanted at various temperatures with Sb and As (see Table 2) were examined for anomalous effects. Very obvious yield deficits were seen, especially from those samples implanted with 2×10^{16} ions cm^{-2} at 40 keV. However, as discussed in Section 4, significant implant-impurity-induced deficits are expected because of the much larger ratio of impurity to substrate scattering cross sections in Si compared to Ge. Although it is tempting to assign the observed deficits to this effect alone, detailed calculations are required to support the assumption. Preliminary results obtained from such calculations are discussed in Section 4.

Figure 5 shows typical spectra from high-temperature (250°C), high-dose, Sb-implanted Si. Comparison between the random spectra from virgin and implanted samples suggests a yield deficit which corresponds in depth with, and reflects the shape of, the implanted Sb distribution. The channelled spectrum indicates that the residual damage consists most probably of an amorphous layer with a thickness of about $2R_p$. The magnitude of the yield deficit does not change appreciably with temperature although the shape alters slightly. Similar effects were seen in spectra from high-dose, As-implanted Si. Higher temperature implants for both As and Sb species showed additional features, notably regions of non-amorphous, deep disorder [Csepregi et al. 1976], redistribution of the implanted species, and incomplete amorphousness of the near-surface region. If there are anomalous yield deficits in the spectra from implanted Si, these features may be relevant, but they have not been investigated further in this study.

4. DISCUSSION

Yield deficits in the high-dose Ge spectra are typically >20 per cent of the surface edge height. Normally the yield from an elemental substrate is independent of its atomic density. However, when composition changes occur due to the presence of an impurity species, the yield is reduced. The yield deficit which results from incorporation of the implanted species is referred to as 'impurity-induced', to distinguish it from the anomalous case in which impurities are absorbed into the porous structure following exposure to air. The magnitude of the impurity-induced yield deficit in ion-implanted samples can readily be calculated.

Implantation profiles are commonly described by a Gaussian form with the peak impurity concentration given by the formula

$$\frac{\phi}{\Delta R_p \sqrt{2\pi}} \tag{1}$$

where ϕ is the fluence or ion dose and ΔR_p is the standard deviation of the projected range R_p. This peak impurity concentration can be used to give a first approximation to the expected impurity-induced yield deficit. However for the present analysis, the peak concentration was determined from the spectral data. This method is more accurate and removes the need for such corrections as those for the difference between actual and nominal implant dose, the loss of implant species due to sputtering effects, and redistribution due to diffusion. The peak Tl concentration in the 1 x 10^{16} Tl cm^{-2} case is 2.6 x 10^{20} Tl cm^{-3} or 0.6 at.%. The magnitude of the yield deficit at the Ge surface for the case of 0.6 at.% Tl is calculated to be 1 per cent of the edge height of unimplanted Ge. This is much less than that observed (see Figure 1) hence the yield is considered anomalous. Similar anomalous behaviour is found for all the high implant dose Ge samples. Of course, the self-implantation results of Appleton et al. [1982] provide striking evidence for the anomalous nature of the deficit.

The situation is more complex for the Si samples. For example, a most obvious yield deficit is expected and found in Si implanted with 2 x 10^{16} Sb cm^{-2} at 40 keV. The corresponding peak Sb concentration is equivalent to 14 at.% Sb in Si. The impurity-induced yield deficit is calculated to have a maximum value of 22 per cent of the Si surface edge. From Figure 5, it can be seen that the yield deficit has a maximum value of ∿ 33 per cent, which is quite different from that calculated, and suggests the presence of an anomalous component in the deficit. In all Sb- and As-implanted samples examined, the measured deficit was larger than the calculated deficit by a factor of up to 1.6. This discrepancy is outside experimental and computational uncertainties. To test the method of calculation, we examined experimental spectra from SiO_2 on Si, and also generated simulated implant spectra using the program of Ziegler et al. [1976]. In both cases, the measured and calculated deficits are identical.

