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June 1984

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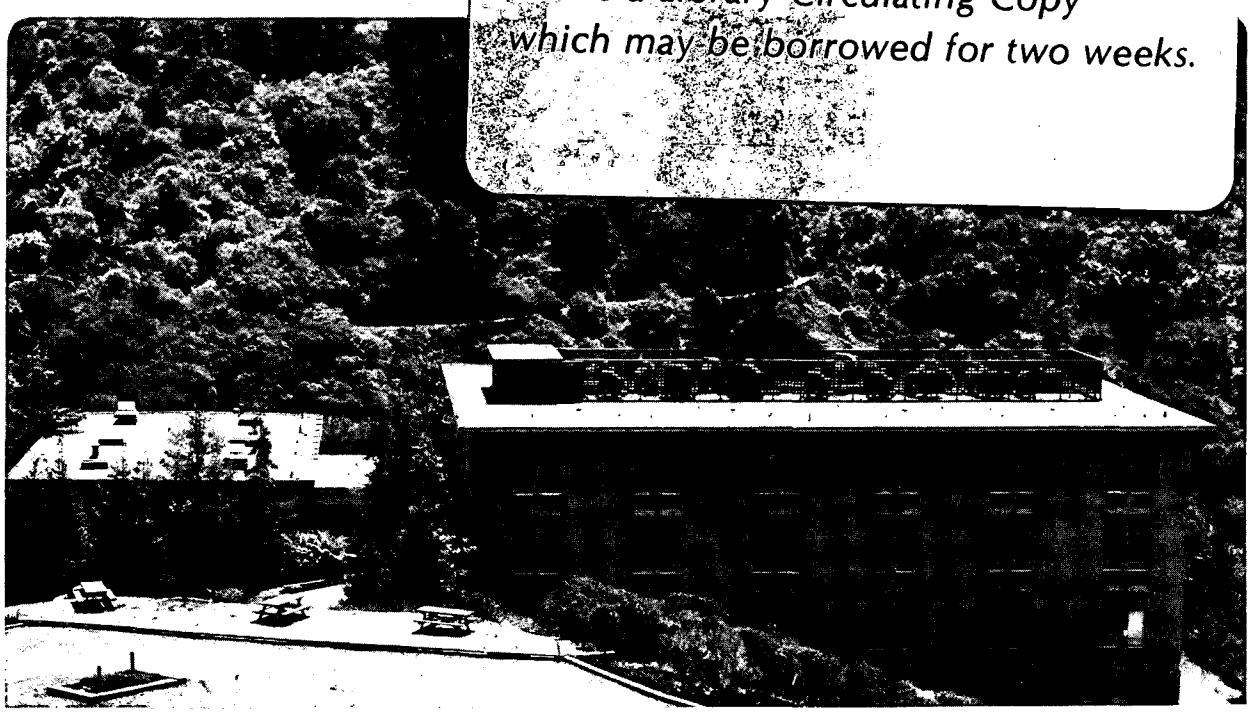

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Near-Surface Defects Formed During Rapid Thermal Annealing of Pre-amorphized and BF_2^+ - Implanted Silicon

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Near-surface defects formed during rapid thermal annealing (950-1150° C, 10 sec.) of pre-amorphized and BF_2^+-implanted (100) Si have been studied by a combination of cross-sectional transmission electron microscopy (XTEM) and secondary-ion mass spectrometry (SIMS). Two types of defects are identified: fine clusters (1.5-4nm in diameter) are shown to be related to flourine; and stacking faults are correlated with the presence of both excess boron above the solid solubility limit and flourine. In addition, high-resolution XTEM images suggest that small crystallites ($\sim$5 nm in diameter) in the surface oxide are B_2O_3. This observation is consistent with the SIMS data which shows segregation of boron to the surface. Finally, the peak flourine concentration is found to be lower in samples which contain a high density ($>10^8$

cm^{-2}) of "hairpin" dislocations, indicating that a pipe diffusion mechanism for the rapid out-diffusion of flourine may be operative.

