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ION BEAM ANNEALING OF Ga-IMPLANTED Si

S. P. Withrow, O. W. Holland, and S. J. Pennycook

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ION BEAM ANNEALING OF Ga-IMPLANTED Si

S. P. Withrow, O. W. Holland, and S. J. Pennycook
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831 USA

Abstract

Rutherford backscattering/ion channeling and transmission electron microscopy have been used to investigate regrowth effects which occur during high-energy ion bombardment of amorphous silicon layers implanted with 1×10^{16} Ga/cm^2. At both 300 and 400°C the Si lattice initially regrows epitaxially. However, at this high dopant level, Ga is segregated at the crystalline-amorphous interface and eventually disrupts epitaxy. Transmission electron microscopy has been used to characterize the lattice morphology and monitor movement of the Ga. The results are compared with thermal annealing effects in Ga-implanted Si samples.

I. Introduction

Ion-induced damage in Si at high fluences normally results in the formation of a continuous amorphous layer at the surface which extends through the implanted ion distribution. Recrystallization of this amorphous layer can occur by solid-phase epitaxial growth (SPEG) onto the single-crystal substrate. Thermally activated growth is characterized by a single activation energy (~2.7 eV) over an extended temperature range from 450 to 1360°C.[1,2] Because of the small activation energy, amorphous layers can be recrystallized with reasonable growth velocities at temperatures as low as 550°C. The SPEG mechanism has been shown to lead to essentially defect-free annealing of the amorphous layer, with good electrical activation of dopant in the recrystallized volume.[3] Furthermore, solute trapping at the growth interface can produce highly supersaturated, substitutional solid solutions.[4,5]

A unique phenomena during SPEG has been observed for Si implanted with high concentrations of low melting point impurities (such as In, Ga, and

Bi).[4,6] Significant redistribution of the dopant occurs due to interfacial transport at the growth interface, which can disrupt normal SPEG and ultimately lead to an amorphous-to-polycrystalline (a-p) transformation. This interfacial transport of dopant has been attributed to the motion of liquid impurity precipitates which form in the a-phase and are collected by the growth interface.[4,7] The formation of these precipitates ahead of the advancing interface has been directly observed by electron microscopy.[8] The liquid droplets are envisioned to move as a result of Si dissolving into the liquid at the amorphous-liquid boundary, and precipitating at the crystalline-liquid boundary. Free-energy constraints on the total surface energy thermodynamically favor the liquid droplets remaining in contact with the growth interface.[7,8] It should be noted that this mechanism is substantially different from impurity segregation phenomena which normally occur at a phase boundary.

There is, however, some controversy in regard to the mechanism for polysilicon nucleation and growth. It has been proposed that polysilicon regrowth originates at the amorphous-crystalline (a-c) boundary during SPEG as a result of an interfacial instability[4] since it was observed that the interface becomes progressively less planar as the quantity of transported dopant increases. At a critical impurity concentration, planar a-c interfacial growth cannot be sustained and further crystallizing occurs by polycrystalline growth originating at the interface. Nygren, however, proposed that SPEG and polycrystalline nucleation/growth were competing processes that depend on temperature and impurity concentration.[9] In this model, the initiation of polysilicon growth is envisioned to occur well ahead of the a-c interface either by explosive crystallization or as a result of a-Si dissolving into molten

impurity precipitates on one side and crystallizing at the other due to a difference in Si solubility in equilibrium with a- and c-phases. This has been shown to happen under certain conditions. In actuality, the models are not so different if the melt-mediated growth proposed by Nygren is considered to originate from the a-c interface. This is not unreasonable since most of the impurity droplets are located at the interface prior to polysilicon growth, and their presence inhibits normal SPEG growth, allowing sufficient time for polynucleation.

