

CONF 891119--41

To be published in the Proceedings of the Materials Research Society Symposium on "Beam-Solid Interactions: Physical Phenomena," held in Boston, Massachusetts, November 27 - December 1, 1989.

CONF-891119--41

DE90 004297

ION BEAM ANNEALING OF Si CO-IMPLANTED WITH Ga AND As

S. P. Withrow, O. W. Holland, and S. J. Pennycook
Solid State Division
Oak Ridge National Laboratory

and

J. Pankove and A. Mascarenhas
Solar Energy Research Institute

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
under
Contract No. DE-AC05-84OR21400
for the
US DEPARTMENT OF ENERGY
OAK RIDGE, TENNESSEE 37831

November 1989

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER *zh*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ION BEAM ANNEALING OF Si CO-IMPLANTED WITH Ga and As

S. P. WITHROW,* O. W. HOLLAND,* S. J. PENNYCOOK,* J. PANKOVE,** and A. MASCARENHAS**

*Oak Ridge National Laboratory, Oak Ridge, TN 37831

**Solar Energy Research Institute, Golden, CO 80401

ABSTRACT

Ion beam annealing of amorphous Si(100) layers formed by co-implantation of overlapping Ga and As distributions is studied. Annealing was done using 750 keV Si⁺ ions with the Si substrate held at 300°C. The samples were characterized using 2.0 and 5.0 MeV He⁺ backscattering/channeling as well as by transmission electron microscopy (TEM). Crystallization of the amorphous Si layer occurs during irradiation via solid-phase-epitaxial growth without impurity precipitation or segregation. Both the Ga and As are nearly substitutional in the Si lattice, even at concentrations in excess of 7 at. % for each species. These results are attributed to compensation effects, most likely through ion pairing of the electrically-attractive dopants.

INTRODUCTION

An ion-implanted amorphous (α -) Si layer on a crystalline Si substrate can be epitaxially regrown by irradiating the interface layer with energetic ions.[1,2] This ion-induced regrowth occurs at Si temperatures lower than is normally achieved using conventional thermal annealing. More interestingly, annealing effects are observed that do not occur thermally. For example, an amorphous Si layer on crystalline Si formed by Ga⁺ implantation regrows under high-energy ion bombardment with more of the Ga incorporated into the lattice than is possible to achieve using thermal annealing at similar dopant concentrations.[2,3] Recently, ion-induced growth of α -Si deposited on a crystalline substrate with a 15 Å silicon oxide was reported; such an oxygen layer prevents regrowth during thermal processing.[1]

In the present work, high-energy Si ion beams were used to regrow Si implanted with overlapping Ga and As distributions. Excellent epitaxial regrowth is observed, even for dopant atomic concentrations as high as 7.5 at. %. Characteristics of both thermal and ion beam annealed (IBA) implanted layers are detailed. It will be shown that the annealing behavior of the co-implanted layers is quite different from layers implanted only with Ga⁺ or As⁺, independent of the annealing technique. The presence of electrically compensating dopants, even at concentrations in excess of solid solubility, is shown to greatly effect dopant behavior during annealing of the α -layers. Differences produced by the annealing techniques are manifest at the highest dopant concentrations which were studied. These differences are detailed and possible explanations for them are given.

EXPERIMENTAL PROCEDURE

Silicon (100) samples were implanted at liquid-nitrogen temperature with ^{69}Ga followed by implantation with ^{75}As ions to produce an amorphous surface layer with overlapping Ga and As distributions. Two dopant concentrations were used. One set of samples was doped with $1 \times 10^{16} \text{ Ga/cm}^2$ at 160 keV followed by an equal dose of As at the same energy. This produces dopant distributions with peak concentrations of approximately 2.75 at. %, [4] and is referred to here as the 2.75% distribution. Silicon was also implanted alternately with $1 \times 10^{16} \text{ /cm}^2$ of Ga and As at energies of 180, 160, and 140 keV to obtain overlapping distributions with a maximum peak concentration of approximately 7.5 at. %. This is referred to as the 7.5% distribution. Regrowth of the α -layers formed by the implantation was induced by irradiation of the implanted sample using ^{28}Si at an ion energy of 750 keV. The sample was held at 300°C during the IBA. Thermally activated regrowth of these α -layers was studied for comparison with the IBA results.

Damage to the Si lattice and the distribution and lattice location of the implanted impurities were determined in as-implanted and annealed samples using Rutherford backscattering/ion channeling. Channeled spectra were acquired with either 2.0 or 5.0 MeV incident beams aligned along the normal $\langle 100 \rangle$ axial direction. Defect morphology in annealed samples was studied using cross-section TEM.

