Lawrence Berkeley National Laboratory

Recent Work

Title

A THREE-STAGE MODEL FOR THE DEVELOPMENT OF SECONDARY DEFECTS IN ION-IMPLANTED SILICON

Permalink

<https://escholarship.org/uc/item/22j38954>

Author

Seshan, K.

Publication Date

1978

Submitted to Radiation Effects

UC-25
LBL-5410
Preprint e.1

A THREE-STAGE MODEL FOR THE DEVELOPMENT OF
SECONDARY DEFECTS IN ION-IMPLANTED SILICON

K. Seshan and J. Washburn

January 1978

RECEIVED
LAWRENCE
BERKELEY LABORATORY

FEB 14 1978

LIBRARY AND
DOCUMENTS SECTION

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-5410
e.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its 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, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

-iii-

A THREE-STAGE MODEL FOR THE DEVELOPMENT OF SECONDARY
DEFECTS IN ION-IMPLANTED SILICON*

K. Seshan** and J. Washburn

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory
and
Department of Materials Science and Engineering
University of California
Berkeley, California 94720

Abstract

A three-stage model to explain how the secondary defects consisting of interstitial dislocation loops evolve from the primary defects in ion-implanted silicon is presented. Crystals implanted to an ion dose below D_c (critical dose which forms a continuously damaged layer), such that the primary damage clusters do not overlap, were studied. The model suggests that the Frenkel pairs formed by ion impact produce submicroscopic clusters of vacancies and interstitials which are stable up to about 900°K. Upon heating to a higher temperature the smallest interstitial clusters emit mobile interstitials and/or the vacancy clusters emit mobile vacancies. The larger clusters grow and convert to dislocation loops. Vacancy loops shrink and disappear; interstitial loops grow because of the excess of interstitials. The total area per unit area of interstitial loops remaining after a high temperature anneal above 1100°K corresponds to the number per unit area of the implanted atoms. The implication of this is that for vacuum and dry

*This work was supported by the U. S. Department of Energy through the Molecular and Materials Research Division of the Lawrence Berkeley Laboratory.

**Based in part on thesis work done to obtain the degree of Doctor of Philosophy at the University of California, Berkeley.

nitrogen anneals the surface is not important as a sink or source for point defects and that the annealing processes occur almost entirely within the buried damaged region.

INTRODUCTION

Although much theoretical^{1,2} and experimental³⁻⁶ work has been done describing primary defects in ion-implanted silicon, there is not a clear description of how these primary defects evolve to produce the secondary defects which are observed when the implanted crystals are annealed. Previously proposed models are unsatisfactory. They often have been based on the observations from one instrumental technique, e.g., electron and nuclear paramagnetic resonance (EPR,NMR),³ infrared absorption (IR),⁴ resistivity,⁵ channeling and Rutherford backscattering (RBS).⁶ Thus these techniques apply to a very limited part of the annealing range. For instance, the Rutherford backscattering and channelling techniques are extremely sensitive in the 300 to 800°K annealing region, but are insensitive above 900°K, where crystallinity is largely restored and the remaining defects are mostly in the form of dislocation loops and stacking faults. EPR and NMR³ detect only electrically active defects and are insensitive to the neutral silicon self-interstitial. Resistivity and carrier concentration measurements⁵ are indirect because they average several different effects of point defects including their mobility, lifetime and total number. No model has been proposed that is consistent with the recently published information on point defects in silicon.⁷⁻⁹

In this paper a three-stage model for the evolution of secondary defects in ion-implanted silicon is proposed, assuming that the incoming ions produce a large number of Frenkel pairs. The steps required to evolve this primary defect distribution into the observed secondary defects are outlined, and experimental evidence to support the

hypotheses is presented. The model is then compared to those previously proposed. The doses considered for this model are all below the critical dose (D_c), so the primary damage clusters do not overlap.

