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Oxygen and Nitrogen Transport in Silicon Investigated by Dislocation Locking Experiments

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The behavior of oxygen and nitrogen impurities in silicon has been investigated using a novel dislocation locking technique. The locking effect of oxygen in Czochralski silicon (CZ-Si) was investigated in the 350-850°C temperature range and was found to display five well-defined regimes as a function of annealing time. Results indicate that enhanced transport of oxygen to dislocations takes place for temperatures below ~700°C. Numerical simulations of the enhanced oxygen transport indicate that the effective diffusivity becomes dependent on oxygen concentration with an activation energy of approximately 1.5 eV. The same technique has been used to investigate nitrogen transport in nitrogen-doped float-zone silicon in the 550-830°C temperature range and shows nitrogen to have a comparable locking effect to oxygen in CZ-Si, despite being present in a concentration that is 2 orders of magnitude lower. The stress required to unlock dislocations at 550°C which have previously been immobilized by nitrogen during an annealing step, initially increases approximately linearly with the duration of the anneal before saturating to a steady-state value of approximately 50 MPa for all anneal temperatures investigated. An expression for the transport of nitrogen to the dislocations was deduced, which has an activation energy of 1.45 eV.
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Oxygen is the major nonelectrically active impurity in Czochralski silicon (CZ-Si) and is normally present in concentrations of 10^{17}-10^{18} cm^{-3}. The presence of oxygen has both beneficial and detrimental influences on the production of integrated circuits using CZ-Si wafers. At the temperatures used for device processing, the oxygen is supersaturated and tends to form precipitates. These precipitates and any associated dislocations and stacking faults are often advantageous, because they act as gettering centers for unwanted metallic impurities. However, for gettering to work effectively the concentration and distribution of precipitates throughout the wafer must be carefully controlled. This in turn requires that the nucleation and growth of the precipitates is also controlled and these processes depend upon the transport of the oxygen through the wafer. Moreover, because the nucleation processes often take place in the 450-650°C temperature range, it is important to have accurate data on oxygen diffusion at these temperatures, and until recently, this has largely been lacking.

The presence of oxygen is also beneficial in that any left in solution is found to strengthen wafers and reduce the incidence of warpage.[1] However, oxygen also has negative effects, such as the production of mobile dislocations which are sometimes induced by large oxide precipitates. These mobile dislocations can weaken wafers and lead to warpage. Their immobilization or retardation can be achieved by the diffusion of oxygen atoms to the dislocation core, effectively resulting in the locking of dislocations.[2-4] Once again, this process depends on the transport of oxygen through the crystal and also on subsequent oxygen-dislocation interactions.

In this paper we present a review of our work concerning oxygen transport in silicon and its interactions with dislocations together with numerical modeling of the decoration and locking of dislocations for heat-treatments representative of actual device processing conditions.

In the case of float-zone silicon (FZ-Si), the oxygen content is usually below the detection limit and no appreciable locking of dislocations can be measured in pure FZ-Si crystals for any temperature and time of annealing.[5] However, the mechanical strength of wafers can be improved by doping the crystals with nitrogen,[4,6,7] which is then thought to decorate and lock the dislocations in a manner similar to oxygen when it is present. In addition to nitrogen doping of FZ-Si, there is increasing interest in nitrogen doping CZ-Si, because it has beneficial effects which include modifying the behavior of intrinsic point defects and the precipitation of oxygen.[8-10] However, as there is little experimental data available on the nature of the nitrogen species in silicon (monomer, dimer, or complex), its transport properties, and its interaction with dislocations, its use as a beneficial addition to silicon is being pursued mainly on an empirical basis at the present time.

In this paper details concerning the transport of nitrogen and its interactions with dislocations in nitrogen doped float-zone silicon (NFZ-Si) are presented. This data was obtained using the dislocation locking technique which was also employed for the measurements concerning oxygen. This technique uses accurate measurements of the stress required to move dislocations previously locked by decoration with oxygen or nitrogen during a high-temperature anneal. The critical stress required to just cause movement of a decorated dislocation is known as the unlocking stress, τ_u. Measurements of unlocking stress are relevant to the strength of wafers during device processing and they are also important because the time evolution of the unlocking stress measured as a function of annealing temperature provides values of the diffusivities of impurities in the range 10^{-12} to 10^{-16} cm^2 s^{-1}. Such relatively slow diffusion is often difficult to measure using other techniques but includes a range of values which is relevant to many of the important impurity-related processes which occur during processing of silicon.

