

***In situ* neutron diffraction study of lattice deformation during oxygen precipitation in silicon**

K. D. Liss and A. Magerl
Institut Laue-Langevin, F-38042 Grenoble Cedex, France

J. R. Schneider
Hamburger Synchrotronstrahlungslabor HASYLAB at DESY, Notkestrasse 85, D-2000 Hamburg 52, Germany

W. Zulehner
Wacker-Chemitronic GmbH, Postfach 1140, D-8263 Burghausen, Germany

(Received 11 December 1990; accepted for publication 29 April 1991)

We present the first *in situ* measurement of the evolution of strain fields due to oxygen precipitation in silicon single crystals by means of high-resolution neutron backscattering. The integrated reflecting power R and the lattice parameter variations $\Delta d/d$ which are directly related to the strain fields have been measured as a function of temperature and annealing time. In the temperature range from 300 to 1185 K, high purity float zone crystals maintain the R -values characteristic for perfect crystals. In contrast, Czochralski-grown crystals which contain on the order of 10^{18} oxygen atoms cm^{-3} (20 ppm), show a steep increase in reflectivity starting at 1160 K, and which goes through a maximum at 1350 K. At 1456 K, partial annealing occurs with a time constant of several hours.

INTRODUCTION

Czochralski-grown (Cz) dislocation-free silicon is used almost exclusively by semiconductor industry in the manufacture of very large scale integrated devices (VLSI). Oxygen is the most important impurity in Cz silicon crystals which typically contain around 10^{18} oxygen atoms cm^{-3} (20 ppm). Upon heat treatment, during device fabrication, oxygen atoms diffuse through the lattice to produce small agglomerates which grow into precipitate particles of silica (SiO_2). At temperatures above 1150 K, the precipitates punch out dislocation loops and/or generate stacking faults by emission and precipitation of Si self interstitials. These defects are getters for unwanted impurities which would have disastrous effects in the electrically active regions of VLSI devices.¹ Therefore information about the defects caused by oxygen precipitation and the accompanying strain field are technologically important.

In order to describe the precipitation process of oxygen in silicon important parameters like the size, number density, shape and crystallographic orientation of the oxide precipitates as well as the oxygen concentration in the matrix have to be determined. This has been achieved in the past by applying a combination of different techniques like anomalous transmission of x rays,² infrared spectroscopy,^{3,4} chemical etching coupled with optical microscopy,^{3,5} and high-resolution electron transmission microscopy.⁶⁻¹⁰ More recently, it has been demonstrated that small angle neutron scattering allows the determination of the size and the number density of the oxide precipitates as well as the solute oxygen concentration remaining in the matrix after heat treatments.^{11,12} In order to get good signal-to-noise ratios in the neutron measurements, large samples, about 10 mm thick, have been used. On the same sample the effect of the observed oxide precipitates on the overall perfection of the crystal has been studied by means

of γ -ray diffractometry¹³ and high-resolution neutron backscattering experiments.¹⁴ The diffuse scattering caused by partial (stacking faults) and perfect (glissile) dislocation loops has been observed using a triple-crystal diffractometer and 150-keV synchrotron radiation.¹⁵ From these measurements it is evident that all the applied diffraction techniques allow for *in situ* studies of the evolution of the various aspects of the defect structure induced by oxygen precipitation in silicon. In the present paper we show first *in situ* measurements of the strain evolution in a temperature range from 300 to 1456 K. The principles of neutron backscattering experiments and their interpretation are given in the next paragraph. This is followed by an experimental section and by a presentation of the results. A qualitative discussion of the data obtained so far will conclude the paper.

NEUTRON BACKSCATTERING EXPERIMENTS

In situ diffraction experiments with thermal neutrons are facilitated because of the weak interaction of neutrons with matter, which allows both to study bulk properties of large samples and to avoid window problems in case the samples have to be mounted in furnaces or cryostats. If diffuse scattering from long range strain fields are studied, high k -space resolution diffractometers and nearly perfect single crystals have to be used because the diffuse scattering is localized in the vicinity of the reciprocal lattice point. Here the diffuse scattering is in competition with the tails of the Bragg peak. However, if samples with a thickness much larger than the extinction length can be used the diffuse scattering is enhanced relative to the Bragg peak because the former is sampled over the whole crystal volume, whereas the latter reaches saturation after a penetration depth of the order of one extinction length. In the present neutron backscattering studies the extinction

length is about $11\ \mu\text{m}$, i.e., approximately 900 times smaller than the sample thickness, which makes the technique very well suited for studies of defect scattering induced by oxygen precipitation in standard Cz silicon crystals.