EXPERIMENTAL

The 100 keV P^+ ions were implanted at room temperature into $\{111\}$ p-type Czochralski grown silicon wafers of 0.1 ohm-cm resistivity to a dose of 2×10^{14} ions/cm². The experimental value of D_c for P^+ ions in silicon is 4×10^{14} ions/cm²; ^{6a} this number is an upper limit because annealing proceeds during implantation. A lower estimate may be obtained by assuming no annealing and defining the critical dose as that required to displace all the target atoms once. Using the formula of Morehead and Crowder,¹⁰ $D_c = E \cdot n / (dE/dx)$ ions/cm², where E is the displacement energy (25 eV for silicon); n is the number of target atoms per cm³ (15×10^{22} cm⁻³), dE/dx is the energy independent energy loss per unit length and is calculated to be 5.1×10^9 eV/cm for P^+ ions in silicon.¹¹ Using these values one finds $D_c = 2.4 \times 10^{14}$ ions/cm². This lower value was chosen to ensure that a continuous damaged layer was not formed. Samples were isochronally annealed between 700 to 1100°K for times between 15 to 30 min. Annealing was done in both vacuum and in dry nitrogen with no significant differences observed. Samples were chemically thinned for electron microscopy.

The as-implanted silicon foils gave diffraction patterns similar to those obtained by Mazey et al.,¹² i.e., broad rings indicative of a heavily damaged layer. The rings were replaced by heavy streaking in the diffraction patterns upon annealing to 700°K. Figure 1 shows a dark field and diffraction pattern of a foil heated to 700°K for 1-1/2 hr. The dark field picture was obtained by imaging part of the streak as shown. The speckled contrast arises from the small defect clusters which are responsible for the streaking. Note the

six extra 111 spots in the diffraction pattern, despite the fact that a fairly thick specimen is being examined, as indicated by the Kikuchi lines. Therefore, these spots and the streaks must arise from small clusters on the $\{111\}$ planes. By assuming the presence of such small clusters and the reciprocal lattice point extensions¹³ they would give rise to, all the extra diffraction spots can be consistently explained, see Fig. 2.

Upon further annealing in the range 900 to 1100°K these primary defect clusters are replaced by secondary defects, resolvable by electron microscopy. A weak beam image of a P^+ ion--implanted silicon foil annealed to 1100°K is shown in Fig. 3. The regular hexagonal shapes of the Frank loops shows that they were still growing at the end of the annealing treatment. The loops lie on all four $\{111\}$ planes. These Frank loops are always found to be interstitial type.^{14,15}

In order to estimate the number of point defects required to form all the loops, the sizes and the numbers of the loops were obtained from weak-beam images. For an 1100°C 15 min anneal, the average loop diameter was found to be 300Å, which corresponds to 1.8×10^4 interstitials per loop. The number of loops per unit area, taking into account that with a $g = 2\bar{2}0$ type reflection two of the four sets of loops are absent by diffraction contrast rules, was 10^{10} loops per cm^2 . The number of point defects involved in the loops is thus 1.8×10^{14} atoms/ cm^2 which is nearly equal to the implanted ion dose of 2×10^{14} P^+ ions/ cm^2 .

Similar results have been published by Bicknell¹⁶ for B^+ ions implanted into silicon at 500°K and annealed at 1100°K. It was

determined from stereo pair measurement that the loops lie about 1000 Å from the implanted surface in a layer 350 to 400 Å thick. The implication of these results is that the annealing of damage and the nucleation of the loops is confined almost entirely to the buried damaged layer with little interaction with the surface.

MODEL

Description of the As-Implanted Silicon

The primary damage clusters lie buried at a depth equal to the ion range $R_p(1000\text{\AA})$ with a spread of $R_p(350\text{\AA})$.^{6a} The clusters do not overlap for the ion doses used so that the integrity of the crystal is never completely destroyed. The repair processes will be assumed to be confined to this buried volume. The number of atoms displaced per ion during the implantation, g , can be estimated from the modified Kinchin and Pease formula^{6a} $g = 0.42 E/E_d$. Using $E = 10^5$ eV for the incoming ion and $E_d = 25$ eV for the displacement energy, g is 1000 atoms per incoming ion. For a dose of 2×10^{14} ions/cm². This gives 2×10^{17} Frenkel pairs or a point defect concentration in the damaged layer of about 2×10^{21} /cm³. A great majority of these must recombine almost immediately as they are produced. This fraction that recombine is difficult to estimate; assuming 99% recombination there would still be 2×10^{19} defects/cm³ remaining after implantation.

