Nitrogen diffusion and interaction with dislocations in single-crystal silicon

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(Received 13 August 2008; accepted 6 November 2008; published online 8 January 2009)

The results of dislocation unlocking experiments are reported. The stress required to unpin a dislocation from nitrogen impurities in nitrogen-doped float-zone silicon (NFZ-Si) and from oxygen impurities in Czochralski silicon (Cz-Si) is measured, as a function of the unlocking duration. It is found that unlocking stress drops with increasing unlocking time in all materials tested. Analysis of these results indicates that dislocation locking by nitrogen in NFZ-Si is by an atomic species, with a similar locking strength per atom to that previously deduced for oxygen atoms in Cz-Si. Other experiments measure dislocation unlocking stress at 550 °C in NFZ-Si annealed at 500–1050 °C. The results allow an effective diffusivity of nitrogen in silicon at 500–750 °C to be inferred, with an activation energy of 3.24 eV and a diffusivity prefactor of approximately 200 000 cm² s⁻¹. This effective diffusivity is consistent with previous measurements made at higher temperatures using secondary ion mass spectrometry. When the results are analyzed in terms of a monomer-dimer dissociative mechanism, a nitrogen monomer diffusivity with an activation energy in the range of 1.1–1.4 eV is inferred. The data also show that the saturation dislocation unlocking stress measured at 550 °C in NFZ-Si is dependent on the anneal temperature, peaking at 600–700 °C and falling toward zero at 1000 °C. © 2009 American Institute of Physics. [DOI: 10.1063/1.3050342]

I. INTRODUCTION

Manufacturers of silicon have recently become interested in the intentional addition of nitrogen to wafers. Nitrogen is known to affect the concentration of vacancies in silicon, and also offers manufacturers additional control over oxygen precipitation processes in Czochralski silicon (Cz-Si). Float-zone silicon (FZ-Si) wafers are now commonly doped with nitrogen, which also increases the mechanical strength of the material by pinning dislocations. However, in spite of its utility, nitrogen’s fundamental properties in silicon remain poorly understood.

The dominant form of nitrogen in silicon has been shown to be an interstitial dimer. The dimer’s binding energy has not been measured, but ab initio theoretical studies calculate that it is high, in the range of 3.67–4.30 eV. Calculations have found diffusion paths for the dimer with activation energies of 2.38–2.69 eV, values which are consistent with high temperature secondary ion mass spectrometry (SIMS) measurements, which found a barrier to diffusion of 2.8 eV. However, other experiments have obtained results that cannot be explained by simple diffusion of the nitrogen dimer, indicating that nitrogen transport in silicon is more complex. It has recently been proposed that nitrogen transport proceeds by a dissociative mechanism, whereby the practically immobile dimer splits into fast-moving monomers, which diffuse with an activation energy of 1.25 eV before recombining. Questions remain over this proposal, however, as the inferred monomer diffusion barrier is considerably greater than the low value of ~0.5 eV calculated by theoretical studies.

Other measurements of impurity transport in silicon have been made using an experimental technique known as dislocation unlocking. Specimens are processed to contain regular arrays of dislocations. They are then annealed, during which impurities diffuse and segregate to dislocations, producing a locking effect. The resolved shear stress required to unlock the dislocations, known as the unlocking stress \( \tau_u \), is then measured by three-point bending normally carried out at 550 °C. This procedure is repeated with many specimens, using a different anneal temperature and duration for each. Analysis of the variation in \( \tau_u \) with these parameters can yield information about the transport of the impurity and its interaction with dislocations.

Dislocation unlocking experiments using Cz-Si to investigate oxygen transport reproduced other transport measurements made at high temperatures, and quantified the enhanced transport due to a fast-moving oxygen dimer at low temperatures. The technique was then extended to measure nitrogen in nitrogen-doped FZ-Si (NFZ-Si), finding an activation energy for nitrogen transport of 1.5 eV. In these NFZ-Si experiments the conditions used for the three-point bending process were varied with the intention of increasing the precision of the measurements. This was done by employing longer times to measure unlocking when lower unlocking stresses were expected. However, as will be shown in the present paper, this contributed to an error in these results. This error did not affect the earlier Cz-Si measurements that showed greater locking stresses and for which roughly constant unlocking times were used.