The physical quantities measured in neutron backscattering experiments have been discussed in detail in Ref. 14 and only a summary will be given here. The k -space resolution element is a plane perpendicular to the reciprocal lattice vector \mathbf{G} with a relative thickness of $\Delta\mathbf{G}/\mathbf{G} \approx 10^{-4}$. By scanning the wavelength of the neutrons this plane of integration in k -space is shifted in a direction parallel to \mathbf{G} through the distribution of both the diffuse, and the Bragg scattering. Therefore the position of the center of the diffraction pattern and its width are directly related to the strain field in the sample. The integral of the measured diffraction pattern can be compared with the integrated reflecting power measured on an as grown, dislocation free Cz silicon single crystal which is expected to be close to the value from dynamical diffraction theory for perfect crystals. The formation of defects leads to an increase of the measured integrated reflectivity. In the present experiment the maximum increase is by a factor of 15, which indicates that an *in situ* measurement of the integrated reflectivity provides a sensitive indicator for the formation of defects during annealing.

EXPERIMENTAL SETUP

The experiment was performed at the backscattering spectrometer IN10 at the Institut Laue-Langevin¹⁶ in a setup similar to the one described in Ref. 14. The two crystal setting¹⁷ is used in which the reflected intensity of the sample is analyzed via the reflection curve of a high quality crystal which also fulfills the function of the monochromator. The scanning variable is the wavelength of the neutrons incident onto the sample which is achieved by mechanical motion of the monochromator mounted on the piston of a modified motorcycle engine. Both the monochromator and the sample are set for back reflection and the mechanical Doppler motion corresponds to a purely longitudinal scan in reciprocal space. The diffraction patterns are recorded in transmission, i.e., one observes dips instead of peaks as a function of wavelength or, alternatively expressed, by the wave vector transfer $\Delta\mathbf{G}$.

The sample was mounted in the standard IN10 furnace which allows for temperatures up to 1500 K. Resistance heated cylindrical niobium foils with a length of 20 cm and niobium heat shields are used for this furnace giving negligible small background scattering. The outer wall consists of a 1.5 mm thick aluminum-based alloy, which again is very transparent for neutrons. The sample is heated in vacuum (10^{-5} Torr) and the temperature is controlled by two thermocouples next to the sample.

Sample sizes were $3 \times 3 \times 1\ \text{cm}^3$ with the big faces cut parallel to (111) planes. The samples were prealigned before mounting the furnace on the spectrometer. Final positioning occurred in the neutron beam with the furnace rigidly connected to a rotational unit and one goniometer arc parallel to the beam direction. Alignment was done at

TABLE I. Impurity concentrations of crystals in units of 10^{15} atoms/cm³.

Impurity	Sample		
	A	B	C
Oxygen	3	910	780
Carbon	5	10	10
Nitrogen	0.2	<0.1	<0.1

room temperature with a monochromator made from a perfect Si crystal. With increasing temperature the mismatch in the lattice constant between sample and monochromator becomes significant and the transmission spectra will leave the observation window offered by IN10. To compensate for this effect a monochromator made from $\text{Si}_{91}\text{Ge}_9$ ¹⁸ which has a correspondingly increased lattice spacing is used for the measurements at higher temperature. Because the $\text{Si}_{91}\text{Ge}_9$ crystal is less perfect than pure Si the instrumental resolution is reduced from $\Delta\mathbf{G}/\mathbf{G} = 7 \times 10^{-5}$ to $\Delta\mathbf{G}/\mathbf{G} = 25 \times 10^{-5}$.

Temperature changes were performed at a constant rate of 1 K/min. Because each diffraction pattern was measured over a period of 15 min it represents an average over approximately 15 K. In the following only the mean value of the temperature will be referred to. Three samples have been thermally cycled which are further on referred to as A, B, and C. Crystal A is cut from high purity float zone material, whereas samples B and C are cut from Cz-crystals. The impurity concentrations are listed in Table I.

RESULTS

On sample A a high-resolution spectrum with a perfect Si monochromator has been taken immediately after alignment of the sample (Fig. 1a). Then the temperature was brought up to 1023 K within 4 hours and held there for 1

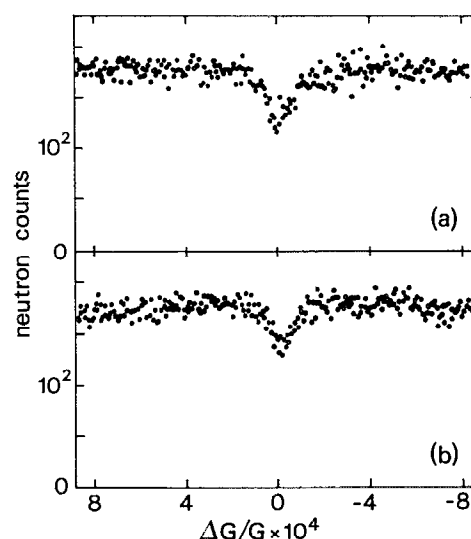


FIG. 1. Neutron spectra taken with a high-resolution Si monochromator at float zone Si crystal A before (a) and after (b) thermal treatment going up to 1185 K.