Optical absorption and paramagnetic resonance^{3,4} studies show that the primary damage consists of central damaged regions surrounded by regions rich in vacancies. The interstitials formed by the implantation are most likely expelled to even greater distances from the regions of heavy damage and cluster or complex with other point defects in the surrounding regions. During annealing interstitials are expected to be released from these clusters.

Stage I 300-600°K (200-350°C)

There is much experimental evidence concerning the behaviour of vacancies. Convincing magnetic resonance³ and optical absorption⁴ studies indicate that upon heating the single vacancy converts to a series of vacancy complexes: divacancies (V-V), A-centers (vacancy-oxygen), E-centers (vacancy-phosphorous), etc. These complexes often exist in different charge states, depending on the type of silicon, and consequently exhibit different migration energies. Upon heating to about 600°K Corbett's data³ indicate that most of these complexes "anneal out."

In contrast there is little evidence concerning the interstitial. Frank and Seeger⁷⁻⁹ suggest that there could be three different interstitial species in this temperature range: the positively, neutral, and negatively charged self-interstitials (I^+ , I^0 , I^-) mobile between 370-420°K, 490-570°K and 490-580°K with migration energies 0.85, 1.7 and 1.8 eV, respectively. Frank⁹ proposes that the annealing of the vacancy complexes could just as well occur by the motion of the self-interstitials.

In the light of the above evidence, we assume that in the early stages the annihilation of Frenkel pairs proceeds by migration of one or more of the point defects. In the intermediate temperature range (~400°K) vacancies complex and interstitials form di-interstitials, etc. Finally some of the divacancies and di-interstitials annihilate while others grow to include three or more defects.

Stage II 600-900°K (350-650°C)

At the lower temperatures 600-700°K (350-450°C), processes operative at the end of Stage I continue: the dissolution of the smallest clusters and the release of mobile interstitials annihilate vacancies or cause other interstitial clusters to grow. The binding energy of an interstitial to a small interstitial cluster E_f^c is certainly smaller than the energy of formation of an interstitial from a regular lattice site. Therefore, based on Frank's data⁹ we expect that interstitials are readily produced as the temperature is raised.

In the temperature range 700-850°K (450-600°C) the mobile point defect species have not been positively identified. This is the temperature range in which heavily damaged silicon begins to recrystallize. There is an increase in resistivity as a result of a decrease in the number of carriers. This reverse annealing has been attributed to the tendency of some dopants, like Boron, to precipitate.^{5,16}

At the highest temperatures 800-900°K (550-650°C) there is electron diffraction evidence for the existence of submicroscopic clusters. Their nature and sizes are too small to be determined by diffraction contrast. We expect that there is some conversion from clusters to very small Frank loops on the four $\{111\}$ planes and that the clusters and loops are of both kinds, with interstitials in slight excess by the number of implanted ions. For a dose of 2×10^{14} ions/cm² the excess is one interstitial in 10^5 atoms.

Stage III 900-1100°K (650-800°C)

At about 900°K repair processes are expected to be nearing completion for doses below D_c ; the increasing carrier concentration indicates that dopant atoms are being restored to substitutional sites and after a 1100°K anneal about 85% of the implanted atoms become substitutional. A coarsening process by which point defects move between small shrinking loops and larger growing loops is operative. This process can take place by a vacancy or an interstitial mechanism.

Two effects are expected to operate which would result in the formation of the observed interstitial defects: First, the dislocations preferentially attract interstitials because of their large strain fields. As a result if any point defects are lost by diffusion away from the damaged layer, a vacancy loop will attract slightly more interstitials than vacancies and shrink. An interstitial loop on the other hand will grow. Second, and more importantly, if the dose is below D_c and the integrity of the crystal is never destroyed, there is a net excess of silicon interstitials when the dopant atoms have all become substitutional. Examination of the diffusion data shows that the dopant atoms (P, B or As) are relatively immobile in this temperature range. Therefore they must find substitutional sites rather close to where they come to rest.

It is proposed that the combination of these two effects eliminates all the vacancy defects before they grow to a size that can be studied by electron microscopy. The density and sizes of interstitial loops observed are consistent with this model.