Dislocation unlocking experiments, made using a standardized experimental technique, are presented in this paper. Measurements of the variation in unlocking stress with three-point bend duration in both Cz-Si and NFZ-Si are presented, and analyzed in terms of a theory of the release of disloca-
locations near the outer knife edges that experienced a stress lower than the locking stress remained locked and did not move, but dislocations near the central knife edge that experienced a stress higher than the locking stress unlocked, and expanded according to the stress they experienced. The unlocking stress \( \tau_u \) is determined by identifying the sets of dislocations that moved under the least stress. This is done after the three-point bend using a preferential etch, a mixture of \( \text{CrO}_3 (0.3M) \) and \( \text{HF} \) (40\%) in the ratio of 5:4, which creates a pit large enough to be visible under an optical microscope at the location of each dislocation.

In previous NFZ-Si dislocation unlocking experiments, the three-point bend duration was varied on an experiment-by-experiment basis to increase sensitivity by using longer times at lower unlocking stresses. In this way the unlocked dislocations always moved a large distance compared to those that remained unlocked. However, it is now known that this contributed to an error in this work,\(^{9,28-31,34}\) since, as will be shown, the measured unlocking stress is dependent on the three-point bend duration. It should be noted that this error did not affect previous dislocation unlocking experiments that measured oxygen locking in Cz-Si.

In the work presented here, the three-point bend conditions have been standardized for each set of experiments. All FZ-Si experiments used a load calculated to give \( \sim 85 \) MPa \( \tau_{\text{max}} \), with a duration of 4 h, apart from those experiments in which the three-point bend duration was intentionally varied to measure its effect. Even when using this standardized unlocking time, careful examination of the specimens using optical microscopy allowed unlocking stresses of as low as 6 MPa to be measured. The Cz-Si experiments were carried out using loads set to give a maximum stress of \( \sim 190 \) MPa for each test.

### II. EXPERIMENTAL METHOD

Specimens measuring approximately \( 28 \times 5 \times 0.6 \) mm\(^3\) were cleaved from different types of silicon (as listed in Table I) with the long axis along the \([110]\) direction, and with the long edge mirror polished to be orthogonal to the top face. A microhardness tester with a Vickers diamond tip was then used to make a line of indents along the length of the specimen, each separated by 250 \( \mu \)m. A 0.1 N load was used for a 5 s dwell time. This created a tangle of dislocations in the damaged region directly underneath each indent. A four-point bend at 600 °C, producing a uniform resolved shear stress of \( \sim 85 \) MPa, was then used for 35 min to expand the dislocations into half-loops with a diameter of approximately 200 \( \mu \)m, thus producing specimens that contained regular arrays of dislocations.

Specimens were then isothermally annealed for a controlled duration. During this anneal, impurities in the silicon diffused and segregated to the dislocations, producing a locking effect. Most anneals were carried out in either standard metallurgical furnaces (argon ambient) or a rapid thermal anneal (RTA) furnace (nitrogen ambient), at temperatures of 500–900 °C for durations of 0–5066 h, and were cooled in air. One set of experiments, with anneals at 725–1050 °C, used water quenching to achieve a faster cooling rate. Specimens annealed in this way were held between pieces of silicon and suspended by wire in a tube furnace that had been positioned vertically. At the end of the anneal period the wire was cut, and the specimen and its mountings fell through the furnace into a water bath below.

After annealing, all specimens were etched using a planar etch solution comprising \( \text{HNO}_3 \) (69\%), \( \text{CH}_3\text{COOH} \) (glacial), and \( \text{HF} \) (40\%) in the ratio of 75:17:8, to remove a \( \sim 20 \) \( \mu \)m layer from the surface. This was to remove the damage associated with the indents, and also to remove the near-surface regions of specimens, which might have been affected by outdiffusion of impurities during the anneal.

After this, specimens were subjected to three-point bend at 550 °C. This exposed the specimens to a stress that varied linearly along their lengths, from the maximum stress \( \tau_{\text{max}} \) at the central knife edge to zero at the outer knife edges. Dislocations from pinning points, while other results, obtained using a constant dislocation unlocking time, are analyzed in terms of nitrogen’s transport in silicon and interaction with dislocations.