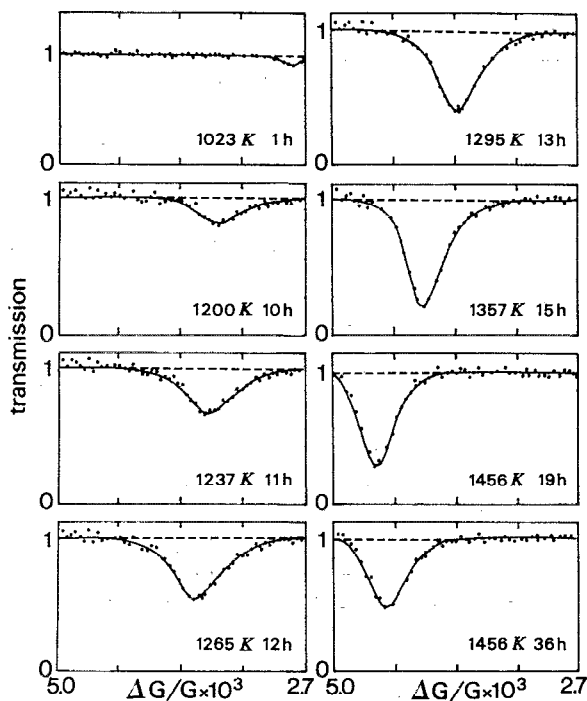


FIG. 2. Neutron spectra taken with $\text{Si}_{0.91}\text{Ge}_{0.09}$ monochromator at Czochralski-grown Si sample *B* for various temperatures of the annealing cycle.

additional hour. Subsequently the temperature was increased to 1185 K and held constant for 4 hours. The neutron spectrum taken after cooling down to room temperature is shown in Fig. 1(b). There is no difference between the two spectra which demonstrates both the reliability of the present setup and the causal relation between the observed changes at annealed Cz-crystals with the formation of lattice strains due to oxygen precipitation.

Figure 2 shows representative examples of neutron spectra taken on sample *B* at various points of a temperature cycle. There is a pronounced evolution of both the position and the shape of the dip. The position relates directly to changes of the lattice parameter which can be determined very accurately by neutron backscattering spectroscopy. A detailed analysis of the diffraction pattern and its relation to the defect structure in the annealed crystal will be presented in a forthcoming paper. At 1023 K the diffraction dip is significantly flatter than in Fig. 1, where a perfect Si monochromator had been used at room temperature. This reduction of the amplitude of the dip is due to the $\text{Si}_{0.91}\text{Ge}_{0.09}$ monochromator, which is of lower resolution as indicated above. Therefore, the total reflected power is distributed over a wider part of the spectrum.

At 1023 K the integrated intensity R of the dip measured on sample *B* is equal to the value R_{perf} measured with IN10 for the dislocation free float zone crystal *A*. In the following the changes of the integrated reflectivity due to the temperature treatment will be discussed in units of R_{perf} . As shown in Fig. 2, R strongly increases with increasing temperature until it reaches a maximum value for

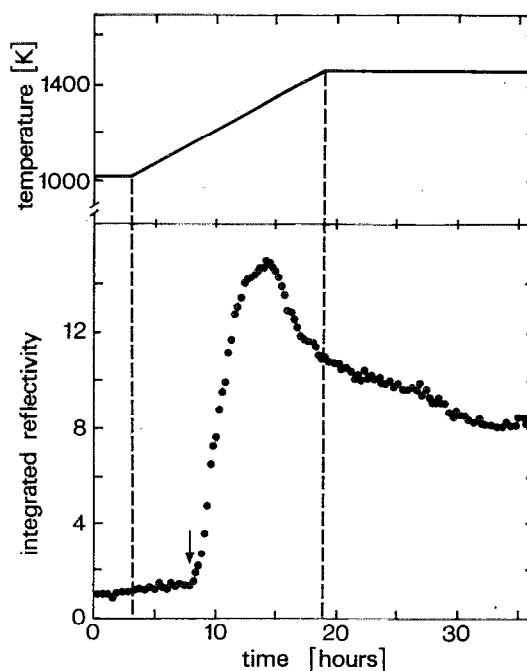


FIG. 3. Temperature profile of the annealing cycle applied to the Czochralski-grown sample *B*. The integrated reflectivity is plotted in units of R_{perf} which is the value measured on an as-grown dislocation-free Si crystal at room temperature. Each point represents a measurement for 15 min. The quoted temperatures are average values over $\pm 7.5^\circ$.

