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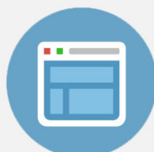
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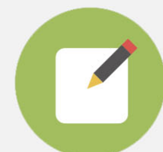

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Electrical activation of bismuth implanted into silicon by rapid thermal annealing and kinetics of defects

J. P. de Souza
Instituto de Física, UFRGS, 91501-970 Porto Alegre, R. S., Brazil

P. F. P. Fichtner
Escola de Engenharia, UFRGS, 90025-190 Porto Alegre, R. S., Brazil

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The rapid thermal annealing (RTA) of Si implanted with Bi^+, to a dose of 5.0×10^{14} cm^{-2} at the energy of 150 keV, was investigated using sheet resistivity, Hall measurements, and channeling analysis. Approximately 95% of the Bi dose is found substitutional and 90% is electrically active after annealing is performed at 600 °C for times longer than 1 min. The electrical activation yield of Bi after RTA at temperatures $\geqslant$700 °C is observed to decrease when increasing the temperature and time of the annealing process. The data taken from electrical measurements and angular scan across the $\langle 100\rangle$ axis are evidence that the electrically inactive concentration of the Bi correlates with the concentration of Bi atoms located slightly displaced from the crystal rows.

I. INTRODUCTION

Bi is an *n*-type dopant in Si substrate that has been disregarded of practical applications mainly due to the low equilibrium solid solubility limit (8×10^{17} cm^{-3} at 1320 °C) in Si crystal.[1] It is known that Bi can be incorporated in metastable solid solution which far exceeds that of equilibrium during liquid phase[2] (1.1×10^{21} cm^{-3}) or solid phase[3] (9×10^{19} cm^{-3}) epitaxial regrowth of amorphous implanted Si layer.

The first studies of the lattice location and electrical activation of Bi implanted into (111)Si revealed that approximately 16% of a dose of 3×10^{14} cm^{-2} implanted at the energy of 40 keV is electrically active after a furnace annealing at 600 °C for 10 min.[4,5] This relatively low activation yield contrasts with the observed high substitutional concentration of 80% of the dose. The substitutional metastable concentration of Bi precipitates during higher temperature thermal treatment. For example, after an annealing at 900 °C only 40% the dose remains substitutional.

Eriksson *et al.*[5] studied the lattice location of hot (450 °C) and room-temperature implanted Bi into (111)Si at an energy of 40 keV. They determined that for doses $<2\times10^{14}$ cm^{-2} 90% of the Bi is located at substitutional sites after hot implant, which corresponds to a maximum substitutional concentration of about 2×10^{20} cm^{-3}. At higher doses a drop off of a substitutional level of Bi was observed to occur. A higher stability of Bi in substitutional lattice sites was observed in the hot implanted samples compared to that in the room temperature implanted samples.[5,6]

Further studies on Bi activation were undertaken by Crowder[7] using Bi^+ implantation at an energy of 240 keV into (111) silicon. He obtained 60% of a Bi dose of 3×10^{14} and 1×10^{15} cm^{-2} electrically activated after an annealing at 600 °C for 30 min. From angular scan measurements across the $\langle 111\rangle$ direction, Davies determined that a significant fraction of the substitutional Bi atoms after hot implantation are slightly displaced from the lattice rows by about 0.2 Å.[8] Picraux *et al.*,[9] using single and double alignment channeling techniques, determined that after an annealing performed at 650 °C for 30 min about 50% of the Bi dose ($2–4\times10^{14}$ cm^{-2}, 150 keV) reside in near substitutional positions located 0.45 Å apart from the lattice rows. The authors suggested the formation of point defect complexes involving Bi atoms and Si vacancy/vacancies in order to release the strain fields associated with the large covalent radius mismatch between Bi (1.70 Å) and Si (1.32 Å).

Subsequent studies focused primarily on the Bi incorporation in the Si lattice (solute trapping) and on push out of Bi atoms towards the surface during laser or electron beam annealing.[2,10–15]

From our knowledge the electrical activation of Bi implanted into (100) Si substrate has not yet been reported in the literature. In the present publication the annealing behavior of Bi implanted into (100) Si during rapid thermal annealing (RTA) is monitored by electrical measurements and aligned Rutherford backscattering spectrometry (RBS).