Experimental

In order that the dislocation unlocking stress could be measured, rectangular specimens with dimensions $0.65 \times 3 \times 25$ mm were cleaved from (100) orientation CZ-Si wafers with oxygen concentrations of 2.6×10^{17} cm^{-3} (low), 6.3×10^{17} cm^{-3} (medium), and 10.4×10^{17} cm^{-3} (high) as measured by Fourier transform infrared spectroscopy (FTIR, DIN 50438/I). The cleaved edges were polished mechanically and chemomechanically. Unpolished wafers of (111) orientation NFZ-Si with a nitrogen concentration of 2.2×10^{15} cm^{-3} (measured by FTIR) were cut into bars with dimensions $2 \times 1 \times 30$ mm. Isotropic etching was used to mirror polish these bars on three sides. For control purposes, specimens from a nitrogen-free FZ-Si wafer were produced in a similar way. In addition, specimens were made from wafers with a high vacancy content ($\sim 10^{15}$ cm^{-3}) in order to investigate the effect of point defects on oxygen transport and locking of dislocations.

The bars were indented at 250 μm intervals using a Vickers diamond tip with 10 g load and a 5 s dwell time. The specimens were then subjected to four-point bending conditions under argon atmosphere at temperatures between 550 and 650°C to produce disloca-

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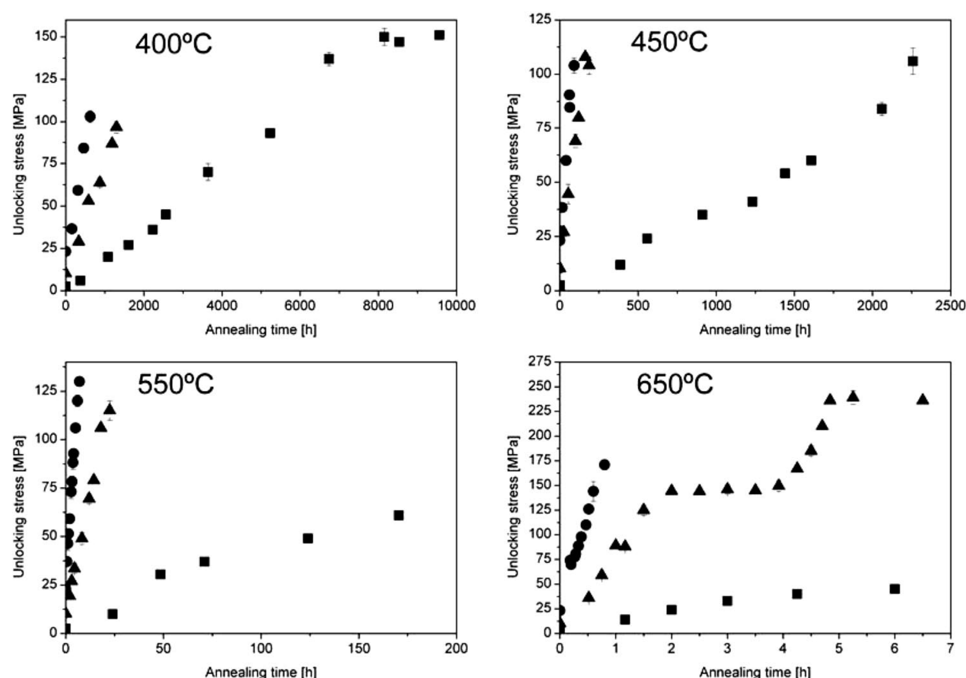

Figure 1. Experimental results for the dislocation unlocking stress as a function of annealing time for CZ-Si with three different oxygen concentrations: (■) Data for specimens with a low oxygen concentration (2.6×10^{17} cm^{-3}), (▲) data for specimens with a medium oxygen concentration (6.3×10^{17} cm^{-3}), and (●) data for specimens with a high oxygen concentration (10.4×10^{17} cm^{-3}).

tion half-loops up to 200 μm diam extending from the indented regions. This was followed by the removal of the surface damage to produce a mirror-finished surface.

