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ON THE SHRINKAGE OF ROD-SHAPED DEFECTS

IN BORON ION IMPLANTED SILICON

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Abstract

Three different types of rod-shaped defects formed during post-implantation annealing of boron implanted silicon are distinguished in annealing experiments carried out on transmission electron microscope specimens. It is shown that rod-shaped defects can be boron precipitates, Frank dipoles or perfect $a/2 \langle 110 \rangle$ dipoles. All shrink from the ends only during annealing. The temperature dependence of shrinkage rate for the first type was determined by measuring dL/dt at three different temperatures for a given isolated defect. Boron diffusion appeared to be the rate determining process. The second type, Frank dipoles, were often observed to unfault, transforming into the third type during annealing. At the time of unfauling the newly formed perfect dipole was always observed to rotate on its glide cylinder to near edge orientation.

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Introduction

In a previous paper,⁽¹⁾ an electron diffraction contrast analysis suggested that there are at least two different kinds of rod-shaped defects that form during post-implantation annealing of boron ion implanted silicon.

The first type show contrast similar to that expected for an elongated dislocation loop on {100} with displacement vector $a/x\langle 100 \rangle$, where a is the lattice constant of silicon and x may not be an integer. The displacement vector is perpendicular to the elongated $\langle 110 \rangle$ direction and loop plane.⁽¹⁾

The above characterization agrees with that of Madden and Davidson.⁽²⁾ They also suggested that these defects should be composed mostly of silicon atoms since similar rods were also observed in Neon⁽³⁾ and high energy electron irradiated silicon.⁽⁴⁾

However a second type showing diffraction contrast characteristic of elongated interstitial Frank loops were also present.⁽¹⁾

A ribbon shaped layer or layers of solute elements can show similar contrast to that expected of an elongated dislocation loop.⁽⁵⁾ For very small ribbon widths there is no way to distinguish between the two by contrast analysis alone. It was also observed that some rod-shaped defects are more complex, because sudden changes in diffraction contrast occur along the length of the same rod.

The present work was undertaken to further identify the nature of these defects. Repeated observations of the same area of a foil during an annealing sequence at different annealing temperatures and for different

times were made. One objective was to determine the apparent activation energy for shrinkage of the various types. The observations also were expected to provide direct information on the evolution of the more complex defects, so that their structure could be more fully understood.

Experimental

a) Specimen Preparation

n-type silicon slices, 5 Ω -cm, of <111> orientation were irradiated at room temperature with boron ions at 100 KV to a dose of $2 \times 10^{14}/\text{cm}^2$.

They were then ultrasonically cut into discs of 3 mm in diameter and annealed in a dry nitrogen flowing atmosphere. The annealed specimens were then chemically polished from the unimplanted side in one part solution A (2.5g iodine and 1100 cc CH_3COOH) and two parts solution B (1HF + 3 HNO_3).

b) Electron Microscopy

The thinned specimens were repeatedly examined in a Philips 301 electron microscope operating at 100 kV following each furnace anneal period.

The annealing temperatures were monitored to an accuracy within 1°C by a chromel alumel thermocouple sealed in a small quartz tube positioned near the specimen. Clean annealing was obtained in dry nitrogen flow not only for bulk specimens but also for thinned specimens up to 1100°C .

All micrographs were taken under two beam diffraction conditions with $s > 0$, where s is the deviation from the exact Bragg diffraction condition.

Great care was necessary to successfully take the specimens out of the microscope, anneal them and then put them back without any mechanical damage or contamination. Exact repetition of orientation and diffracting conditions were obtained in a given series by making use of the Kikuchi map.