II. EXPERIMENTAL DETAILS

The Si wafers used in this work were of *p* type and (100) oriented with nominal resistivity of 2.5 Ω cm. Van der Pauw[16] structures, having low sheet resistance contact areas (<20 Ω/□, phosphorus doped) and blanket wafers, were implanted at nominal room temperature with $^{209}Bi^+$ to a dose of 5×10^{14} cm^{-2} and energy of 150 keV. The corresponding mean projected range and standard deviation of the implantation profile are, respectively, 570 and 150 Å.[17] The samples were annealed in a halogen lamp furnace in the temperature range of 600–900 °C for times from 5 to 480 s in argon atmosphere. The Van der Pauw devices were electrically characterized by sheet resistivity and Hall measurements. Random and $\langle 100\rangle$ aligned Ru-

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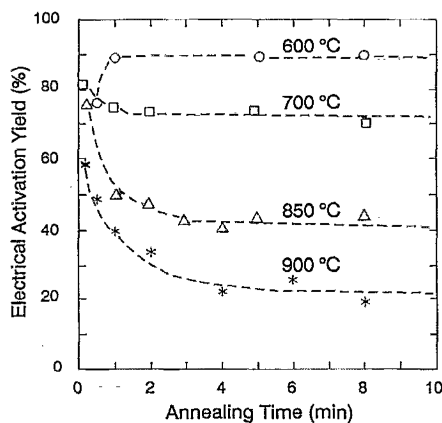

FIG. 1. Electrical activation yield obtained from sheet resistance and Hall measurements in samples annealed at 600, 700, 850, and 900 °C for times from 5 to 480 s.

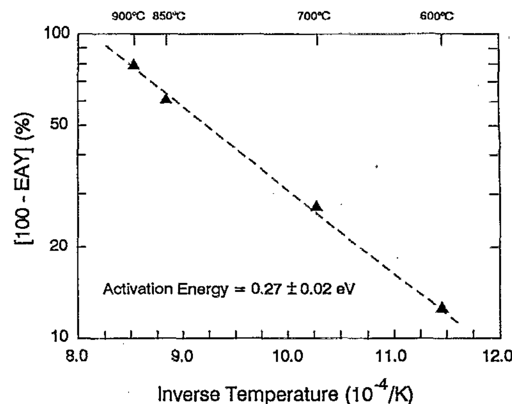

FIG. 2. Arrhenius plot of the electrically inactive fraction of the implanted Bi dose after 300 s annealing at temperatures of 600, 700, 850, and 950 °C.

therford backscattering spectrometry (RBS) were performed on the blanket samples using 760 keV He^{++} beam from the ion implanter.

III. RESULTS

Figure 1 shows the electrical activation yield (EAY) versus the annealing time after RTA performed at 600, 700, 850, and 900 °C. The EAY is considered hereafter as the ratio of the sheet carrier concentration obtained from sheet resistivity and Hall measurements and the implanted dose. An EAY of about 90% was evaluated after annealing at 600 °C for times longer than 1 min. The prolongation of the annealing time up to 60 min did not influence the EAY. This EAY value corresponds to an estimated active concentration of 1.2×10^{20} cm^{-3} at the implanted profile peak, which is well above the equilibrium solid solubility limit (8×10^{17} cm^{-3} at 1320 °C, see Ref. 1).

The EAY of Bi varied with the annealing time and annealing temperature for RTA conducted at $T\geqslant700$ °C. In this temperature range a maximum of EAY occurs after the shortest annealing time (5 s). The prolongation of the annealing time up to ~3–4 min conducts to the reduction of the EAY from the initial values of 83%, 76%, and 58% to 72%, 42%, and 22%, respectively, at 700, 850, and 900 °C. For times from 3–4 to 8 min the EAY remains apparently constant. Sheet resistances of 350, 370, 450, and 590 Ω/□ and Hall mobilities of 40, 47, 70, and 90 cm^2/V s were typical in samples annealed, respectively, at 600, 700, 850, and 900 °C for times longer than 4 min.

The Arrhenius plot of the percentual inactive fraction of the implanted dose evaluated after 5 min annealing at different temperatures is shown in Fig. 2. From the slope of the straight line fitted to the data in Fig. 2 an activation energy of 0.27 ± 0.02 eV is evaluated.