Recently, it has been shown that SPEG kinetics can be enhanced significantly when the growth interface is irradiated with high-energy ions.[10–13] The apparent activation energy for SPEG in Si via this ion beam annealing (IBA) is reduced to 0.33 eV,[14] thus allowing SPEG of amorphous layers to occur at much lower temperatures. This allows phenomena such as dopant redistribution, solute trapping, and supersaturated alloying, etc., associated with SPEG, to be studied at lower temperatures. In particular, it is of interest to extend the study of SPEG in Si implanted with low melting point impurities to determine the behavior at lower growth temperatures. Low-temperature growth offers the possibility of affecting solute trapping at the interface, leading to higher impurity saturation in the regrown Si. Furthermore, it provides additional flexibility in studying the novel crystallization mechanism during the a-p transition.

II. Experimental Procedure

Silicon (100) crystals were implanted at liquid nitrogen temperature with 180-keV ^{69}Ga ions up to a dose of $1 \times 10^{16}/cm^2$. Regrowth of the silicon crystal lattice was induced by irradiation of the implanted sample using 370-keV

^{28}Si ions at a dose rate of 4×10^{12} ions/cm^2 s while the sample was held at temperatures ranging from 300 to 400°C. Part of the sample was masked during irradiation so that effects due only to macroscopic sample heating could be experimentally determined.

Damage to the Si lattice and the distribution and substitutionality of the implanted Ga were measured in the as-implanted and regrown samples using Rutherford backscattering/ion channeling of 2.0-MeV He^+ ions. Spectra were obtained with the incident beam aligned along the <110> axial direction or by rotating the sample in the beam to approximate scattering from an amorphous matrix. Lattice morphology and Ga precipitation in the sample were studied using cross-section transmission electron microscopy.

III. Results and Discussion

Backscattering yield spectra following ion-assisted growth at 300°C of a Si sample implanted with 180-keV, 1×10^{16} Ga/cm^2 are shown in Fig. 1. Following the Ga implantation, an amorphous layer is present at the surface which extends to a depth of ~0.32 μ (measured at the half height of the low-energy edge of the amorphous Si layer). The effect of different fluences of 370-keV Si ions on the layer is clearly seen. Irradiation with 1×10^{16} Si/cm^2 stimulates regrowth to within 0.23 μ of the surface. At this depth the a-c interface is just below the Ga implant (see Fig. 2). The slope in the scattering yield in the vicinity of the a-c interface indicates that the transition region between the amorphous and crystalline phases has remained sharp. During Si ion irradiation the substrate lattice shows damage at the end of range of the high-energy ions. Irradiation with a higher Si fluence causes a greater amount of regrowth of the a-layer. After 3×10^{16} Si/cm^2, the layer has

regrown through much of the as-implanted Ga distribution, approaching within 0.08 μ of the Si surface. The a-c interface is still seen to be reasonably sharp. It should be noted that the growth rate per unit dose is lower at this higher dose than for the $1 \times 10^{16}/cm^2$ fluence. Presumably this is because the regrowth penetrates the Ga distribution and is affected by the high impurity concentration. A similar effect has been observed for thermally activated SPEG;[2] this result is, however, in contrast to results obtained for B- and P-doped Si which were found to enhance the growth rate.[14] After irradiation with 5×10^{16} Si/cm^2 it is clear that ion-assisted growth of the amorphous layer has been interrupted. Little or no additional growth appears to have occurred between 3 and $5 \times 10^{16}/cm^2$. However, the change in slope in the scattering yield in the transition region indicates a much broader and poorly defined interfacial region.

It is of interest to correlate the behavior of the Ga impurity with the regrowth behavior of the Si substrate described above. Random and <110>-aligned Rutherford backscattering (RBS) spectra from the Ga-region for conditions corresponding to those in Fig. 1 are shown in Figs. 2 and 3. Essentially no redistribution of Ga occurs until the a-c growth interface penetrates the Ga profile. This can be seen in Fig. 2 by comparing the scattering yield from Ga in an as-implanted sample with one after IBA with 1×10^{16} Si/cm^2. After IBA with 3×10^{16} Si/cm^2, however, the random and aligned yields in this figure clearly show significant redistribution of the Ga toward the surface. A large Ga peak is seen at a depth of ~0.07 μ, which is coincident with the a-c interfacial position for this bombardment dose, but no significant movement of Ga to the surface has occurred. This interfacial transport of Ga is similar to that which occurs during thermally activated growth.[4] The maximum total