The RBS spectra of 1.3 x 10^{17} cm^{-2} He-implanted Ge show no yield deficit. There are a number of reasons for this. First, the implantation energy and corresponding particle range is such that surface and near-surface effects are unlikely. The channelled spectrum (Figure 4) indicates little surface damage. The stopping power of the He in the near-surface region is less than the maximum and mainly electronic. Second, the implantation temperature is not well known. The Ge sample was surrounded by a cold (77 K) electron suppression shield to reduce its temperature. On the other hand, the power dissipated by the beam (≈7 W cm^{-2}) was enough to raise the temperature significantly [Dearnaley 1978]. Although standard deviation ΔR_p and dose were unusually large in this experiment, the peak concentration was only 1.6 x 10^{21} cm^{-3} (based on Equation 1) and R_p was 5.7 μm. Consequently, no impurity-induced yield deficit was anticipated. Of course, lower He implantation energies could give rise to an anomalous deficit.

A very plausible explanation for the anomalous yield deficit observed in the Ge RBS spectra is the incorporation of large concentrations of light contaminants into the near-surface region of the implanted Ge. It is to be noted here that, owing to the dependence of the Rutherford cross section on atomic number, low mass impurities cannot be seen in the RBS spectra. Oxygen and carbon have been identified by Appleton et al. [1982] using nuclear reaction analysis. Other low mass contaminants such as N and H may also be present but have not as yet been investigated. Microscope studies (TEM by Appleton et al. [1982] and SEM by Wilson [1982]), indicated that Ge samples implanted at room temperature have a complex damaged surface region composed of three distinct layers. The uppermost layer is highly porous, part amorphous, part polycrystalline, and contains many surface craters. Below this is a more uniform amorphous layer separated from the single crystal substrate by a dislocation-rich, single-crystal region. It appears that on annealing, only the deeper layers regrow epitaxially while the upper porous, contaminated layer recrystallises in a polycrystalline manner.

Another striking feature of the Ge RBS spectra is the loss of implant species. It is likely that this is due to sputtering enhanced by the increased surface area. Sputtering calculations, assuming a normal surface, give implant species losses much less than that observed. For example, the sputtering yield for 90 keV Tl-implanted Ge is about 6 Ge atoms per incident Tl ion [Anderson and Bay 1982]. Based upon this, a dose of 1×10^{16} Tl cm^{-2} ought to result in the collection of more than 80 per cent Tl whereas only 32 per cent was found. It is suggested that the exposure of a larger surface area through the development of a porous structure leads to enhanced loss of material by sputtering (both Ge and Tl).

As far as we are aware, anomalous yield deficits corresponding to porous near-surface layers have not been observed for room-temperature implants into Si. Our observation of an anomalous yield deficit in Si for elevated implant temperatures suggests that mobile defects may contribute to the generation of a porous structure. We have suggested elsewhere [Lawson et al. 1983] that such a process explains the temperature dependence of the effect in Ge. This defect mobility would be expected to be lower in Si than in Ge at the same temperature, consistent with the relative amorphous/crystalline transition temperature [Wilson 1982] in these materials.

5. CONCLUSIONS AND SUMMARY

It has been shown that room-temperature ion-implantation into Ge can produce an anomalous yield deficit and associated loss of implant species. Both become more significant as the dose increases. It is noted that the extent of the yield deficit is considerably greater than the R_p, and coincident with the extent of implantation damage.

Furnace annealing of Ge above the amorphous/crystalline transition temperature does not reduce the magnitude and distribution of the deficit, although the implant-damage width decreases noticeably. There is a dramatic reduction in the epitaxial regrowth process in the region of the yield deficit. This feature will obviously be very significant should Ge become technologically more important.

The anomalous yield deficit appears to result from the absorption of low mass impurities on exposure to air. The loss of implant species is explained by enhanced sputtering from a porous surface layer. The lack of complete annealing arises, in part, from polycrystallinity in the near-surface region, a high fraction of near-surface, low mass impurities, and also from a porous structure.