### III. RESULTS

#### A. Time dependence of unlocking stress

Four sets of silicon specimens have been tested to investigate the effect of variation in three-point bend duration on measured unlocking stress. Anneal conditions were standardized for each set of experiments, although the different silicon types were given different anneals: 96 h at 600 °C for FZ-1, 48 h at 750 °C for NFZ-2 and NFZ-3, and 1 h at 650 °C for Cz-1. The results are presented in Fig. 1. They show that unlocking stress falls with increasing three-point bend duration, for all types of silicon tested. This indicates that accurate comparisons of unlocking stress between different specimens can only be made if the duration of the unlocking step is the same in each case. Given the scatter in the data, it is not clear whether the unlocking stress falls toward zero with increasing three-point bend duration, or whether there is also a component of unlocking stress that is independent of three-point bend duration.

#### B. Regime 1 NFZ-Si dislocation unlocking results

Dislocation unlocking stress measurements at 550 °C in NFZ-3 (\([\text{N}]=2 \times 10^{15} \) cm\(^{-3}\)) have been made at anneal temperatures of 500, 600, 675, 750, 825, and 900 °C, and typical results are shown in Fig. 2. Initially, nitrogen diffuses to

<table>
<thead>
<tr>
<th>Designation</th>
<th>Manufacturer</th>
<th>Doping (cm(^{-3}))</th>
<th>([\text{N}]) (10(^{15}) cm(^{-3}))</th>
<th>([\text{O}]) (10(^{17}) cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FZ-1</td>
<td>A</td>
<td>[P]=2 \times 10^{12}</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>NFZ-1</td>
<td>B</td>
<td>[B]=1.3 \times 10^{12}</td>
<td>0.3</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>NFZ-2</td>
<td>B</td>
<td>[P]=2 \times 10^{14}</td>
<td>Unknown</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>NFZ-3</td>
<td>A</td>
<td>[P]=6 \times 10^{13}</td>
<td>2</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cz-1</td>
<td>C</td>
<td>[B]=1.5 \times 10^{15}</td>
<td>&lt;0.1</td>
<td>6.32</td>
</tr>
</tbody>
</table>
and accumulates at the dislocation cores, producing a locking effect that increases with increasing anneal duration (known as regime 1). The unlocking stress then takes a constant value for all subsequent anneal times (regime 2). The initial rise in dislocation locking stress (regime 1) is strongly thermally activated. The gradient \( d \sigma_u/dt \) can be plotted in an Arrhenius plot for the temperatures where it is evident (500–750 °C), to discern an activation energy for the dislocation locking process. When this is done, an activation energy of 3.24 ± 0.25 eV is found. Regime 1 was not experimentally accessible at temperatures higher than this, as the required anneal times were too short for the available furnaces.

A numerical simulation can be used to model the regime 1 results, to find values for the effective diffusivity of nitrogen. The simulation, which was also used to model previous Cz-Si experiments,26,27 calculates the number of atoms that accumulate at the dislocation core after annealing at different temperatures for different durations. Diffusion of a single species with concentration of \( 2 \times 10^{15} \) cm\(^{-3} \) is modeled. For this reason the values obtained are referred to as effective diffusivities, since there is uncertainty as to the nature of nitrogen’s transport mechanism, as explained above. Dislocation unlocking stress is calculated by multiplying the number of impurity atoms at the dislocation core by the locking strength per atom. This value is not known for nitrogen, but analysis of the time dependence of the dislocation unlocking stress, presented in Sec. IV A, indicates that it is similar to that for oxygen atoms, which is known to be 7 Pa cm.26 This value has therefore also been used for the simulation of nitrogen locking in this work.