Ga concentration in the regrown layer at a depth of 0.15 μ is $5 \times 10^{20}/cm^3$. The substitutional fraction of Ga at this depth was calculated[15] from the aligned spectrum to be ~70%. The total Ga concentration trapped in the regrown Si is more than twice that reported for thermally activated growth.[4] The substitutional amount is also larger by about ~40%. The scattering yield from Ga after IBA with 5×10^{16} Si/cm^2 is shown in Fig. 3. Ga is seen to have moved to the surface, although there is still a Ga peak at 0.07 μ similar to that seen in Fig. 2. Comparing the Ga scattering yield in Fig. 2 to that in Fig. 3 shows that the movement of Ga toward the surface apparently occurs after a breakdown of the epitaxial regrowth of the Si lattice. Amorphous-to-crystalline interfacial growth appears to occur to about 0.07 μ from the surface, where a Ga peak in observed, before stopping. The peak height in Fig. 3 at 0.07 μ is reduced over that in Fig. 2, indicating that Ga originally at the interface is transported to the surface after the interfacial growth was interrupted. A comparison of the total Ga yield in the as-implanted spectrum and in the random spectra following IBA indicates no Ga has been lost from the sample. In addition, no change in the as-implanted Ga distribution as a result of heating to 300°C was observed in RBS spectra. The sample was held at 300°C ~40 minutes per $1 \times 10^{16}/cm^2$ Si dose.

Transmission electron microscopy (TEM) of Si samples ion beam annealed with 5×10^{16} Si/cm^2 at 300°C showed that an a-p transition has occurred in the near-surface region down to 0.07, after SPEG was observed to stop. The redistribution of the Ga to the surface correlates with this polysilicon formation similar to observations for thermally activated SPEG.[4]

Figure 4 shows a cross-sectional transmission electron micrograph of the Si crystal after irradiation with 3×10^{16} Si/cm^2. Several interesting features

are immediately obvious. While there is extensive damage in the region near the end of range of the 370-keV Si ions, no defects are seen in the regrown region. Somewhat more surprising, no Ga precipitates are observed in this region. As indicated above, a significant fraction of the Ga in this region is not in substitutional sites. Either the nonsubstitutional Ga is located in very small precipitates (<10 Å radius), or it is interstitially dissolved. This behavior is quite different from that reported by Narayan et al.[4] who observed large precipitates in thermally regrown layers which had been similarly implanted. Also, the interfacial structure is of interest. A continuous amorphous layer is seen ahead of the interface. However, nucleation of polycrystalline Si has clearly occurred in the interfacial region where misoriented polysilicon grains are observed. Hence, polysilicon growth originates from the a-c interface and SPEG becomes inhibited. This polysilicon growth results in significant redistribution of the Ga which was originally at the a-c interface.

Ion-assisted growth at 400°C in Ga-implanted Si has also been studied. At this temperature, interfacial SPEG stops at ~0.12 μ from the surface, indicating that the interfacial breakdown is accelerated at higher temperatures. This is in contrast to the behavior with thermally activated SPEG. In the latter case, the activation energy for SPEG (2.7 eV) is greater than that for the a-p transition (~1.5 eV), so higher tem-peratures would favor SPEG.