No anomalous deficit was seen in Ge implanted with 2.0 MeV He ions. It appears that the damage produced by these highly energetic ions is deep (a few micrometres) and no porous surface region is created to absorb low mass impurities. Furthermore, the implantation temperature may be above the amorphous/crystalline transition temperature.

For Si, our experimental data suggest the presence of anomalous yield deficits but the effect is not as large as has been observed in Ge. More experimental work will be undertaken to identify clearly this anomalous component, with particular attention to high-dose Si into Si implants. In addition, a search will be made for the anomalous deficit in ion-implanted GaAs.

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7. REFERENCES

Andersen, H.H. and Bay, H.L. [1982] - In Sputtering by Ion Bombardment (ed. R. Behrisch), Topics in Applied Physics Vol.47, Springer-Verlag, Berlin, p.145.

Appleton, B.R., Holland, O.W., Narayan, J., Schow III, O.E., Williams, J.S., Short, K.S. and Lawson, E.M. [1982] - Appl. Phys. Lett., 41(8)711.

Csepregi, L., Kennedy, E.F., Lau, S.S., Mayer, J.W. and Sigmon, T.W. [1976] - Appl. Phys. Lett., 29(10)645.

Dearnaley, G. [1980] - Site Characterization and Aggregation of Implanted Atoms in Materials. In Lectures presented at the NATO Advanced Study Institute, Aleria, Corsica (September 1978). Series B: Physics, (ed. A. Perez and R. Coussement), Plenum Press, N.Y. p.33.

Gibbons, J.F., Johnson, W.S. and Mylorie, S.W. [1975] - Projected Range Statistics. Halstead Press, Pennsylvania.

Lau, S.S., Mayer, J.W. and Tseng, W. [1980] - In Handbook of Semiconductors (ed. S.P. Keller), North Holland, Amsterdam, Vol.3, Ch.7.

Lawson, E.M., Short, K.T., Williams, J.S., Appleton, B.R., Holland, O.W., and Schow III, O.E. [1983] - Nucl. Instrum. Methods, 209/210:303.

Mayer., J.W., Eriksson, L. and Davies, J.A. [1970] - Ion Implantation in Semiconductors. Academic Press, New York.

Williams, J.S. [1978] - Nucl. Instrum. Methods, 149:207.

Wilson, I.H. [1982] - J. Appl. Phys., 53(3)1698.

Ziegler, J.F., Lever, R.F. and Hironen, J.K. [1976] - Computer Analysis of Nuclear Backscattering. In Ion Beam Surface Layer Analysis, (eds. O Meyer, G. Linker, F. Kappeler), Plenum Press, New York, pp.163-183.

TABLE 1
NOMINAL IMPLANTED AND MEASURED DOSES FOR
VARIOUS SPECIES IN GERMANIUM

Species	Energy (keV)	R_p (nm)	ΔR_p (nm)	Nominal Dose (cm^{-2})	Measured Dose (cm^{-2})	Loss (%)
Tl	90	22.1	8.1	1.0×10^{16}	3.2×10^{15}	68
				3.0×10^{15}	3.3×10^{15}	-
				5.0×10^{14}	3.1×10^{14}	-
Bi	90	21.9	8.0	1.0×10^{16}	8.4×10^{15}	16
				3.0×10^{15}	3.7×10^{15}	
Sb	70	21.9	9.6	1.2×10^{16}	6.1×10^{15}	50
				6.0×10^{15}	5.1×10^{15}	-
In	70	22.3	9.9	1.0×10^{16}	5.3×10^{15}	47

TABLE 2
IMPLANTATION DETAILS - Sb AND As IMPLANTED INTO Si
AT ELEVATED TEMPERATURES

80 keV		40 keV	
Dose	Temperature	Dose	Temperature
(100) and (111) Sb		(111) Sb	
R_p = 38.5 nm	ΔR_p = 11.8 nm	R_p = 23.0 nm	ΔR_p = 7.1 nm
	°C		°C
2×10^{15} cm^{-2}	150	2×10^{16} cm^{-2}	250
	200		300
	250		350
	300		400
	350		450
	400		
		(111) As	
		R_p = 26.9 nm	ΔR_p = 9.9 nm
			°C
		2×10^{16} cm^{-2}	150
			200
			250
			300
			350
			400