Results and Discussion

General Observations

In order to determine the temperature range where rod-shaped defects would start to shrink, a 20-minute isochronal annealing sequence from 800°C up to 1017°C with 50°C temperature intervals was first performed. The following results were obtained:

The two types of diffraction contrast are shown in Figs. 1 and 2. Type a and type A defects are parallel to each other along $\langle 110 \rangle$ but show opposite contrast (one shows weak outside contrast while the other has strong inside or vice versa). Type a were observed to shrink much faster than type A and completely disappeared by about 900°C. Type A showed irregular shrinkage rates as in Fig. 1(a) and (b), and some were still present up to 1017°C. Also they sometimes showed clear stacking fault fringes [as shown in Fig. 1(e)]. This is consistent with the conclusions of the previous contrast analysis that one kind of linear defect is a faulted Frank dislocation dipole.⁽¹⁾ The widths of type a defects, as indicated by the diffraction contrast, remained the same as they became progressively shorter in length (Fig. 2). However the widths of type A sometimes increased (Fig. 1). Isolated type a defects shortened in length at a constant rate which depended on the annealing temperature.

Transformation of a type A defect is shown in Fig. 2. The defect, A, suddenly changed into a perfect dislocation loop which rotated into a $\langle 112 \rangle$ direction with its new Burgers vector perpendicular to its new

elongated direction. Occasionally, it was also observed that a portion of what was originally a type a defect transformed into a perfect dislocation loop which also rotated to a $\langle 112 \rangle$ direction as shown in Fig. 3.

In Fig. 4, a perfect dislocation loop B is apparently formed adjacent to the rod-shaped defect a. It grew on its right end as the defect a was shrinking.

Annealing Kinetics of Type a Defects

Isothermal annealing sequences were carried out in the temperature range from 750°C to 850°C to determine the apparent activation energy for shrinkage of type a defects. Shrinkage rates for type A defects were found to be too erratic in this temperature range to permit apparent activation energy determination.

Dislocation loops tend to shrink during annealing due to the line tension of the dislocation and the energy of the stacking fault, if any. The type a rod-shaped defects have very narrow spacing and straight edges along $\langle 110 \rangle$ directions (Fig. 5). For the following discussion, the interstitial self-diffusion mechanism has been assumed to operate in the temperature range from 750°C to 850°C.⁽⁷⁾ However it is still not known whether the diffusion mechanism for silicon or boron is interstitial or vacancy type in this temperature range.

Assuming that the ends of the dislocation loops act like point sources for interstitials migrating to the foil surfaces, the shrinkage rate can

be expressed as:

$$\frac{dL}{dt} = -\pi B^2 N_0 D^{SD} \left[1 - \exp \left(-\frac{\mu_V}{2kT} \right) \right] \quad (1)$$

where D^{SD} is the self-diffusion coefficient for silicon, N_0 is the atomic density (5×10^{22} atom/cm³), B^2 is the cross sectional area of an atom on the loop plane, $\mu_V^{(6)}$ is the chemical potential of interstitials at the end of the dislocation loop:

$$\mu_V = \frac{G b^2 B^2}{4\pi(1-\nu)R} \ln \frac{R}{r_0} + \gamma B^2 \quad (2)$$

where G and ν are the shear modulus and Poisson's ratio of silicon, b is the Burgers vector of the dislocation loop, r_0 and $2R$ are the dislocation core radius and width of the loop, γ is the stacking fault energy of silicon. The factor 2 occurs in the exponent in Eq. (1) because each lattice point is associated with two atoms if the diamond cubic lattice is assumed to be based on FCC.

Alternatively if the defect is a rod shaped boron precipitate n layers thick, the shrinkage rate can be expressed as:

$$\frac{dL}{dt} = - \frac{2 B^2 N_0 D^B}{n} (C_s - C_o) \quad (3)$$

where D^B is the diffusion coefficient for boron in silicon, C_s and C_o

are the impurity concentrations at the defects and far from the defects respectively.

The boron density in silicon after boron ion implantation at 100 KV to a dose of 2×10^{14} B/cm³, if distributed uniformly through a depth of 4000Å, would be only about 5×10^{18} B/cm³, as compared to the solid solubility of boron at 800°C $\approx 10^{20}$ B/cm³. Therefore, boron precipitates should tend to redissolve by thermal diffusion during annealing. Even though the observed shrinkage occurred only at the ends, there may be some change in composition along the length during annealing.