Heating to yet higher temperatures, over 1100°K causes the interstitial loops to become circular and shrink. Experimental results on the kinetics of shrinkage give an activation energy of 5.5 eV;¹⁷ from Seeger's data⁸ this corresponds to the shrinkage via the motion of the extended high temperature self-interstitial.

The essentials of the model are summarized in Fig. 4a. Figure 4b shows how the regions delineated by electron microscopy and resistivity measurements⁵ and point defect studies^{8,9} compare with each other. It is interesting to note that in the region 300-500°C where important crystalline reorganization occurs the mobile point defects cannot be identified by resonance or other measurements.

DISCUSSION

We have presented a model for the formation of secondary defects in ion-implanted silicon in which both interstitial and vacancy clusters play a significant role. This is in contrast to those previously proposed in the literature which emphasize one or the other type of point defect. Our model applies to doses less than the critical dose D_c , where the integrity of the crystal is never destroyed.

An important assumption of the model is that for vacuum and dry nitrogen anneals, all the repair processes are confined to the damaged layer, which is about 350Å thick buried about 1000Å from the surface, and that there is almost no migration of point defects to or from the surface. This hypothesis is consistent with the experimental results of Tamura,¹⁹ who shows that by annealing in an oxidizing atmosphere, such that vacancies do migrate to the surface,²⁰ the secondary defects are drastically affected. Although he has made no quantitative estimates, we expect that under these conditions the number of interstitials in the defects would be larger than the number of implanted atoms.

Several significant conclusions follow if, we assume that in Stage I and Stage II the point defect motion is largely confined to a 350Å thick damaged layer. The distance moved by the interstitial and by the vacancy, in Stages I and II calculated by using the value of the migration energy alone, is found to be several microns. The contradiction with the assumption is removed if we assume that in Stage I the annihilation of Frenkel pairs, involving very short range diffusion, is the dominant process. In Stage II we assume that numerous clusters are present and that defects still migrate primarily from cluster to cluster.

In this process the coefficient of diffusion must involve both the migration energy E_m and the formation energy of a defect from its cluster E_f^c , which will be smaller than the equilibrium formation energy E_f . E_f^c may be estimated by assuming that the diffusion distance is 350Å during 1 min. This gives a value of E_f^c as 3 eV. Since the energy of formation of divacancies E_f^{2v} is 3.4 eV,^{4b} we conclude, consistent with EPR data,⁴ that the formation of divacancies from larger clusters and their subsequent motion is involved in Stage II.

In Stage III, assuming an interstitial diffusion mechanism as suggested by Seeger,⁸ with E_m^I equal to 3.38 eV and E_f^I equal to 2.5 eV, we can estimate the diffusion distance, d , at 1100°K during a typical anneal; since D , the diffusion coefficient at 1100°K is 1.04×10^{-16} cm²/sec, the value of the distance d , given by $d = \sqrt{Dt}$, is 30Å. This is an underestimate since the interstitials evolve from loops and clusters involving less than the full formation energy. Nevertheless this calculation does indicate that the diffusion processes in Stage III are confined to distances of the order of hundreds of Angstroms. Wu¹⁷ has shown that the shrinkage rates of defects is affected by the presence of others nearby. This is direct evidence that there is significant diffusion between the defects.

It is not clear at which temperature a simple coarsening of interstitial clusters starts. It is possible that at a low temperature at the end of the divacancy annealing stage 600°K all the Frenkel pairs have annihilated and there is left only the excess interstitials which then coarsen in the temperature region 600-1100°K. To prove this point it would be necessary to show that all the clusters at

600°K are interstitial and that the number of interstitial atoms stays essentially constant during subsequent heating. It is difficult to confirm either statement by using techniques presently available. Therefore we assume that vacancy and interstitial clusters are both present and that annihilation processes continue to the middle of Stage II. In this case coarsening starts at or above 900°K.