The simulation was used to produce fits to the experimental dislocation unlocking data at 500, 600, 675, and 750 °C, the four temperatures at which regime 1 was evident. The values for nitrogen’s effective diffusivity used as the fitting parameter are shown in Table II, and displayed in an Arrhenius plot in Fig. 3 with data from other work. It can be seen that the effective diffusivity values inferred from the dislocation unlocking data are consistent with the higher temperature measurements. The expression for nitrogen’s effective diffusivity found from these results is

\[
D_{\text{eff}} = 200000 \exp\left(-\frac{3.24 \text{ eV}}{kT}\right) \text{cm}^2 \text{s}^{-1}.
\]

The value of the activation energy is accurate ±0.25 eV, while the prefactor is accurate only to an order of magnitude or more.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Effective diffusivity (cm(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>( 1.75 \times 10^{-16} )</td>
</tr>
<tr>
<td>600</td>
<td>( 2 \times 10^{-14} )</td>
</tr>
<tr>
<td>675</td>
<td>( 1 \times 10^{-12} )</td>
</tr>
<tr>
<td>750</td>
<td>( 2.5 \times 10^{-11} )</td>
</tr>
</tbody>
</table>

FIG. 1. Variation in unlocking stress (measured at 550 °C) with three-point bend duration for four different types of silicon.

FIG. 2. Dislocation unlocking stress measured at 550 °C in NFZ-3, annealed at 500 and 675 °C. Also included are numerical simulations of regime 1, with the indicated effective diffusivity of nitrogen as the sole fitting parameter.

FIG. 3. The effective diffusivity of nitrogen in silicon found in this and other work (Refs. 19, 39, and 40).
C. Regime 2 NFZ-Si dislocation unlocking results

Figure 4 shows the regime 2 data taken with NFZ-3, plotted against anneal temperature, along with results obtained using fast-quench annealing. The latter results contain an error of ±5 °C in the anneal temperature, compared to ±5 °C for the data taken using the standard annealing techniques. The results show that dislocation unlocking stress, measured at 550 °C, is dependent on anneal temperature, peaking at 600–700 °C and falling toward zero at 1000 °C.

IV. DISCUSSION

A. Time dependence of unlocking stress

The results showing a time dependence of the unlocking stress can be understood in terms of a theory of the release of dislocations from pinning points. If it is assumed that the interaction between the dislocation and the pinning points is of a short range nature, and the pinning points are arranged discretely, then the releasing rate \( \Gamma \) of the dislocation is

\[
\Gamma = LNv \exp\left(-\frac{[E - (\pi b^2/N)]}{kT}\right).
\]

where \( L \) is the length of the dislocation, \( N \) is the line density of the pinning points, \( v \) is the frequency of dislocation vibration, \( E \) is the maximum interaction energy of the pinning point and the dislocation, \( \tau \) is the applied resolved shear stress, and \( b \) is the magnitude of the dislocation’s Burgers vector. Rearranging gives the expression

\[
\tau = \frac{NkT}{b^2} \ln \Gamma + \frac{N}{b^2}[E - kT \ln(Nv)].
\]

The dislocation releasing rate \( \Gamma \) can be thought of as a reciprocal “unlocking time” \( 1/t \), so Eq. (3) predicts that the applied stress required to unlock dislocations (i.e., the unlocking stress) should fall off with increasing unlocking duration, as is seen in the results presented in Fig. 1. If \( \tau_0 \) is plotted against \( \ln \Gamma \), as shown in Fig. 5, the gradient of the plot can be used to infer the value of \( N \), the line density of the pinning points, using a value of \( b=3.8 \) Å.

Table III shows the pinning point line densities for the four types of silicon tested in this way. It can be seen that the three NFZ-Si types (with nitrogen locking) have line densities of one pinning point every ~10 nm, whereas the Cz-Si (with oxygen locking) has a pinning point density approximately four times greater than this. These small spacings strongly indicate that dislocation locking in these materials is not by precipitates. It is therefore believed that a species comprising single atoms or a small number of atoms is responsible for the effect. The indirect nature of these experiments means that the exact form of the locking species (e.g., monatomic or diatomic) cannot be determined. These results also confirm the previous observation, that for these annealing conditions, oxygen dislocation locking is likely to be by an atomic species rather than by precipitates.

Since, for the annealing conditions used, the measured unlocking stresses in the Cz-1 specimens are also approximately four times greater than those in the three NFZ-Si types, these results indicate that the locking stress per pinning point for nitrogen is similar to that for oxygen, which is known to be 7 Pa cm, as mentioned in Sec. III B above.