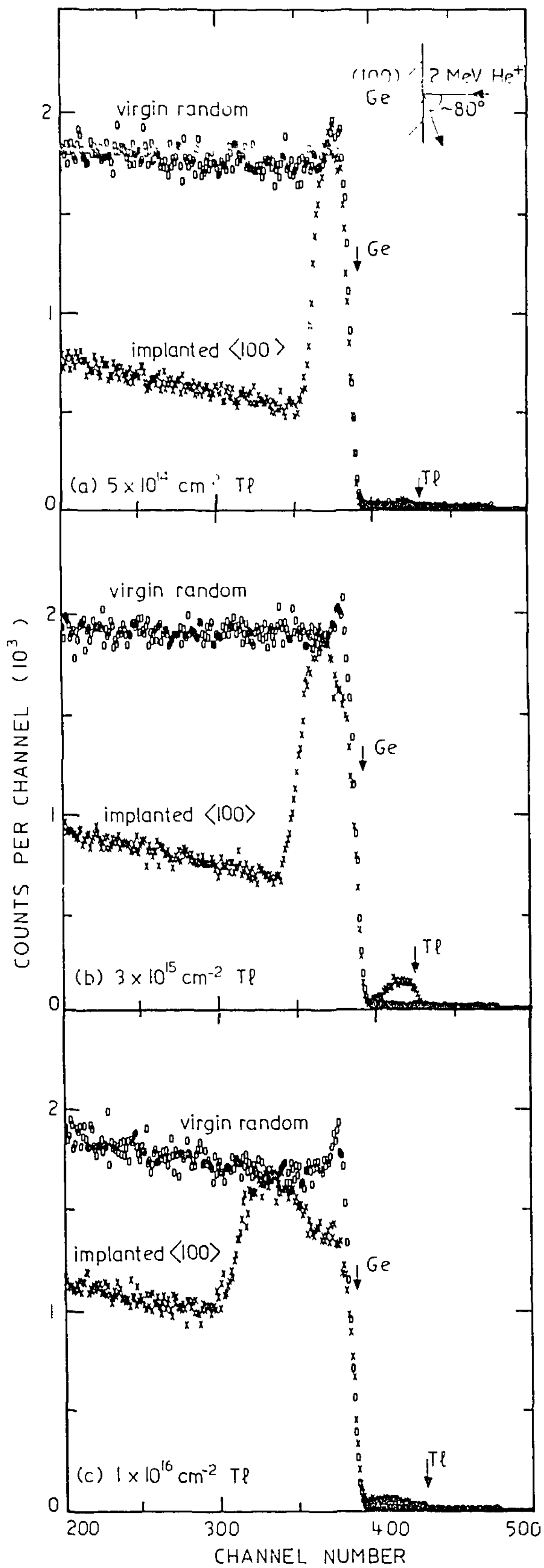

FIGURE 1. DOSE DEPENDENCE OF RBS NEAR-SURFACE YIELD DEFICIT FOR (a) 5×10^{14} cm^{-2}, (b) 3×10^{15} cm^{-2}, (c) 1×10^{16} cm^{-2}, 70 keV Tl IMPLANTATION INTO (100) Ge AT ROOM TEMPERATURE