The aligned RBS spectra from an as-implanted and from samples annealed for 5 min at the different temperatures are shown in Fig. 3. The low backscattering yields of Si in the spectra of the annealed samples ($\chi_{min}<5\%$) evidence solid-phase epitaxy (SPE) regrowth of the amorphized layer with residual defect concentration below the detection limit of our RBS technique ($\approx$0.02 at. % for displaced Si atoms). The apparent substitutional concentrations of Bi evaluated from the data of Fig. 3 are 95%, 98%, 87%, and 70%, respectively, in samples annealed at 600, 700, 850, and 900 °C. The apparent substitutional concentration after 600 °C anneal (95%) practically coincides with the measured EAY of 90%. However, in the samples annealed at temperatures $\geqslant$700 °C the apparent substitutional fraction of the dose is always higher than the corresponding EAY (Fig. 1). The random RBS spectra (not shown) did not evidence redistribution of the implanted Bi profile during the experienced annealing cycles.

The angular scans across the ⟨100⟩ axis from samples submitted to RTA at temperatures of 600, 700, 850, and 900 °C for 300 s are shown respectively, in Figs. 4(a)–4(d). In Figs. 4(a)–4(d) the Si yield corresponds to the integrated counts in a channel window on the Si backscattering signal extending over substrate depths where Bi atoms are present. The Bi yield corresponds to the integrated counts in a channel window comprising the Bi back-

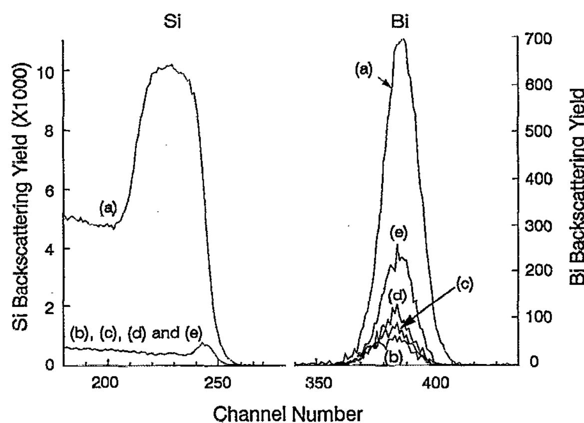

FIG. 3. ⟨100⟩ aligned RBS spectra taken from an as-implanted sample (a), and from samples submitted to an annealing for 300 s at 600 °C (b), 700 °C (c), 850 °C (d), and 900 °C (e).

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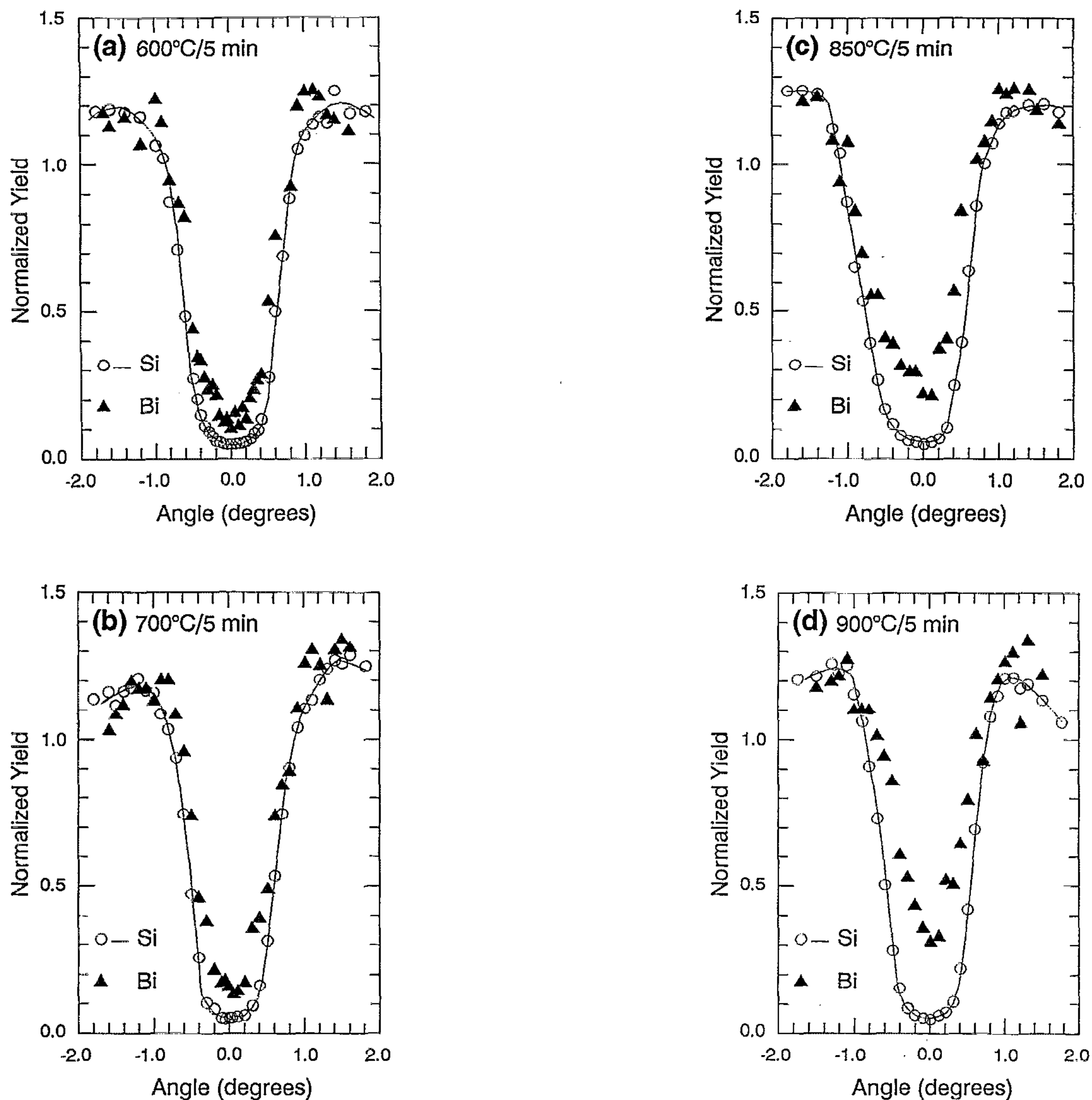