the spectrum taken at 1357 K. Further increase in temperature reduces the amplitude of the dip. This trend continues for many hours even with the temperature kept constant at 1456 K. A more detailed presentation of the evolution of the integrated reflectivity R is given in Fig. 3. The salient observations are summarized in the following statements:

- (1) Annealing for several hours at 1023 K has no significant effect on the integrated reflectivity.
- (2) A gradual increase in temperature up to 1160 K causes a slight, but significant increase in R .
- (3) At 1160 K the integrated reflectivity starts to grow rapidly and reaches a saturation value of $R = 15 \times R_{\text{perf}}$ at 1350 K.
- (4) A continued increase in temperature up to 1456 K reduces the integrated reflectivity rapidly to a value of $R = 11 \times R_{\text{perf}}$. Holding the sample at this temperature results in a further decrease of R . After 15 hours an equilibrium value of $R = 8.5 \times R_{\text{perf}}$ seems to be reached.

A similar temperature cycle was applied to sample *C*, the evolution of the measured integrated reflectivity is presented in Fig. 4, again in units of R_{perf} . The maximum temperature was limited to 1350 K corresponding to the highest R value observed at sample *B*. Up to this temperature the evolution of R for both samples is very similar. Again a pronounced break point is observed at 1160 K (see arrow in Fig. 4) and the same maximum value of $R = 15 \times R_{\text{perf}}$ is found at 1350 K. However, no significant change in the measured integrated reflectivity occurs even after waiting for several hours at that temperature, i.e., at 1350 K no relaxation of the lattice is observed.

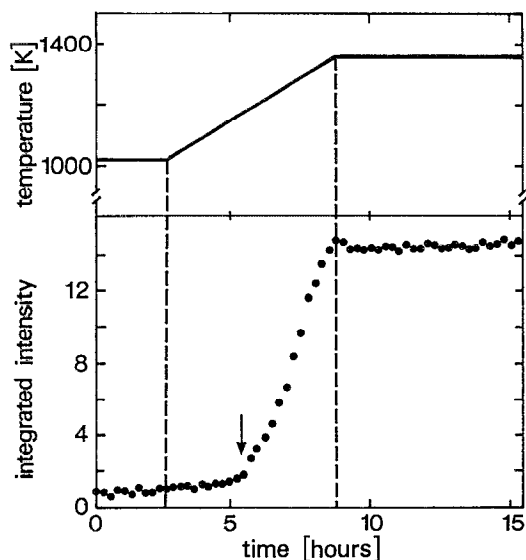


FIG. 4. Temperature profile of the annealing cycle applied to the Czochralski-grown sample C. The integrated reflectivity is plotted in units of R_{perf} , which is the value measured on an as-grown dislocation-free Si crystal at room temperature. Each point represents a measurement over 15 min. The quoted temperatures are average values over ± 7.5 .

DISCUSSION

The integrated reflectivity of a neutron beam diffracted from a perfect Si crystal is rather low and the pronounced enhancement of the integrated reflectivity R observed in the present work originates from lattice distortions related to oxygen precipitates and their secondary defects in Si. With the neutron backscattering spectrometer IN10 one is mainly sensitive to longitudinal deformations, i.e., fluctuations of the lattice parameter measured in the near vicinity of the 111 Bragg peak. Indeed it has been shown recently¹⁴ that the longitudinal deformations dominate the distortion scattering due to oxygen precipitation. The results of these first *in situ* neutron backscattering experiments on annealed Cz silicon can be related qualitatively to the mechanisms induced by oxygen precipitation described in the literature.