Significant redistribution of the Ga occurs when the regrowing interface moves through the implanted region during 400°C ion beam annealing. The total concentration of Ga remaining in the regrown Si is lower at 400°C by more than a factor of 2 from that observed at 300°C. As at the lower temperature, Ga segregates at the interface. It was shown for the

300°C anneal that the polysilicon growth originates from an instability at the SPEG interface, presumably due to the build up of Ga. The critical concentration of Ga needed to produce the a-p instability, as measured in Fig. 3, is $7 \times 10^{20}/cm^3$. This is the same maximum concentration seen in spectra obtained at 400°C in which the measurement of Ga at the surface suggests that the a-p transition has occurred. This critical concentration of Ga at the interface occurs deeper in the sample for 400°C IBA since a higher fraction of the Ga encountered by the SPEG interface is transported at this temperature. The processes favoring interfacial transport versus trapping in the regrown Si are not understood. Very little Ga goes substitutional in the Si for IBA at 400°, in contrast to the lower temperature results.

IV. Conclusions

Solid-phase epitaxial growth of an amorphous, highly Ga-doped Si layer occurs during bombardment with high-energy Si ions. Defect-free growth, without Ga precipitates, precedes until the onset of an amorphous-to-polycrystalline transition at the interface. This transition occurs when the concentration of Ga transported at the interface as the Si regrows reaches a critical concentration and additional ion bombardment leads to redistribution of Ga through the polycrystalline region to the sample surface. The amount of Ga trapped in the regrown layer is somewhat greater than reported for thermal annealing and is dependent on the temperature of the IBA. Mechanisms favoring transport of Ga or trapping in the regrown Si are not known.

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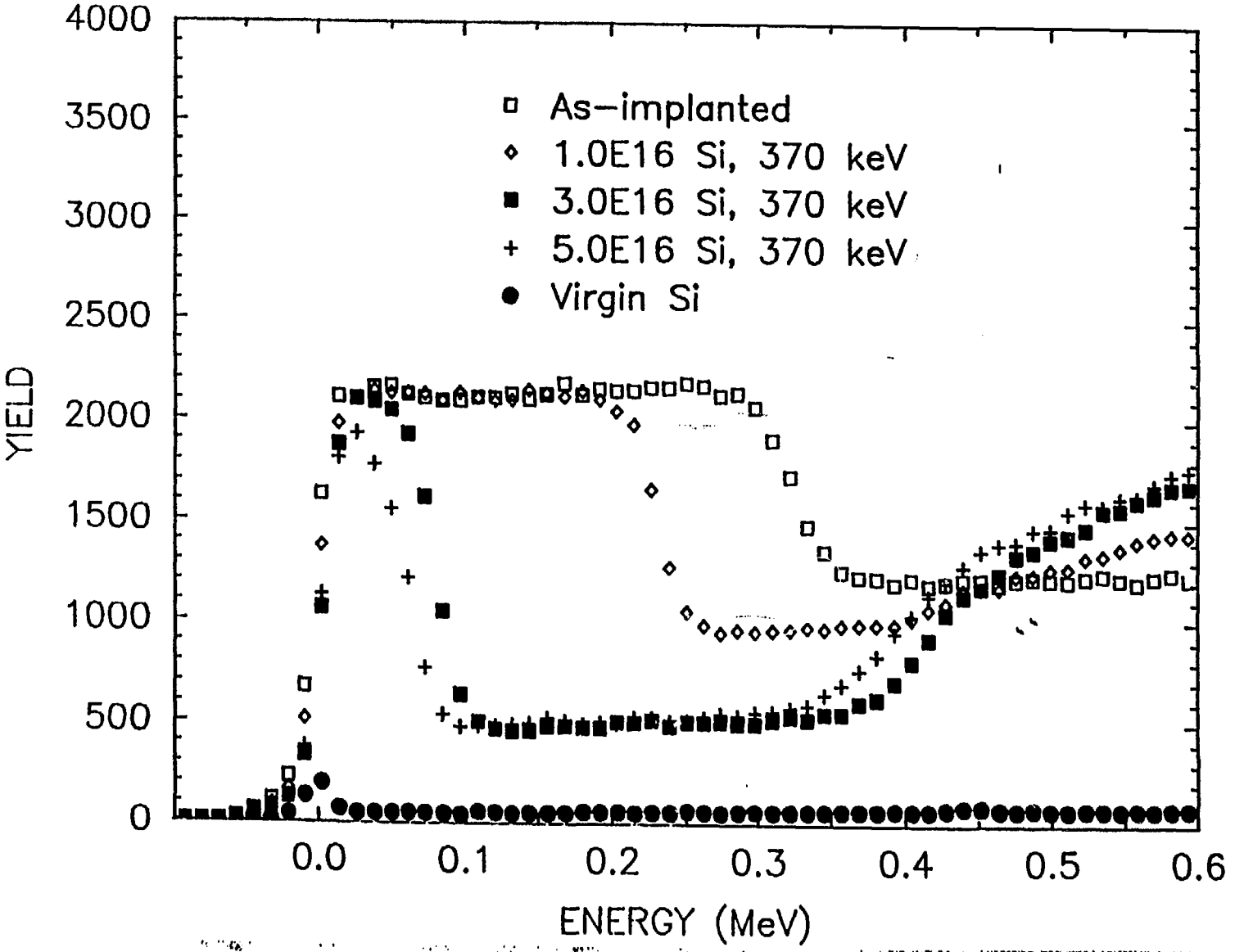
Figure Captions