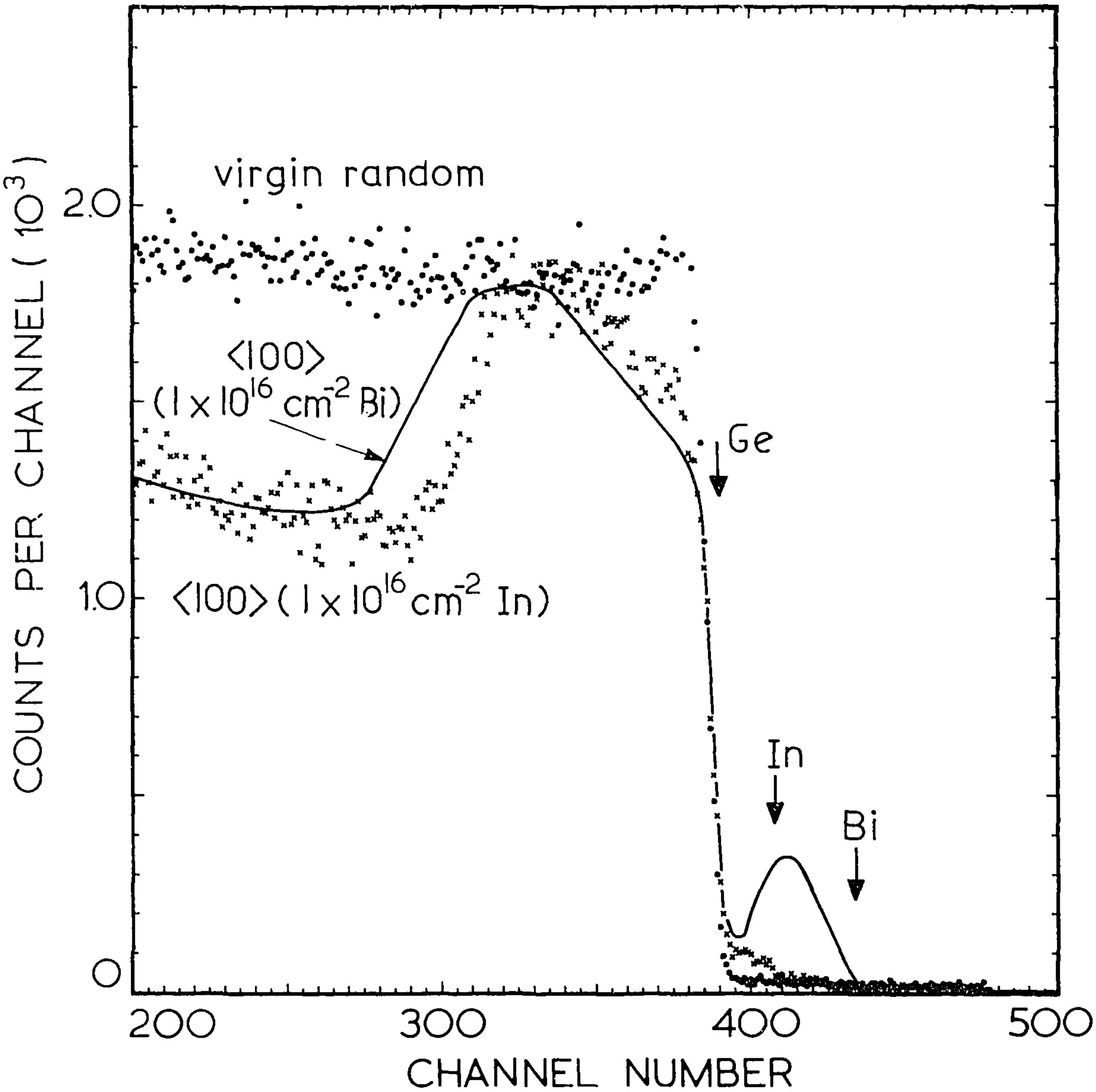

FIGURE 2. SPECIES DEPENDENCE OF THE NEAR-SURFACE YIELD DEFICIT FOR 1 × 10^{16} cm^{-2} Bi AND In-IMPLANTED (100) Ge

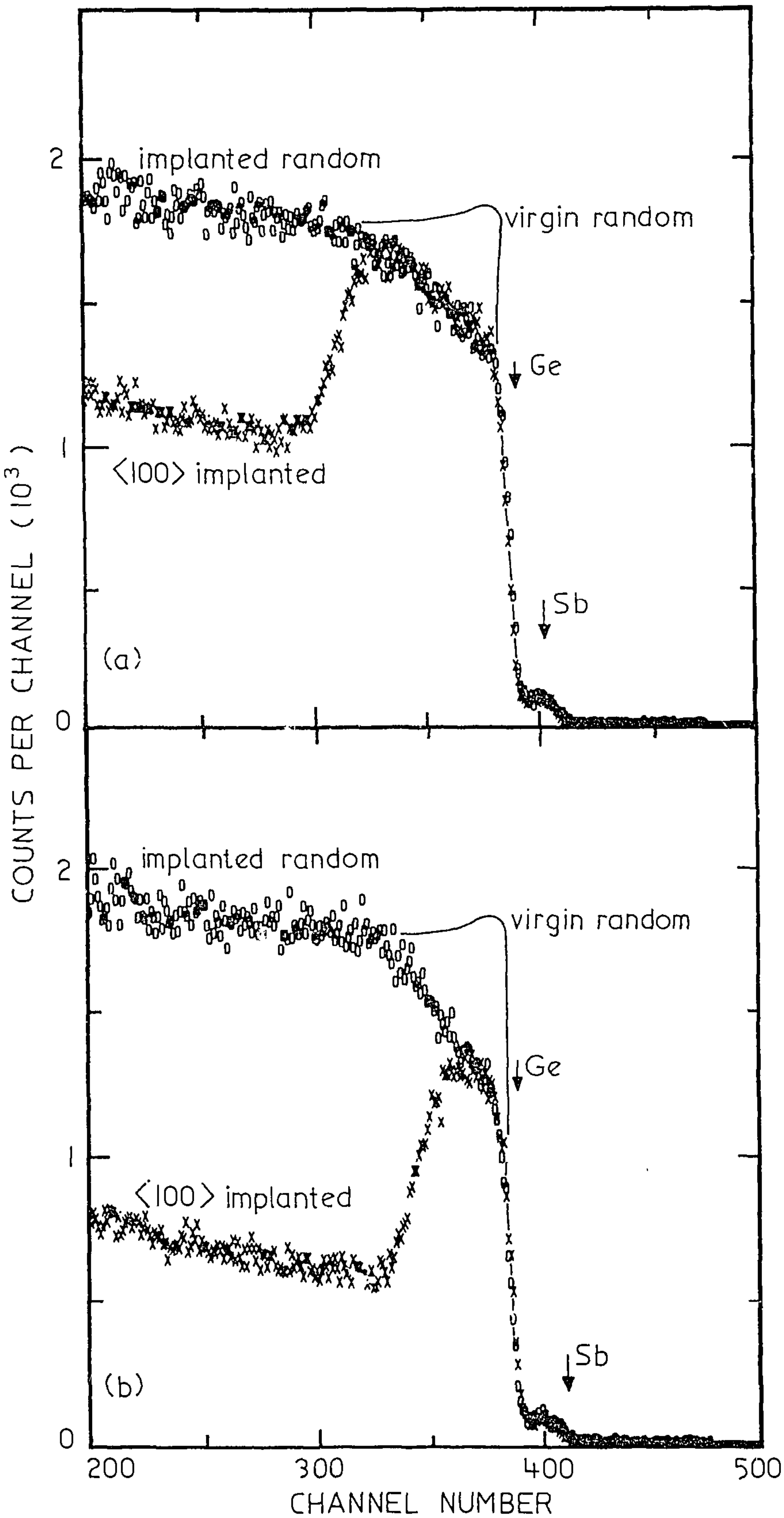

FIGURE 3. NEAR-SURFACE YIELD DEFICIT AND DAMAGE PROFILE (a) BEFORE AND (b) AFTER 350 AND 400°C, 1/2 h ANNEALING OF 1.2×10^{16} cm^{-2}, 90 keV Sb-IMPLANTED (100) Ge