The specimens were then annealed in an argon atmosphere at temperatures between 350 and 850°C for times between 10 s and 10,000 h. After annealing, the surface layer was removed to eliminate the effect of oxygen or nitrogen out-diffusion. For CZ-Si a 50 μm layer was removed by mechanical and chemomechanical polishing. For NFZ-Si a 30 μm layer was removed by chemical etching.

The bars were then subjected to a three-point bend at 550°C in an argon atmosphere under a carefully chosen load. The stress distribution in a three-point bend increases linearly from the external to the internal knife-edge, so each set of dislocation half-loops arising from a single indent experiences a different stress. At this stage, dislocation loops exposed to a stress less than the unlocking stress remain immobile, while those exposed to a stress greater than the unlocking stress move. The unlocking stress is found by noting the position on the specimen dividing those dislocations which have moved from those which have not. Thus, these measurements provide a value of the stress required, at 550°C, to unlock dislocations decorated with impurity atoms. This stress is a function of the temperature and duration of the previous anneal step during which impurities diffuse to the dislocation. Although most experiments involved measuring the unlocking stress at 550°C, in some cases it was measured at different temperatures and these results are presented in a separate section. The unlocking stress measured at any particular temperature is proportional to the concentration of impurities segregated to the dislocation core, and thus the dependence of this stress on the anneal temperature and duration can be used to infer information about the transport of the impurities to the dislocations. Upon cooling, a preferential etch was used to reveal the positions of the dislocation half-loops.

Oxygen in CZ-SI

Results and discussion.— Experimental results of unlocking stress as a function of annealing time are shown for selected temperatures in Fig. 1. Results for other temperatures are published elsewhere.[5,11] The unlocking stress as a function of annealing time is found to have five well-defined regimes, as depicted schematically in Fig. 2. In the first regime, oxygen is building up at the dislocation core due to the diffusion process. The steady-state regime (regime 2) is due to the establishment of a local equilibrium between the oxygen at the core and the background oxygen concentration. In this regime the value of the unlocking stress is dependent on the annealing temperature and the oxygen concentration. In the next stage, locking increases as a function of annealing time due to the onset of oxygen precipitation at the dislocation core (regime 3). With increasing annealing time the unlocking stress saturates again (regime 4). Finally, the unlocking stress decreases rapidly with increasing annealing time (regime 5).

No locking was found in samples of NFZ-Si. The dislocations in these specimens were mobile irrespective of the annealing temperature and the stress applied. Samples from CZ-Si wafers with a high vacancy concentration provided similar values for the unlocking stress to those without, suggesting that native point defects have no or negligible influence on oxygen transport at these temperatures. However, the effect of vacancies on the unlocking stress in NFZ-Si was not investigated in this work.

In regime 1, oxygen diffuses to the dislocation core and its concentration is limited by this process. The rate of increase in the

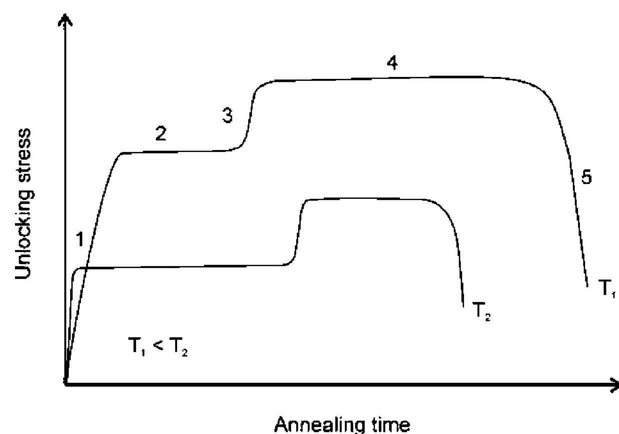

Figure 2. The locking effect due to oxygen in CZ-Si as a function of annealing temperature and time, depicted schematically.