RESULTS AND DISCUSSION

Rutherford backscattering spectra which show the amorphous layer regrowth in a 2.75 at. % sample as a function of ion beam annealing dose are given in Fig. 1. The yield from Si, obtained using 2.0 MeV ^4He backscattered at 153° , is shown in Fig. 1a. As seen in the No IBA spectrum, the amorphous-crystalline (α -c) interface in the Si substrate is at a depth of $\sim 0.3 \mu\text{m}$ after implantation with Ga and As, measured by the half-height of the buried edge of the amorphous Si surface layer. With increasing Si bombardment dose, this interface moves toward the sample surface with essentially no change in the slope of the buried edge indicating that the α -c interface remains planar during regrowth. At the highest Si dose used, $9 \times 10^{16} \text{ Si/cm}^2$, the initially amorphous surface layer has regrown nearly to the substrate surface. The yield in the Si surface peak in the most completely annealed sample is approximately twice that of the virgin, suggesting either surface damage or incomplete lattice annealing. The chi min value [5] for the regrown silicon is 6.5% or about twice the 3.4% value measured from the virgin.

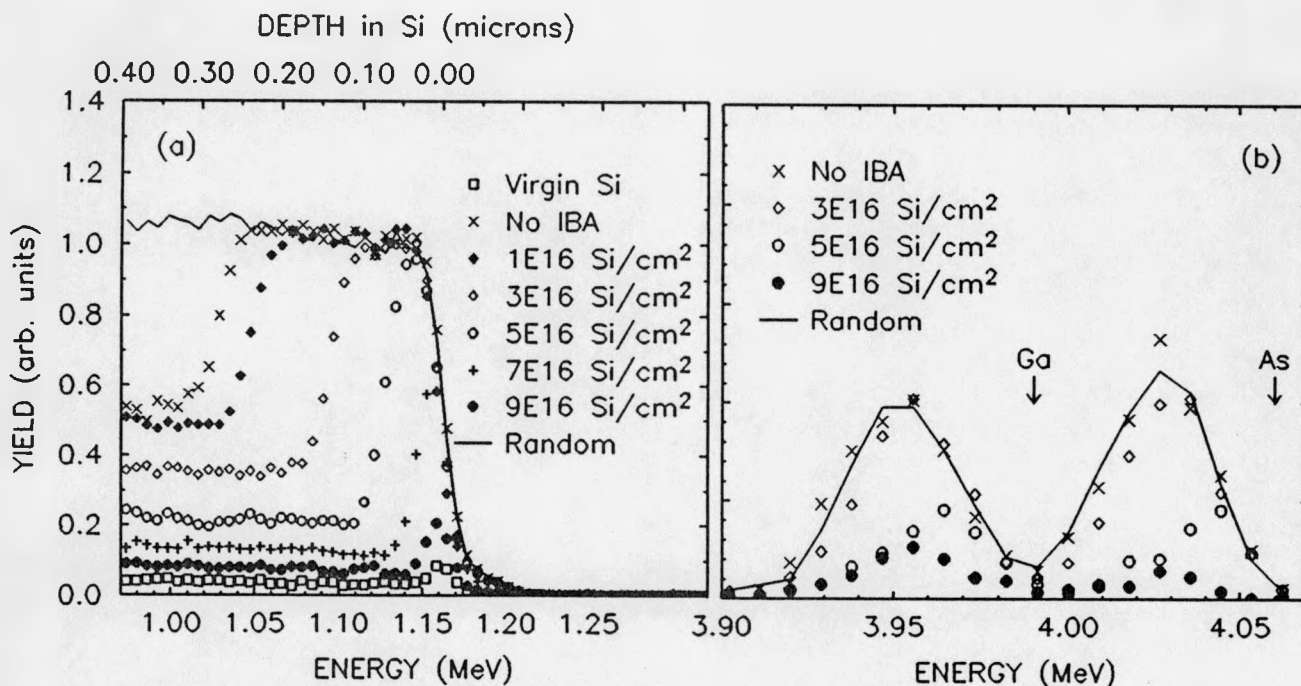


Fig. 1. RBS <100> channeling spectra following IBA at 300°C of a Si substrate implanted with 1×10^{16} Ga/cm² followed by 1×10^{16} As/cm², both at 160 keV. The random spectrum was obtained from a sample annealed with 9×10^{16} Si/cm². (a) Backscattering from Si. (b) Backscattering from Ga and As. The energy at which 5.0 MeV ⁴He backscatters from Ga and As at the surface is marked.