FIG. 4. Angular scan across ⟨100⟩ axis from samples annealed for 300 s at 600 °C (a), 700 °C (b), 850 °C (c), and 900 °C (d).

scattering peak in the RBS spectra. Both Si and Bi backscattering yields were normalized to their respective random yields. Similar critical angles for channeling are observed in the Si angular scans irrespectively of the annealing temperature [see Figs. 4(a)–4(d)]. The Bi angular scan of the sample annealed at 600 °C practically coincides with that of Si [see Fig. 4(a)]. However, the critical angle for channeling in the Bi angular scan progressively reduces and the minimum yield increases with the increasing of the annealing temperature [Figs. 4(a)–4(d)].

IV. DISCUSSION

The data presented in Fig. 1 demonstrate that Bi can be activated at a concentration of 1.2×10^{20} cm^{-3} after SPE regrowth of the amorphized Si layer at 600 °C. This electrically active concentration is considerably higher than those determined by Baron *et al.*[5] (2×10^{19} cm^{-3}) and by Crowder[7] (4×10^{19} cm^{-3}) in (111) Si. The higher activation level found in the present work possibly results from the better crystal quality after SPE regrowth of (100) Si compared to that of (111) Si.

Considering that the flux distribution of alpha particles peaks in the center of the channel and approaches zero close to the rows in the axial channeling, the sensitivity in detecting the presence of atoms displaced a few tenths of an Å apart from the lattice rows is strongly reduced by the axial channeling technique.[18] Consequently, the substitutional concentrations determined from the data of Fig. 3 overestimate the actual substitutional concentrations. This fact explains the higher concentration of apparently substitutional Bi atoms compared to the electrically active concentration.

The decreasing of the EAY with the annealing time and temperature (see Fig. 1) correlates with the narrowing of the channel width in the angular scans of Bi in Figs. 4(a)–4(d). Since the narrowing of the channel width results from the displacement of Bi atoms from substitutional

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lattice sites to near substitutional sites, the reduction of the EAY of Bi with the prolongation of the RTA time and/or temperature should be associated with the Bi atom movement. As pointed out by Picraux *et al.*[9] during the annealing, substitutional Bi atoms and point defects probably interact forming an electrically inactive defect complex in order to relax the strain field originated by the large covalent radius mismatch (0.39 Å) between substitutional Bi and Si atoms. The evaluated activation energy of 0.27 $\pm$0.02 eV should be associated with this phenomenon.

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