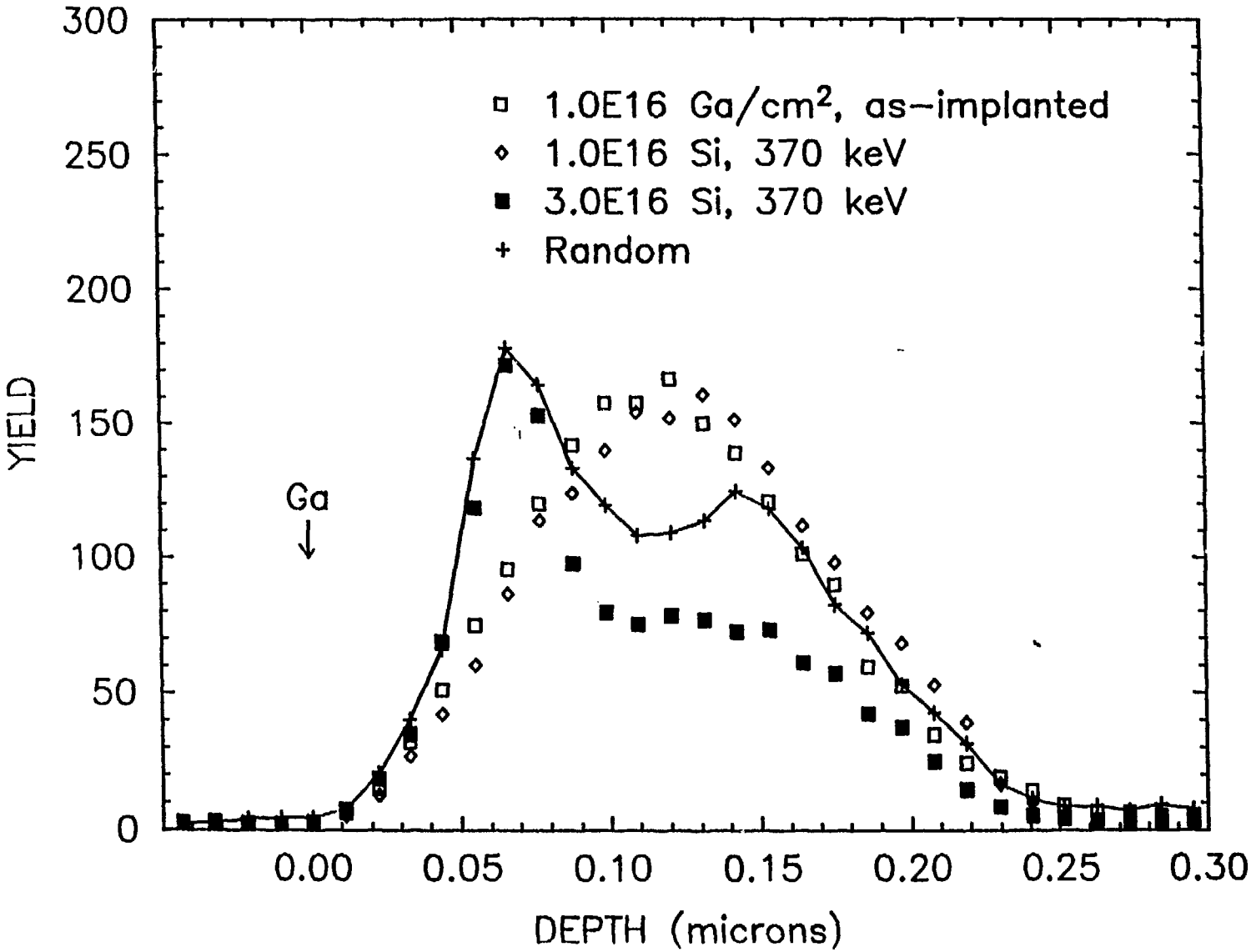
1. RBS spectra following IBA at 300°C of a Si substrate implanted with 180-keV, 1×10^{16} Ga/cm^2. The Si region is shown for <110> channeling spectra from an as-implanted sample and for different high-energy Si ion fluences.