Aligned backscattering yields from the implanted Ga and As are given in Fig. 1b. The spectra were obtained using 5.0 MeV ⁴He channeled along the <100> axis with the detector at 160°C. The use of the higher energy He ions permits the separation of the Ga and As signals. The aligned yield is seen to decrease with increasing Si dose as the α -c interface in the Si lattice moves through the implanted region. The yields after irradiation with 5×10^{16} Si/cm² are peaked to the high energy edge, indicating that the regrowth is incomplete and has not moved completely thru the distributions. It is clear, however, that after a 9×10^{16} Si/cm² irradiation the growth has advanced completely through the implanted region. A comparison of the as-implanted Ga and As distributions with those following IBA at the highest Si dose indicates that no redistribution or loss of either element occurs during annealing. Also, the Ga is 80% substitutional while the As is 96% substitutional.[6] It is not clear whether the lower substitutionality for the Ga indicates that Ga atoms are slightly displaced from the substitutional site, or if some fraction is interstitially dissolved or precipitated. It should be noted that these substitutional fractions represent concentrations which not only greatly exceed the retrograde maximum of these dopants in Si, but also greatly exceed the concentrations of any metastable solid solution which

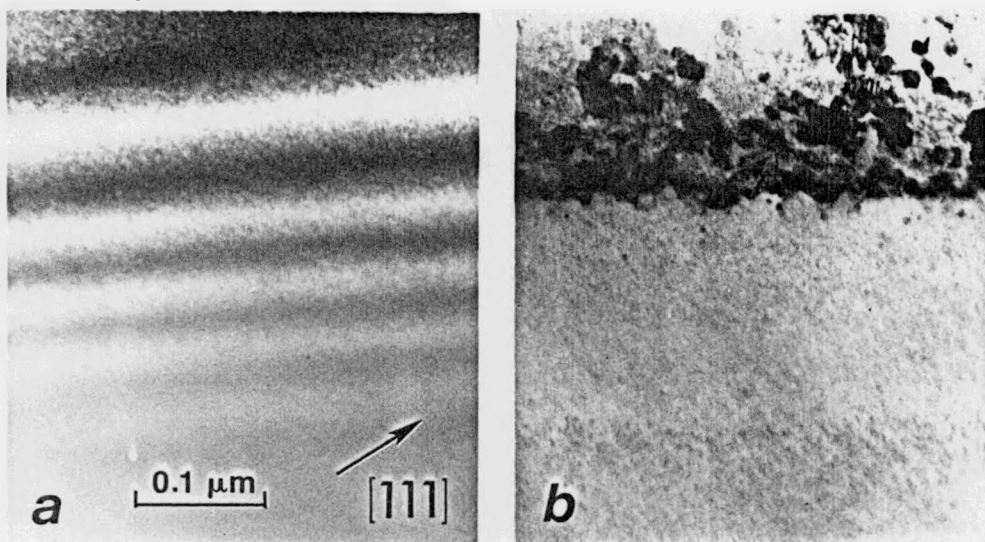


Fig. 2. (a) Cross-section TEM micrograph from the sample in Fig. 1 following beam annealing with 9×10^{16} Si/cm². (b) Micrograph from a sample implanted at 3×10^{16} Ga plus 3×10^{16} As and thermally annealed at 600°C for 1 h.

has been previously formed for Si:Ga. Thermal annealing at 600°C of the 2.75% sample produced similar results (not shown), so clearly the presence of the compensating dopants is responsible for the large solubilities.

A cross-section TEM micrograph from a sample implanted with 1×10^{16} /cm² of both Ga and As and then ion beam annealed with 9×10^{16} Si/cm² is given in Fig. 2a. No defects are visible in the regrown surface region. The micrograph was obtained under dynamical diffraction conditions to be sensitive to the presence of coherent precipitates. However, no precipitates are observed, even though about 20% of the Ga and a small amount of the As are not located on Si lattice sites as seen from the RBS results in Fig. 1b.