REFERENCES

1. R. S. Nelson, Radiat. Eff. 32, 19 (1977).
2. E. C. Baranova, V. M. Gusev, Y. U. Martynenko and I. B. Haibullin, Radiat. Eff. 25, 157 (1975).
3. (a) J. W. Corbett and J. C. Bourgoin in Point Defects in Solids, J. H. Crawford and L. M. Lifkin, eds. (Semiconductors and Molecular Crystals, Plenum Press, NY, London, 1975), Vol. 2, Chapter 1.
(b) H. C. Casey and G. L. Pearson in Diffusion in Semiconductors, ibid, Chapter 2.
4. (a) F. L. Vook, H. J. Stein and J. A. Borde, Appl. Phys. Lett. 14, 328 (1969).
(b) F. L. Book and H. J. Stein, Radiat. Eff. 6, 11 (1970).
5. R. W. Bicknell and R. M. Allen, Radiat. Eff. 6, 45 (1970).
6. (a) J. W. Mayer, K. Erikson and J. A. Davies, Ion Implantation in Semiconductors (Academic Press, 1970).
(b) L. Csepregi, W. K. Chu, H. Muller, J. W. Meyer and T. W. Sigmon, Radiat. Eff. 28, 227 (1976).
7. A. Seeger, Radiat. Eff. 9, 15 (1971).
8. A. Seeger and W. Frank, Proc. Intern. Conf. on Defects in Semiconductors, Reading, 1972 (The Institute of Physics, London, 1973), p. 262.
9. W. Frank, Institute of Physics Conference Series No. 23 (Institute of Physics, London, 1973), Chapter 1, p. 23.
10. F. F. Morehead, Jr. and B. L. Crowder, Radiat. Eff. 6, 27 (1970).
11. K. Seshan, Ph. D. Thesis, University of California, Berkeley, LBL-2728 (1975).

12. D. J. Mazey, R. S. Nelson and R. S. Barnes, Phil. Mag. 17, 1145 (1968).
13. P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley and M. Whelan, Electron Microscopy of Thin Crystals (Butterworths, London, 1965).
14. M. L. Jenkins, D. J. H. Cockayne and M. J. Whelan, J. of Microscopy 98(II), 155 (1973).
15. K. Seshan and J. Washburn, Radiat. Eff. 26, 31 (1975); K. Seshan and J. Washburn, Phys. Stat. Sol. (a) 26, 345 (1975).
16. R. W. Bicknell, Proc. R. Soc. A 311, 75 (1969).
17. W. K. Wu, Ph. D. Thesis, University of California, Berkeley, LBL-3758 (1975); W. K. Wu and J. Washburn, J. Appl. Phys. 48(10), 3742 (1977).
18. S. Mader and A. E. Michel, Phys. Stat. Sol. (a) 33, 793 (1976).
19. M. Tamura, Phil. Mag. 35(3), 663 (1977).
20. I. R. Saunders and P. S. Dobson, Phil. Mag. 20, 881 (1969).

FIGURE CAPTIONS

Fig. 1. A dark field image of an implanted foil annealed at 700°K. Notice the fine speckles which are interpreted as clusters, giving rise to the streaking and the six extra 111 spots in the diffraction pattern, Fig. 1(b). The diffraction pattern also shows the aperture used to obtain the dark field image.

Fig. 2. Model for the origin of the streaks in Fig. 1(a,b).

(a) Reciprocal lattice cell fcc crystal with the 111 plane indicated, i.e., the triangles in continuous line in (b).

(c) Shows clusters on the 4 $\{111\}$ planes. The direction of the reciprocal lattice extensions due to the platelets are drawn in dashed lines in (a) and (b) and explain the $\{111\}$ streaking. (d) Shows the origin of the extra 111 spots which arises from the extension of the 111 point on the second laue layer to intersect the Ewald sphere.

Fig. 3. Secondary defects obtained when 111 silicon is implanted to a dose below critical dose and annealed at 1100°K. the weak beam image clearly shows the hexagonal (Frank loops (α, β) lying on the inclined planes and marked consistent with the Thomson tetrahedron marked in the figure. These loops are all of interstitial type. The diffraction condition is shown in the bottom left.

Fig. 4. (a) A summary of the three-stage model. (b) A summary of work of two previous models by Bicknell and Allen⁵ and Frank.⁹

XBB 747-4767

Fig. 1

XBL 747-6779

Fig. 2

0 0 0 0 4 6 0 -19-5 9 3

XBB 770-10928

Fig. 3

XBL 7711-10864

Fig. 4a

XBL 7610-4978

Fig. 4b

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720