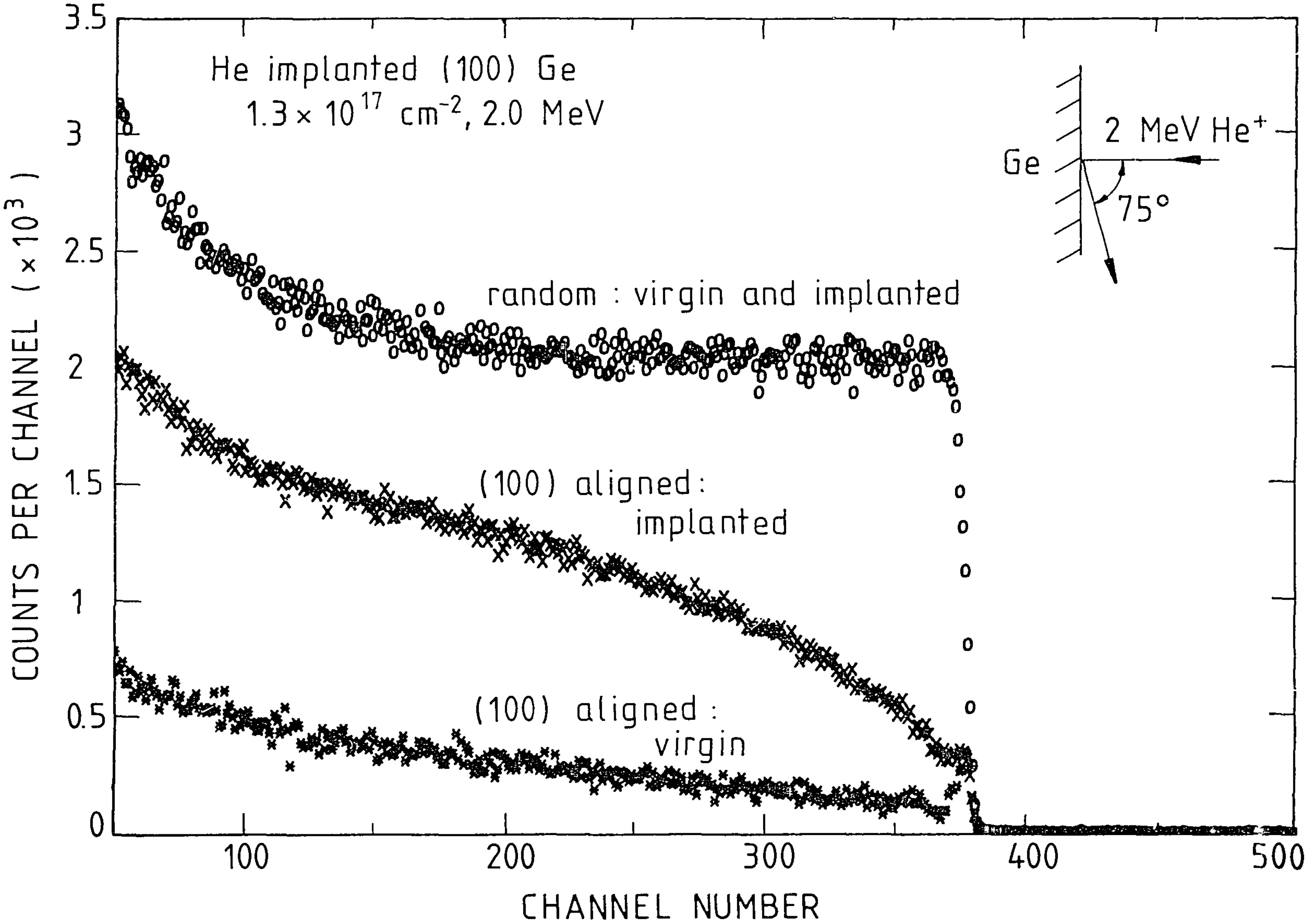

FIGURE 4. RANDOM AND CHANNELLED SPECTRA OF Ge IMPLANTED WITH 1.3×10^{17} cm^{-2} He AT 2.0 MeV