Rutherford backscattering/channeling results from a 7.5 at. % distribution sample are given in Figs. 3a and b, respectively, following irradiation with 7×10^{16} Si/cm² at 300°C. As was found for the lower dopant concentration, the Si lattice again regrows epitaxially under ion bombardment. In Fig. 3a the α -c interface is ~ 0.05 μ m from the surface after 7×10^{16} Si/cm². A comparison of the channeled and random spectra in Fig. 3b shows that the Ga and As are incorporated into the lattice as the interface moves through the dopant distributions. Also shown in Fig. 3 are results obtained following a 600°C thermal anneal on a sample implanted to the same high distribution of Ga and As. Regrowth occurs up to a depth at which the α -c interface has just penetrated into the implant distributions. These thermal annealing conditions are sufficient to completely regrow an undoped, 0.3 μ m amorphous Si layer.

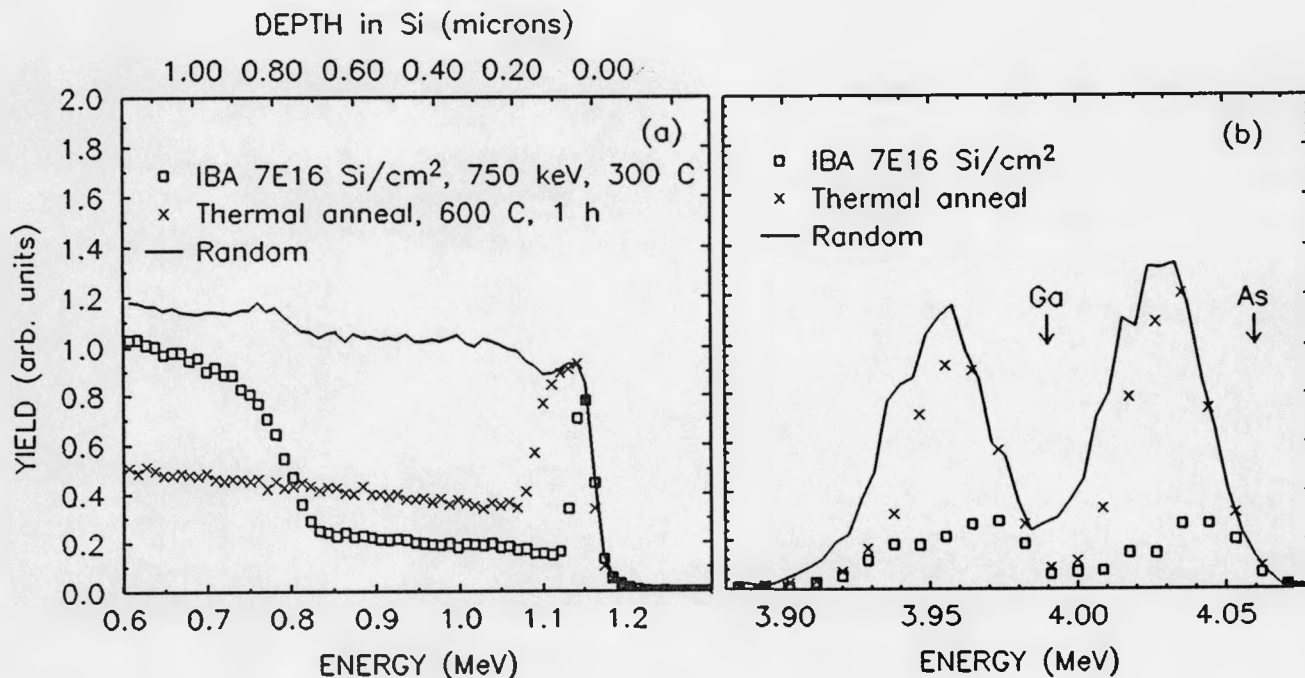


Fig. 3. Comparison of Si ion beam annealing to thermal annealing of a sample implanted with 3×10^{16} Ga plus 3×10^{16} As. (a) Backscattering from Si. (b) Backscattering from Ga and As.

In the present case, however, an amorphous-to-polycrystalline transition has been initiated, as discussed below.

In Fig. 2b is shown a cross-section micrograph from a sample thermally annealed at 600°C for one hour following implantation with the 7.5% distribution of Ga and As. As can be seen, the interface is not planar, and epitaxial regrowth has stopped at 140 nm from the surface where the initiation of polycrystalline growth has occurred.

The mechanisms involved in ion beam annealing of doped Si are not well understood, although it is generally believed that the interaction of the impurities with defects generated by the incident beam must play a significant role. Effects attributed to compensating dopants have been previously observed on the kinetics of ion-induced[7] and thermally-induced[8] regrowth of α -layers. In the present work, annealing effects involving interactions between the implanted Ga and As atoms are likely occurring. Because of the attractive interaction between the opposite ionic charges, ion pairing is to be expected when a sufficient concentration of acceptors and donors is present.[9] Even for the lower,

2.75 at. % distribution here, the separation of the as-implanted Ga and As dopants is on average no more than next next nearest neighbors.