Difficulties encountered when forming shallow ($<0.5\mu m$) p^+-n junctions for silicon device applications have resulted in the implementation of several novel implantation and annealing techniques: for example, implantation of the BF_2^+ molecular ion results in higher beam currents and allows higher beam energies than the equivalent B^+ implantation[1]; amorphizing the substrate surface layer prior to BF_2^+ implantation ("pre-amorphization") eliminates boron channeling and encourages the substitutional incorporation of boron during subsequent solid phase epitaxial growth[2-4]; and rapid annealing techniques reduce the redistribution of boron normally encountered during furnace annealing[5,6]. However, the processes listed above result in p^+-n junctions with increased chemical and structural complexity. Recently, Maszara etal[7] and Carter etal[8] have demonstrated the presence of at least three distinct defect layers in pre-amorphized, BF_2^+-implanted, and rapid-thermally-annealed (RTA) silicon. Since these defects may influence the electrical properties of the diodes through increased leakage currents or by the nucleation of larger defects during subsequent processing, a detailed understanding of the origins of these defects and their interactions with introduced impurities is necessary. In this letter, defect-impurity interactions in the near-surface region (0-200 nm) of shallow p^+-n junctions are identified by comparison of secondary-ion mass spectrometry (SIMS) profiles of boron and flourine with cross-sectional transmission electron microscope (XTEM) images from the same samples.

Surface layer amorphization of (100) silicon wafers to depths of 400-900 nm was accomplished either by triple-energy Si^+ self-implantation (350, 150 and 70 keV to doses of 10^{16}, $2x10^{15}$ and $5x10^{15}$ cm^{-2}, respectively) or by single-step Ge^+ implantation (300 keV to a dose of 10^{16} cm^{-2}). A continuous amorphous layer could be formed by Ge^+ implantation at (nominal) room temperature (RT) and liquid nitrogen temperature (LNT). However, a continuous amorphous layer could be formed by self-implantation only at LNT with a good thermal contact[8]. Following pre-amorphization, the shallow boron profile was obtained by implantation of 42 keV BF_2^+ to a dose of $2x10^{15}$ cm^{-2} at either RT or LNT. Solid phase epitaxial regrowth of the amorphous layer was induced by rapid thermal annealing (RTA) with incoherent light at temperatures of 950 - 1150°C for 10 seconds. The distributions of boron and flourine before and after RTA were obtained by SIMS (Cameca IMS model 3F). Plan-view TEM and XTEM provided the determination of defect distributions. Specimens for XTEM were prepared by argon ion milling at LNT (5kV, specimen current ∿20μA, 15° tilt). Cross-sectional high-resolution TEM (XHRTEM) was performed with a JEOL 200-CX (spherical aberration coefficient, C_S = 1.2 mm) at 200 keV. A through-focal series of high-resolution images was recorded for each area of interest in <110> zone-axis orientation with an objective aperture which contained nine beams. Images recorded at defocus values in the range of -70 to -90 nm were selected for presentation below.

The XHRTEM image of Fig. 1 shows the near-surface region of a wafer which was pre-amorphized with Si^+, implanted with BF_2^+, and then annealed by RTA at 1150°C. Two types of near-surface defects (designated

"type III" in references 7 and 8) are visible: A distribution of fine clusters (1.5 - 4nm in diameter) centered at ∿20 nm below the silicon surface, and stacking faults bounded by Shockley partial dislocations. Both types of surface defects were observed in all samples which had been pre-amorphized with Si^+, implanted with BF_2^+ at either RT or LNT, and then annealed in the temperature range 950-1150°C. The defect densities estimated from plan-view micrographs are listed in Table 1. The SIMS data (Fig. 2) from the same wafer as imaged in Fig. 1 reveals a substantial loss of flourine, both to the surface and into the bulk, during RTA. However, a well-defined flourine peak remains at a depth of ∿20 nm. The boron profile also shows significant in-diffusion during RTA, although the peak boron concentration (∿5×10^{20} cm^{-3} at a depth of ∿35 nm) remains unchanged and at a level which is substantially above the boron solid solubility limit at 1150°C (∿2-3 x 10^{20} cm^{-3})[9]. In addition, the boron profile indicates a segregation of boron to the thin (5-10 nm) surface oxide that forms during RTA in an oxidizing atmosphere. Examination of the surface oxide by XHRTEM revealed the presence of small randomly-oriented crystallites (∿5 nm in diameter) with a lattice fringe spacing of 0.205 ± 0.015 nm corresponding to the {111} spacing of B_2O_3.