It should also be noted that the pinning point density in the NFZ-Si specimens is dependent on the anneal conditions that were used, with a higher concentration of pinning points leading to a larger unlocking stress. The thermally activated unpinning analysis of the time dependence of the unlocking stress was used above to deduce that the NFZ-1 specimens (annealed at 600 °C) have a pinning point density of \( 14 \times 10^7 \) m\(^{-1}\), whereas for NFZ-2 and-3, annealed at 750 °C, the value is lower (approximately \( 9 \times 10^7 \) m\(^{-1}\) for both). This agrees well with the experimental unlocking data presented in Fig. 4, which show that the strength of nitrogen dislocation locking is greater at 600 °C than at 750 °C for different types of silicon.

<table>
<thead>
<tr>
<th></th>
<th>NFZ-1</th>
<th>NFZ-2</th>
<th>NFZ-3</th>
<th>Cz-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 ± 2 × 10^7 m(^{-1})</td>
<td>9 ± 3 × 10^7 m(^{-1})</td>
<td>9 ± 2 × 10^7 m(^{-1})</td>
<td>40 ± 10 × 10^7 m(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>
NFZ-3, and increases confidence in the accuracy of the thermally activated unpinning analysis used to deduce the density of pinning points.

**B. Regime 1: Transport of nitrogen in silicon**

The effective diffusivity of nitrogen found in this work, given in Eq. (1), is broadly consistent with measurements made at higher temperatures, as shown in Fig. 3. This indicates that a single mechanism is likely to be responsible for nitrogen transport from 500 °C up, toward the melting point. Dislocation unlocking experiments are sensitive to overall nitrogen transport, and only give direct information about the specific nature of the transport mechanism if the scaling with nitrogen concentration is investigated, which has not been done here (although other dislocation unlocking measurements in silicon ion implanted with high concentrations of nitrogen have recently provided evidence for dissociative nitrogen transport\(^{27}\)). However, the diffusivity prefactor of \(200\,000\,\text{cm}^2\,\text{s}^{-1}\) is unusually high for simple diffusion in silicon, and it is not clear what physical mechanism could lead to such a high value for the nitrogen dimer, indicating that simple dimeric diffusion is unlikely.

Alternatively, the results can be analyzed in terms of a dissociative mechanism of nitrogen transport,\(^{21-23}\) where a practically immobile dimer splits into fast-moving monomers, which diffuse until they recombine. If transport is occurring by the diffusion of both monomers and dimers, then the total flux of atoms is given by

\[
J = D_1 \frac{dC_1}{dx} - 2D_2 \frac{dC_2}{dx},
\]

where \(D_1\), \(D_2\) and \(C_1\), \(C_2\) are the diffusivities and concentrations of the monomer and dimer, respectively. This equation can be approximated by the expression

\[
J \approx -D_{\text{eff}} \frac{dC}{dx},
\]

where \(C=C_1+2C_2\) is the total nitrogen concentration, and

\[
D_{\text{eff}} = \frac{C_1D_1 + 2C_2D_2}{C_1 + 2C_2}.
\]

As mentioned above, the nitrogen interstitial dimer is known to be the dominant form,\(^{12,13}\) i.e., \(C_2 \gg C_1\), so \(D_{\text{eff}}\) can be approximated as

\[
D_{\text{eff}} \approx \frac{C_1D_1}{2C_2} + D_2.
\]

Now, in equilibrium, the concentration of monomers and dimers is related by

\[
C_2 = \frac{g_2}{g_1} \frac{\Omega_0}{\Omega_1} \exp \left( \frac{\Delta G_2}{kT} \right),
\]

where \(g_1\) and \(g_2\) are the number of available sites per unit cell for the interstitial monomer and dimer, \(\Omega_0\) is the unit cell volume, and \(\Delta G_2\) is the dimer binding energy (the full dynamic partition functions have been neglected as they are unlikely to alter the result significantly). Equations (7) and (8) are now combined. Critically, the dimer diffusivity \(D_2\) is neglected, reflecting the assumption that the nitrogen dimer is practically immobile. This gives the expression

\[
D_{\text{eff}} \approx \frac{C_1D_1}{2C_2} = \frac{g_1}{2 \sqrt{g_2} \Omega_0} \exp \left( -\frac{\Delta G_2}{2kT} \right) D_1.
\]