Thermally-activated recrystallization of Ga-only implanted Si results in the formation of precipitates ahead of the growing α -c interface.[3,10] This occurs when the Ga concentration in the α -layer exceeds 1.2 at. %. The Ga precipitates, which are molten at the regrowth temperature ($>450^{\circ}\text{C}$), have been shown to be transported with the growth interface leading to a marked redistribution of the Ga. Also, if sufficient Ga is gettered at the growth interface, it can interrupt the epitaxial growth and lead to the formation of polycrystal. The presence of As in the experiments here, which can lead to ion pairing with Ga atoms, is thought to be a competing process with precipitation. Such competition between ion pairing and precipitation has been observed for the Sb/B system, and increased solubility was observed when both species were present at similar concentrations.[11] Therefore, ion pairs of Ga/As are thought to form in the amorphous layer ahead of the growth interface. These pairs immobilize the Ga and prevent precipitation of the excess Ga. In the 2.75% sample, this competition apparently results in insufficient precipitation during either ion-induced or thermally-activated growth to adversely affect the epitaxy so that both annealing techniques produce a 'defect-free' layer supersaturated with As and Ga trapped onto (or near) substitutional sites. The competition between ion pairing and precipitation is expected to depend on the annealing temperature and the impurity concentration. Therefore, it is not surprising that differences between ion-induced epitaxy, and solely thermal growth should appear as the implanted concentrations increase. In the 7.5% sample, thermal annealing resulted in an amorphous-to-polycrystalline transformation suggesting the possibility that second-phase particles are present in the α -layer which interfere with epitaxial growth.

CONCLUSIONS

High-energy ion beam bombardment at 300°C of an amorphous Si layer incorporating overlapping distribution of Ga and As results in epitaxial regrowth of the Si onto the crystalline Si substrate and substitutional incorporation of both species. No significant redistribution of the dopants occurs. The effect has been observed for initial concentrations of Ga and As greater than 7 at. % each. In contrast, an amorphous-to-polycrystalline transition is initiated when Si implanted with Ga and As to 7.5 at. % is thermally annealed. These results also differ markedly from effects of beam irradiation of Si implanted only with Ga, indicating that the presence of the As influences the Ga behavior. Additional work is being undertaken to study the thermal stability of beam-annealed layers and to determine the nature of the interaction between the dopants.

ACKNOWLEDGMENTS

Researchers from Oak Ridge National Laboratory gratefully acknowledge support by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES

1. See, for example, F. Priolo, C. Spinnella, A. La Ferla, and E. Rimini, *Journal of Applied Surface Science*, in press, and references therein.
2. S. P. Withrow, O. W. Holland, and S. J. Pennycook, *Journal of Applied Surface Science*, in press.
3. J. Narayan, O. W. Holland, and B. R. Appleton, *J. Vac. Sci. and Technol. B* **1**, 871 (1989).
4. A. J. Armini and S. N. Bunker, *Mater. Sci. and Eng.* **A115**, (1989), p. 67; Implant Sciences, Corp., Danvers, MA, Ion Implant Profile Code.
5. Chi min is the ratio of RBS yield just behind the surface peak in the channeled spectrum to the yield in the random spectrum.
6. S. T. Picraux, p. 229 in: New Uses of Ion Accelerators, ed. by J. Ziegler (Plenum Press, New York, 1975).
7. F. Priolo, A. La Ferla, and E. Rimini, *J. Mater. Res.* **3**, 1212 (1988).
8. See, for example, A. Lietoila, A. Wakita, T. W. Sigmon, and J. F. Gibbons, *J. Appl. Phys.* **53**, 4399 (1982); I. Suni, G. Göltz, M. G. Grunaldi, and M-A. Nicolet, *Appl. Phys. Lett.* **40**, 269 (1982).
9. H. Reiss, C. S. Fuller, and F. J. Morin, *Bell Syst. Tech. J.* **38**, 535 (1956).
10. E. Nygren, J. S. Williams, A. Pogany, R. G. Elliman, G. L. Olson and J. C. McCallum, *Mat. Res. Soc. Symp. Proc.* **74**, (1987) 307.
11. R. J. Culbertson and S. J. Pennycook, in Materials Research Society Symposium on Fundamentals of Beam-Solid Interactions and Transient Thermal Processing, Boston, 1987.