Samples pre-amorphized with Ge^+ instead of Si^+ contained a higher density of fine clusters and a much lower density of stacking faults (see Table 1). The fine clusters imaged in Fig. 3 are peaked at a depth of ∿25 nm. Frank loops (Burgers vector, $\vec{b} = a/3 \langle 111 \rangle$) resulting from the condensation of excess interstitials created during implantation[10] are also visible at a depth of ∿400 nm. The SIMS profiles

in Fig. 4 indicate that the flourine profile has a peak at $\sim$25 nm below the surface with a peak concentration of $\sim 10^{21}$ cm^{-3}. In addition, after RTA in the temperature range 950-1150°C, the samples pre-amorphized with Ge^+ show a more pronounced in-diffusion of boron as compared with samples pre-amorphized with Si^+. As shown in Fig. 4, RTA at 1100°C for 10 seconds is sufficient to reduce the peak boron concentration to a level below the solid solubility limit at 1100°C.

The strong correlation between high concentrations of flourine ($>10^{19} cm^{-3}$) and the presence of fine clusters suggests that the clusters are flourine-related. This relationship was conclusively established by the fact that implantation of flourine alone into amorphized substrates was found to result in a band of fine clusters whereas implantation of boron alone yielded an essentially defect-free surface region. The inset XHRTEM image of a fine cluster [Fig. 3] indicates that the fine clusters cannot be characterized by a displacement vector but rather that the fine clusters may be silicon-vacancy clusters occupied by flourine.

The combination of the TEM images and the SIMS data show that the stacking faults are present in regions which contain both boron in concentrations above the solid solubility limit and flourine. Implantation of boron alone into pre-amorphized substrates, even at doses as high as 1×10^{16} cm^{-2}, was observed to result in fault-free surface regions after RTA. This result suggests that the flourine and the excess boron may interact to form stable clusters which are accommodated structurally by the cores of Shockley partial dislocations nucleated at the advancing amorphous-crystalline interface.

Finally, it is interesting to note that the peak flourine concentration after RTA varies with the density of "hairpin" dislocations. These hairpins[7,8,11] have a characteristic "V" shape with the vertex originating near the original amorphous-crystalline interface and the arms extending to the surface. For example, samples pre-amorphized with Si^+, implanted with BF_2^+ at RT, and annealed at 1150°C have a peak flourine concentration of $\sim 6 \times 10^{19}$ cm^{-3} and a hairpin density of $\sim 2 \times 10^8$ cm^{-2}, whereas, for samples implanted with BF_2^+ at LNT, the peak flourine concentration is $\sim 5 \times 10^{20}$ cm^{-3} and the hairpin density is $<10^7$ cm^{-2}. Similarly, samples pre-amorphized with Ge^+ have hairpin densities of $<10^7$ cm^{-2} and contain high peak concentrations of flourine (e.g. $\sim 10^{21}$ cm^{-3} for RTA at 1100°C). This correlation between the density of hairpins and the flourine concentration indicates that the flourine may be out-diffusing by pipe diffusion via the arms of the hairpin dislocations. In-diffusion of boron appears to be affected somewhat by the presence of hairpins. In addition, boron in-diffusion is significantly enhanced by the presence of germanium. This effect may be related to the fact that substitutional Ge and B create strain fields of opposite sign. Thus, in-diffusion of boron may serve to relieve stresses in the Ge^+-implanted samples.

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TABLE I. Defect and impurity densities following BF_2^+ implantation at RT and RTA in the temperature range 950-1150°C for 10 seconds.

Pre-amorph. ion and temp.	Stacking Fault density [cm^{-2}]	Cluster density [cm^{-2}]	[F] at peak [cm^{-3}]	[B] at peak [cm^{-3}]
Si^+ (LNT)	$1x10^9$-$5x10^{10}$	$<1x10^{11}$	$6x10^{19}$-$1x10^{20}$	$5x10^{20}$
Ge^+ (RT)	$<1x10^8$	$1x10^{12}$	$1x10^{21}$	$1x10^{20}$

Figure Captions

Fig. 1. High-resolution XTEM micrograph of surface region after RTA at 1150 °C of Si^+-amorphized and BF_2^+-implanted silicon. Distribution of fine clusters centered at depth of ∿20 nm and stacking faults are visible.

Fig. 2. Flourine and boron SIMS profiles from sample imaged in Fig. 1. Note flourine peak and boron segregation to surface during RTA.

Fig. 3. Bright-field ($\vec{g}$ = 220) XTEM micrograph of surface region after RTA at 1100 °C of Ge^+-amorphized and BF_2^+-implanted silicon. Distribution of fine clusters is centered at ∿25 nm below oxide (dark-band)-silicon interface. Interstitial loops are visible at ∿400 nm below surface. Inset XHRTEM micrograph shows fine cluster at a depth of 14.5 nm.