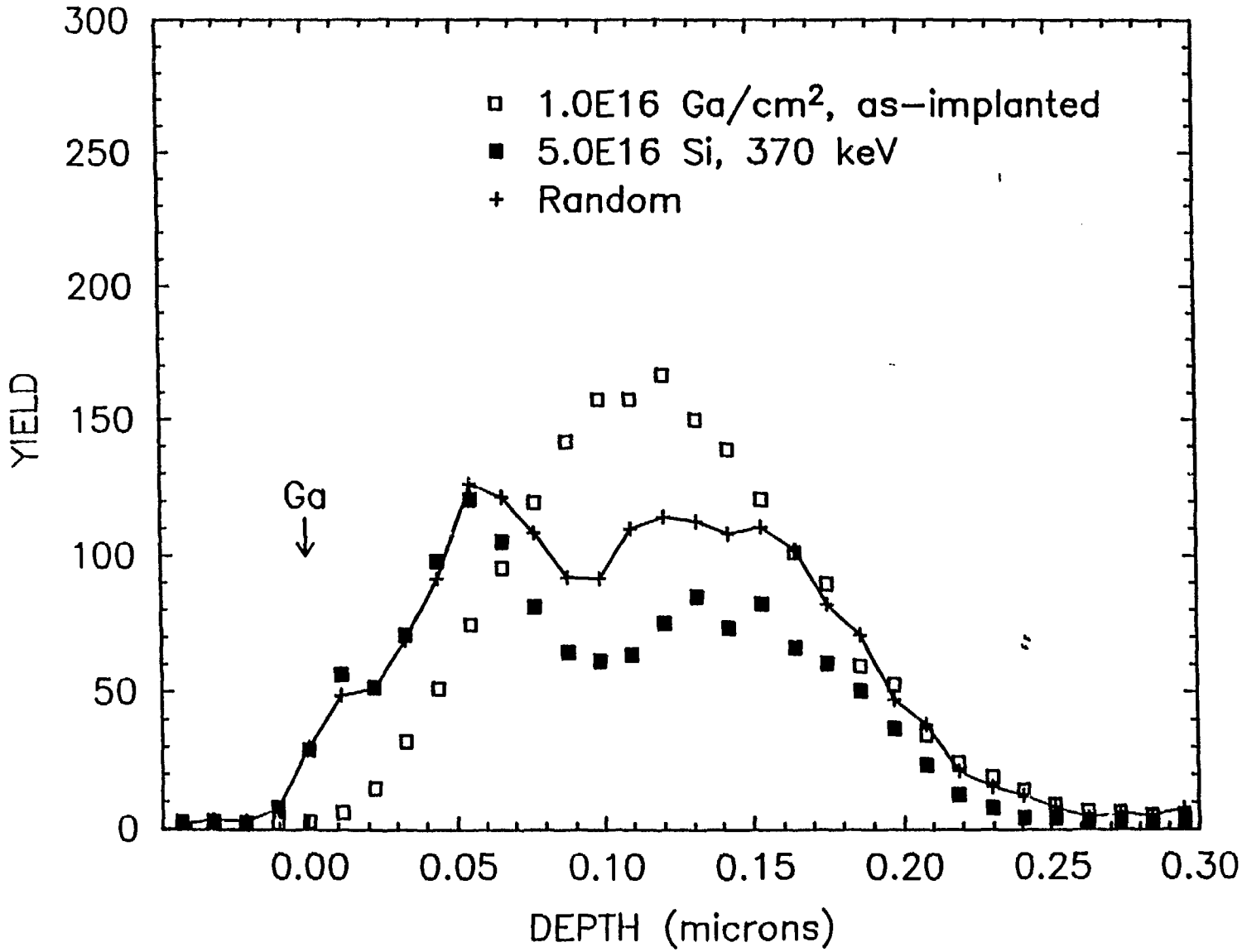
2. Comparison of RBS <110> channeling spectra from the Ga region of spectra given in Fig. 1 from an as-implanted sample and for samples ion beam annealed with Si fluences of 1 and 3×10^{16}/cm^2. A random spectrum following the higher annealing fluence is also shown.