In order to avoid the errors inherent in comparing shrinkage rates of different defects which generally will have different widths and be at different depths the shrinkage rates of the same defect were measured at different annealing temperatures. Even in this case the position of the interstitial source (end of the rod) changes during shrinkage which can still lead to erratic shrinkage rates if interstitial sinks other than the surface of the foil are present near the shrinking rod.

A typical annealing sequence is shown in Fig. 6. Small interstitial type dislocation loops, e.g., 1 and 2 in Fig. 6, are growing while the type a rod defects are shrinking. Also a small perfect dislocation loop, 3, is nucleated or grows to a visible size and continues to grow while rod-shaped defect a_1 is shrinking. The growth of these dislocation loops is caused by their acting as interstitial sinks. The presence of such a dislocation loop generally was found to cause a nearby rod-shaped defect

to shrink rapidly as long as its end was near the loop. This is shown by the behavior of defect a_1 in Fig. 6 which is near a number of loops. Its shrinkage rate is shown as curve 1 in Fig. 7. Sometimes, nearby dislocation loops even caused a single rod defect to break up into two during annealing as shown by loop 2 in Fig. 6.

For rod-shaped defects such as a_2 and a_3 in Fig. 6 which were far away from internal interstitial sinks, the shrinkage rates were very regular as shown by curves 2 and 3 in Fig. 7. This behavior has been confirmed by observation of many other similar defects. It was also observed that the type A rod-like defects such as A in Fig. 6 occasionally would for a time shrink rapidly at the ends while at the same time becoming wider. This kind of unstable shrinkage behavior is not yet understood. For some reason jog nucleation becomes possible on the long side permitting it to become an interstitial sink. This erratic behavior made consistent measurements of shrinkage rates for type A defects impossible.

From Eqs. (1) or (3) in the previous sections, the shrinkage rate (length change) of isolated rod-like defects should be constant for a given defect at constant temperature. The temperature dependence of the shrinkage rate for a given defect should, therefore, be determined only by the diffusion coefficient, i.e., D^{SD} or D^B .

Plotting the logarithmic shrinkage rates of type a rod-like defects with respect to the reciprocal of the annealing temperatures, an Arrhenius plot was obtained which gave an activation energy of 3.5 ± 0.1 eV (Fig. 8).

This corresponds closely to that for diffusion of boron atoms in silicon⁽⁸⁾ but is much too small for silicon diffusion under thermal equilibrium conditions.

Putting reasonable values into Eq. (3), the calculated shrinkage rate fits the observed rate if sheets of boron atoms of a few layers thickness were assumed. From this temperature dependence and the magnitude of the shrinkage rate of type a, rod-shaped defects, it was concluded that they are initially elongated coherent precipitates of boron atoms several layers thick on {100} planes. This conclusion receives further support from a High Voltage Electron Microscopy (HVEM) experiment. In this experiment, two samples without any prior processing were irradiated in the high voltage electron microscope. Sample A was a boron doped <111> oriented silicon of resistivity $0.75 \Omega\text{-cm}$ ($2.5 \times 10^{16} \text{ B/cm}^3$) and sample B was phosphorous doped, of resistivity $2 \Omega\text{-cm}$ ($2.7 \times 10^{15} \text{ P/cm}^3$).

Long needle shaped rod-like defects were observed to develop in sample A held at 620°C during irradiation with 650 KV electrons as shown in Fig. 9. No such defects were observed for sample B irradiated under similar conditions.⁽⁹⁾ Also the number of defects started to saturate after continuous irradiation for about 20 minutes. This suggests that the number of these defects was controlled by the presence of a species that was being depleted.

Boron precipitates should tend to redissolve by thermal diffusion at higher annealing temperatures, because the concentration of boron atoms a short distance away from the precipitates is always much lower

than the solid solubility of boron in silicon. The fact that internal interstitial sinks such as dislocation loops often were observed to be active suggests that the foil surfaces were relatively poor sinks. The formation of an interstitial may be able to take place readily only at the ends of a rod-shaped precipitate because of perfectly coherent low energy interfaces on the long sides. The redissolved boron atoms finally occupy regular substitutional lattice sites resulting in the observed increase in conductivity.