Fig. 4. Flourine and boron SIMS profiles from sample imaged in Fig. 3. Note flourine peak and pronounced in-diffusion and surface segregation of boron.

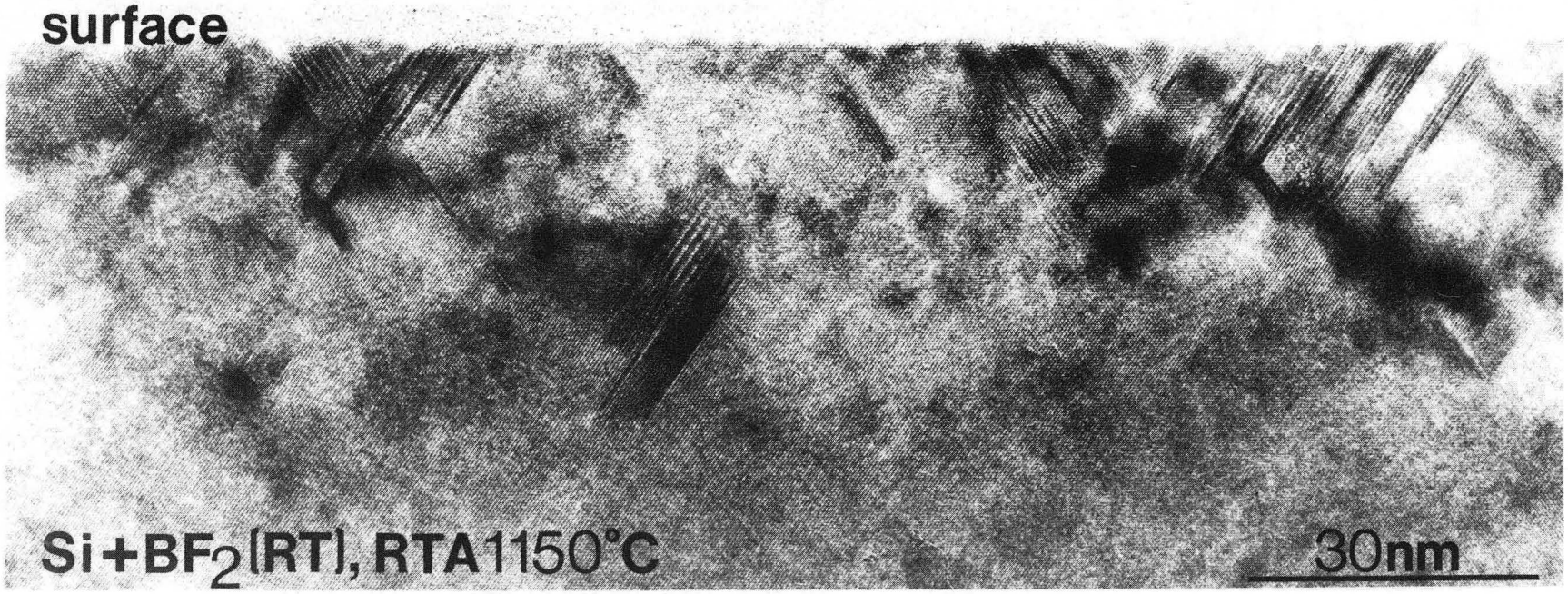

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Fig. 1

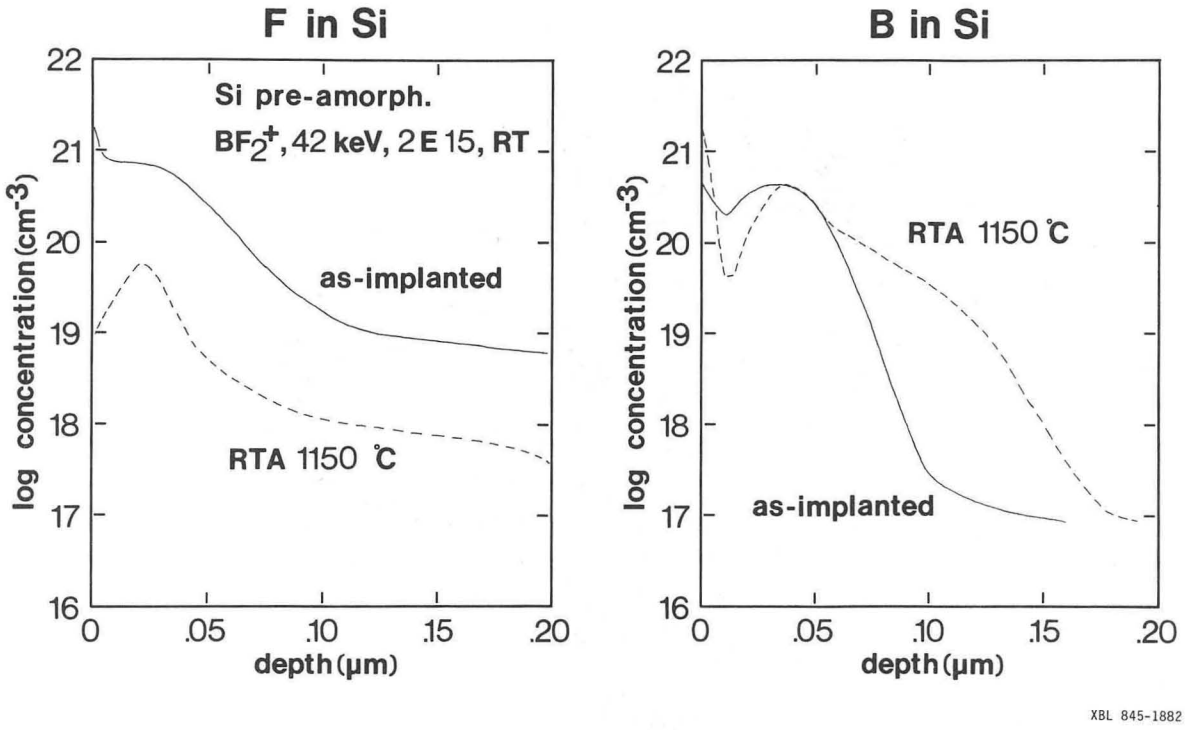
F in Si
Si pre-amorph.
BF2+, 42 keV, 2 E 15, RT
as-implanted
RTA 1150 °C
log concentration (cm-3)
depth (μm)
B in Si
RTA 1150 °C
as-implanted
log concentration (cm-3)
depth (μm)
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Fig. 2