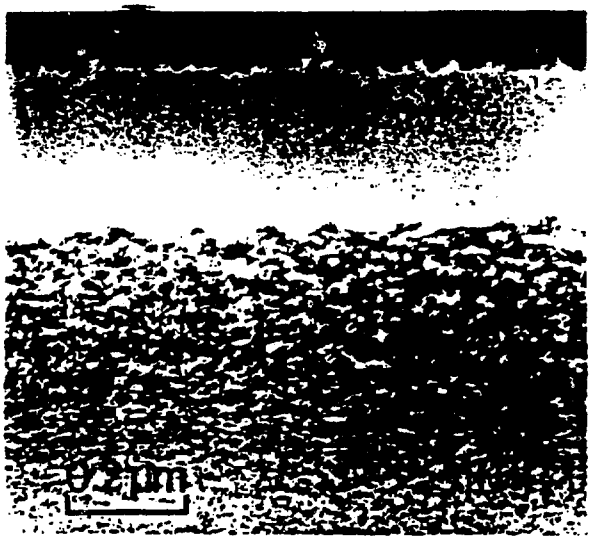
3. Comparison of random and <110>-channeling RBS spectra from the Ga region of a sample implanted with 1×10^{16} Ga/cm^2 and then ion beam annealed at 300°C with 370-keV Si ion at a fluence of 5×10^{16}/cm^2.

4. Cross section transmission electron micrograph of a Si sample implanted with 180-keV, 1×10^{16} Ga/cm^2, followed by IBA at 300°C with 370-keV Si ions at a fluence of 3×10^{16}/cm^2.


As–implanted
1.0E16 Si, 370 keV
3.0E16 Si, 370 keV
5.0E16 Si, 370 keV
Virgin Si
YIELD
ENERGY (MeV)
0
500
1000
1500
2000
2500
3000
3500
4000
0.0
0.1
0.2
0.3
0.4
0.5
0.6


1.0E16 Ga/cm², as-implanted
1.0E16 Si, 370 keV
3.0E16 Si, 370 keV
Random
Ga
YIELD
DEPTH (microns)
300
250
200
150
100
50
0
0.00
0.05
0.10
0.15
0.20
0.25
0.30


1.0E16 Ga/cm², as–implanted
5.0E16 Si, 370 keV
Random
Ga
YIELD
DEPTH (microns)
300
250
200
150
100
50
0
0.00
0.05
0.10
0.15
0.20
0.25
0.30


0.2μm