This can then be compared to the expression for nitrogen’s effective diffusivity inferred from the dislocation unlocking measurements described above, Eq. (1). \(\Delta G_2\) has never been measured but is calculated to be high, in the range of 3.67–4.30 eV,\(^{14,16}\) and the monomer and dimer degeneracies are \(g_1=12\) and \(g_2=6\), respectively.\(^{16}\) Using these values, an expression for the diffusivity of the nitrogen monomer can be inferred,

\[
D_1 = 30 \exp \left( \frac{-(1.1 - 1.4\,\text{eV})}{kT} \right) \text{cm}^2\,\text{s}^{-1}.
\]

This is broadly consistent with the expression given by another analysis in the literature.\(^{23}\) The activation energy for diffusion is greater than those calculated for the nitrogen monomer by theoretical groups, who find values of 0.4–0.5 eV.\(^{14,16,24,25}\)

**C. Regime 2: Interaction between nitrogen and dislocations**

The results presented in this work have shown that nitrogen locks dislocations at anneal temperatures of 500–1000 °C, a result that is consistent with previous work.\(^7\) However, nitrogen’s locking strength (measured at 550 °C) is dependent on anneal temperature, peaking at 600–700 °C and falling toward zero above 1000 °C. This is in contrast to the results found by previous nitrogen dislocation unlocking experiments, which found a constant locking strength at anneal temperatures of up to 1200 °C.\(^{30}\) The difference is accounted for by the faster postanneal cooling methods used in this present work: For an accurate result to be seen, cooling from high temperature must be fast enough to prevent significant amounts of nitrogen segregating to the dislocations during cool down after the anneal. Such fast cooling was thought to be unnecessary in the previous work because the earlier erroneous nitrogen diffusivity measurements\(^9,28-31\) had indicated that transport at high temperatures was orders of magnitude slower than has been shown in the present work.

It will be noted that nitrogen’s dislocation locking strength behaves differently from that of oxygen in Cz-Si. Previous work has shown that oxygen’s locking strength decreases with increasing anneal temperature for all temperatures measured,\(^26\) whereas Fig. 4 shows that this is not the case with nitrogen, where locking strength takes its highest value at 600–700 °C and is weaker at both lower and higher anneal temperatures.

**V. CONCLUSIONS**

Dislocation unlocking stress has been measured in FZ-Si, NFZ-Si, and Cz-Si specimens annealed for a variety of durations at different temperatures. It is found that dislocation unlocking stress falls with increasing unlocking duration
in NFZ-Si and Cz-Si materials. If analyzed in terms of a theory of thermally activated release of dislocations from pinning points, the results indicate that dislocation locking in NFZ-Si is by an atomic species rather than by precipitates, although the experiments could not distinguish between monoatomic and diatomic locking. The results also indicate that the locking strength per nitrogen atom is similar to that for oxygen atoms.

Other experiments measured dislocation unlocking stress at 550 °C in NFZ-Si specimens annealed at temperatures of 500–1050 °C. The data allow an effective diffusivity of nitrogen with an activation energy of 3.24 eV to be deduced in the 500–1050 °C range, a result that is consistent with previous measurements at higher temperatures using SIMS. If analyzed in terms of dimer-monomer dissociative transport, the results allow a diffusivity of the nitrogen monomer with an activation energy of 1.1–1.4 eV to be inferred. The NFZ-Si measurements also show that nitrogen’s saturation dislocation locking strength at 550 °C is dependent on the temperature of the previous anneal, peaking at 600–700 °C and falling toward zero at 1000 °C.

ACKNOWLEDGMENTS

The authors would like to thank Professor R. Jones of the University of Exeter for helpful discussions. C.R.A. gratefully acknowledges the EPSRC-GB for financial support.

37C. R. Alpass, J. D. Murphy, A. Jain, and P. R. Wilshaw, ECS Trans. 16, 249 (2008).