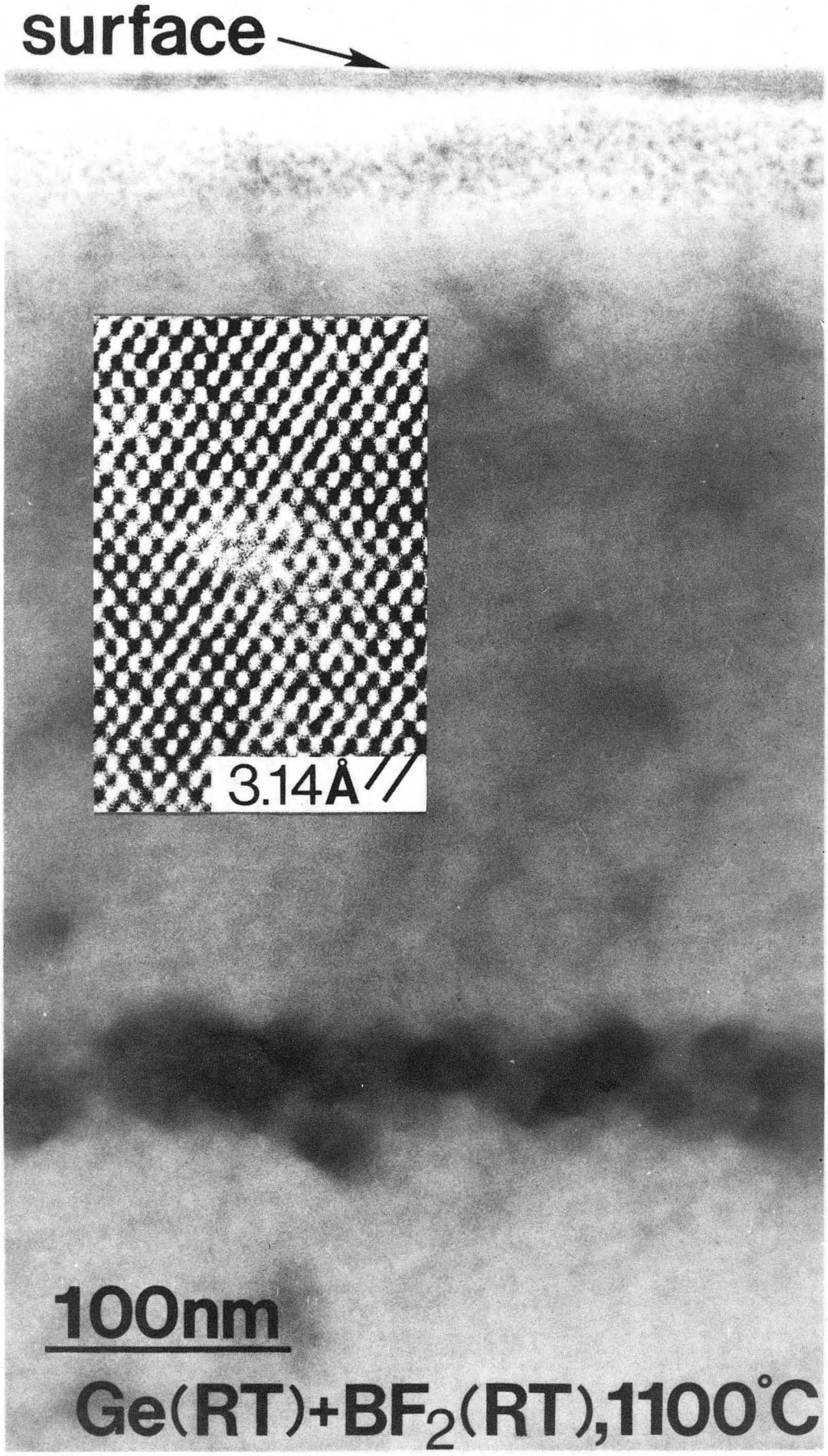

Fig. 3

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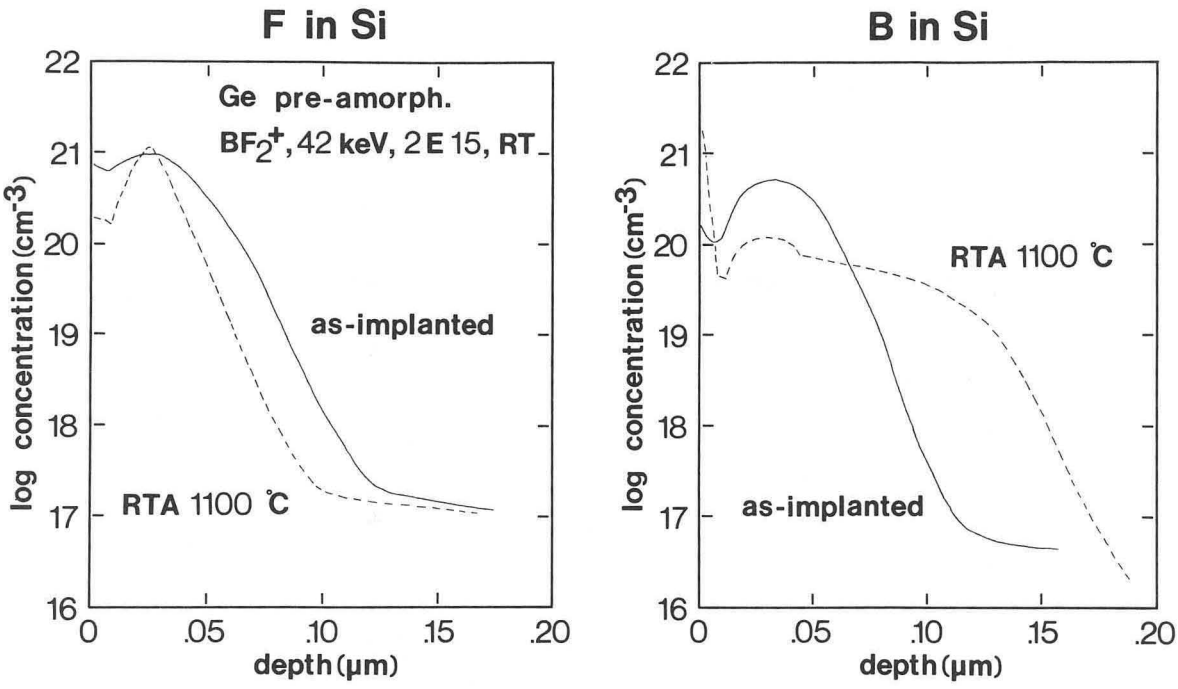

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Fig. 4

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