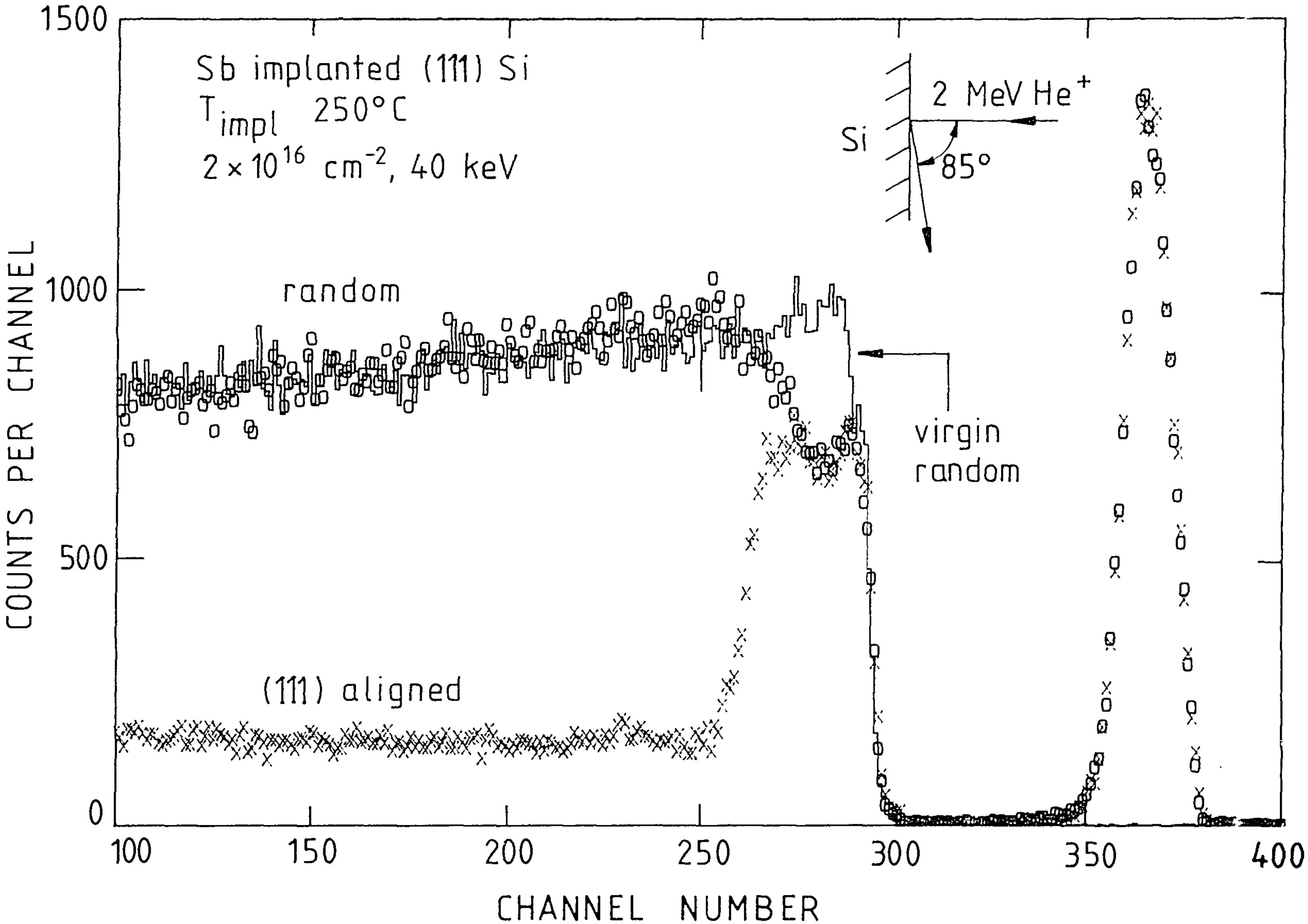

FIGURE 5. SPECTRA FROM A (111) ORIENTED Si SAMPLE IMPLANTED (2×10^{16} Sb cm^{-2}, 40 keV) AT AN ELEVATED TEMPERATURE (250°C)