An anneal at 1023 K for several hours initiates the formation of cushion shaped SiO_2 precipitates on [100] planes.⁹⁻¹¹ The induced strain, however, is too weak to be detected by means of the neutron backscattering spectrometer IN10. With increasing temperature the average size of the precipitates increases and so does the induced lattice strain. However, the host lattice remains coherent so that only a weak although significant increase of the integrated reflectivity up to a temperature of 1160 K is observed. At that temperature and above the silicon lattice has become sufficiently soft so that the strain fields around the SiO_2 clusters can relax by the emission of dislocation loops and/or self interstitials which subsequently agglomerate to stacking faults on {111} planes. This is considered to be the origin of the rapid increase in integrated reflectivity. Also the increase of oxygen solubility with temperature has to be considered as a competing process for strain relief. R

reaches a maximum value at 1350 K where the system seems to be in a stable configuration, because no lattice relaxation is observed even after annealing for several hours (see Fig. 4). At higher temperatures, however, a decrease of the integrated intensity is observed. The effect is rather pronounced for temperatures increasing up to 1456 K. On a flatter slope R continues to decrease as a function of time even if the temperature is kept constant at 1456 K. This relaxation process could be caused by the increased softness of the Si lattice and the higher oxygen solubility at that temperature. Additionally, the mobility of the lattice defects increase. This allows annihilation processes to occur as it is the case when two dislocations with Burger's vectors of opposite sign meet on the same slip plane or when small dislocation loops emit interstitial atoms to large stacking faults.

CONCLUSION

For the first time the formation and the annealing of strain fields in Czochralski-grown silicon crystals have been followed on line during a high temperature treatment. The strain fields are directly related to the formation of oxygen precipitates and to the elastic/plastic behavior of the host lattice. Measurement times of 15 minutes per spectrum are adequate for the present study, although it could be reduced to 5 minutes or less. The transparency of Si for neutrons allows the investigations of massive samples (up to 10 cm thickness) which may be of interest for technical applications.

¹ For a review, see various contributions in Landolt-Börnstein, *New Series III/22B*, edited by O. Madelung and M. Schulz (Springer, Berlin, 1989).

² J. R. Patel and B. W. Batterman, *J. Appl. Phys.* **34**, 2716 (1963).

³ F. M. Livingston, S. Messoloras, R. C. Newman, B. C. Pike, R. J. Steward, M. J. Binns, W. P. Brown, and J. G. Wilkes, *J. Phys. C* **171**, 6253 (1984).

⁴ R. C. Newman, M. Clayburn, S. H. Kinder, S. Messoloras, A. S. Oates, and R. J. Stewart, *Proceeding of the 5th International Symposium on Silicon Materials Science and Technology*, edited by H. R. Huff, T. Abe, and R. Kohlbesen (The Electrochemical Society, Pennington, 1986), p. 766.

⁵ S. M. Hu, *Appl. Phys. Lett.* **36**, 561 (1980).

⁶ K. Wada, N. Inoue, and K. Kohra, *J. Cryst. Growth* **49**, 749 (1980).

⁷ K. Wada, H. Nakanishj, T. Takaoko, and N. Inoue, *J. Cryst. Growth* **57**, 537 (1982).

⁸ W. Bergholz, J. C. Hutchinson, and P. Pirouz, *J. Appl. Phys.* **58**, 3419 (1985).

⁹ A. Bourret, *Microscopy of Semiconducting Materials 1987* (Institute of Physics, London, 1987), p. 49.

¹⁰ W. Bergholz, M. J. Binns, G. R. Booker, J. C. Hutchinson, S. H. Kinder, S. Messoloras, R. C. Newman, R. J. Stewart, and J. G. Wilkes, *Philos. Mag. B* **59**, 499 (1989).

¹¹ S. Messoloras, J. R. Schneider, R. J. Stewart, and W. Zulehner, *Semicond. Sci. Technol.* **4**, 340 (1989).

¹² S. Gupta, S. Messoloras, J. R. Schneider, R. J. Stewart, and W. Zulehner, *Semicond. Sci. Technol.* **5**, 783 (1990).

¹³ J. R. Schneider, O. D. Gonçalves, A. J. Rollason, U. Bonse, J. Lauer, and W. Zulehner, *Nucl. Instrum. Methods Phys. Res. B* **29**, 661 (1988).

¹⁴ A. Magerl, J. R. Schneider, and W. Zulehner, *J. Appl. Phys.* **67**, 533 (1990).

¹⁵ J. R. Schneider, H. Nagasawa, W. Drube, R. Frahm, V. Etelaniemi, L. E. Berman, J. B. Hastings, D. P. Siddons, and W. Zulehner, *Hamburger Synchrotronstrahlungslabor HASYLAB at DESY, Jahresbericht 1988*, p. 277.

¹⁶ *Neutron Research Facilities at the ILL High Flux Reactor*, edited by B. Maier (Institut Laue-Langevin, Grenoble Cedex, 1983).

¹⁷ M. Birr, A. Heidemann, and B. Alefeld, *Nucl. Instrum. Methods* **95**,

435 (1971).

¹⁸ A. Magerl and C. Holm, *Nucl. Instrum. Methods Phys. Res. A* **220**, 414 (1990).