The irregular and generally slower shrinkage rate for type A, rod-shaped defects, such as A in Figs. 1 and 6 made apparent activation energy measurement impossible in this temperature range. However, from the stacking fault fringe contrast as shown in Fig. 1-e and from their frequent sudden transformation over their entire length to perfect dislocation dipoles that rotated on their glide cylinders to a $\langle 112 \rangle$ orientation it was concluded that this type of defect was primarily formed from interstitial silicon atoms and that it was essentially a Frank dislocation dipole.

It is possible that all rod-shaped defects are initially thin boron containing precipitates but that during the early stages of growth some transform into faulted dipoles because they are nucleated in or grow into a region of high silicon interstitial concentration. This might explain the observation in Fig. 3 where part of a type a defect apparently "unfaulted" in a manner usually associated with type A defects. The fact that some

individual defects are more complex is also consistent with the changes in diffraction contrast that were sometimes observed along the length of a single rod. A typical example is shown in Fig. 10. The defects marked 1 and 2, classified as type a defects, show variation in contrast along their lengths. Also shown in this figure is the complex contrast shown by defect 3 which is similar to defect B in Fig. 4, i.e., a perfect dislocation loop adjacent to a type a defect.

Acknowledgements

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Figure Captions

- Fig. 1 Isochronal annealing sequence of rod-shaped defects of type a and type A in boron ion implanted silicon. Picture (a) was bulk annealed at 800°C for 20 minutes before thinning. Figs. b through e were taken after thin foil annealing at 850°C, 900°C, 952°C, and 1017°C for 20 minutes respectively.
- Fig. 2 Similar annealing sequence as in Fig. 1. Note that type A rod-shaped defect suddenly changes into an elongated perfect dislocation loop and rotates into $\langle 112 \rangle$ orientation. The dotted line shows its previous position.
- Fig. 3 The separation of a perfect dislocation loop from a type a defect. Defects a_1 and a_2 are not a single defect. Defect a_1 bent at the arrow as shown in (a) and formed a new dislocation loop B. Loop B is along $\langle 112 \rangle$ perpendicular to its new Burgers vector. Defects a_1 , a_2 , and B are either out of contrast or show very weak residual contrast when the diffraction vector is along the projection of its long axis as shown in Figs. g and h.
- Fig. 4 Similar annealing sequence as in Fig. 1, showing the growth of a perfect dislocation loop B adjacent to a type a rod-shaped defect.

Fig. 5 Schematic illustration of a rod-shaped defect of length L and width $2R$ at the center of a foil of thickness $2l$.

Fig. 6 Annealing sequence of rod-shaped defects: (A) is after bulk annealing at 800°C for 30 minutes, (B) is the same but for reversed g vector, (C), (D), and (E) were after annealing as thin foils at 802°C for 25, 50 and 75 minutes respectively. (F) was then annealed at 802°C for 50 minutes more and then at 750°C for 70 minutes. All pictures were taken under identical diffraction contrast conditions to (A) except for (B).

Fig. 7 The shrinkage rate of several rod-shaped defects at different annealing temperatures. 1, 2, 3, 4 are type a defects and 5 shows erratic shrinkage of one type A defect.

Fig. 8 Logarithmic shrinkage rate with respect to the reciprocal of absolute annealing temperature for type a defects.

Fig. 9 Sequence showing nucleation and growth of linear boron containing precipitates in the 650 KV electron microscope for boron doped silicon at 620°C . The time intervals between each picture are as indicated.

Fig. 10 Weak beam dark field picture showing complex contrast of some defects after post-implantation annealing of boron ion implanted silicon.

XBB 765-4223

Fig. 1

a

d

b

e

c

f

XBB 765-4224

Fig. 2

XBB 765-4221

Fig. 4

XBL 7411-7614

Fig. 5

XBB 765-4220

Fig. 6

Fig. 7

XBL7411-7567

Fig. 8

XBB 753-1857

Fig. 9

XBB 7610-9071

Fig. 10

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