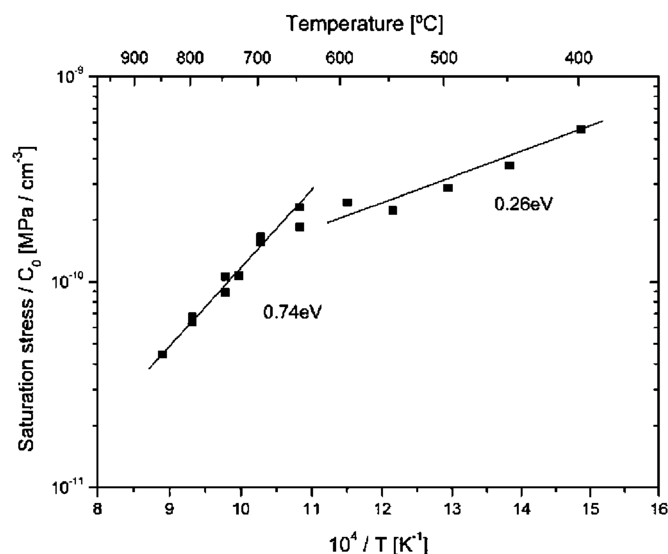

Figure 3. The saturation stress due to a local equilibrium between the oxygen at the dislocation core and the background oxygen concentration normalized by the oxygen concentration as a function of reciprocal temperature.

unlocking stress was found to be approximately linear with annealing time. At temperatures below ~650°C, the activation energy for transport of oxygen to the dislocation was found to be approximately 1.5 eV for all three oxygen concentrations investigated.

In regime 2, the unlocking stress, τ_u, saturates and the oxygen atoms at the dislocation core establish a Maxwell-Boltzmann distribution between those at the core and those in the bulk. This can be expressed in terms of the binding energy between an oxygen atom and a dislocation, ΔG.[12] Assuming that the unlocking stress is proportional to the number of oxygen atoms at the dislocation core, τ_u can be written as

$$\tau_u \propto C_0 \exp\left(-\frac{\Delta S}{k}\right)\exp\left(\frac{\Delta H}{kT}\right) \quad [1]$$

where C_0 is the oxygen concentration at the far field of diffusion, ΔS is the entropy change, and ΔH is the enthalpy change between an oxygen atom in the bulk and at the dislocation core.

From an Arrhenius plot of the values of the saturation unlocking stress in regime 2, the value of the oxygen-dislocation binding enthalpy, ΔH, can be determined (Fig. 3). Two different values are found, one for the high-temperature regime (~650-850°C) and one for the low-temperature regime (350-550°C). At high temperatures the binding enthalpy is 0.74 ± 0.01 eV. At low temperatures the binding energy was found to be 0.26 ± 0.04 eV.

Modeling and discussion.— During regimes 1 and 2, oxygen diffusion to the dislocation core can be described by

$$\frac{\partial C_0}{\partial t} = D_0 \nabla \left[\nabla C_0 + \frac{C_0 \nabla(\Delta G)}{kT}\right] \quad [2]$$

where D_0 is the oxygen diffusivity. Equation 2 was solved numerically using a cylindrical domain with the dislocation core at its center. The outer calculation boundary was chosen to be sufficiently large that the zero flux boundary condition could be used.

The boundary between the bulk material and the dislocation core was modeled such that both capture and remission of atoms to/from the core were considered. It was assumed that the capture is controlled by the oxygen concentration next to the core, C_1, the concentration of available sites at the core, C_a, and the concentration of occupied sites at the core, C_c. That is

$$\text{capture} \propto C_1 \frac{C_a - C_c}{C_a} \quad [3]$$

Emission of oxygen atoms from the core is assumed to be a function of the oxygen concentration in the core and their escape probability

$$\text{emission} \propto C_c \exp\left(-\frac{\Delta G}{kT}\right) \quad [4]$$

During simulations D_0 was treated as a fitting parameter.

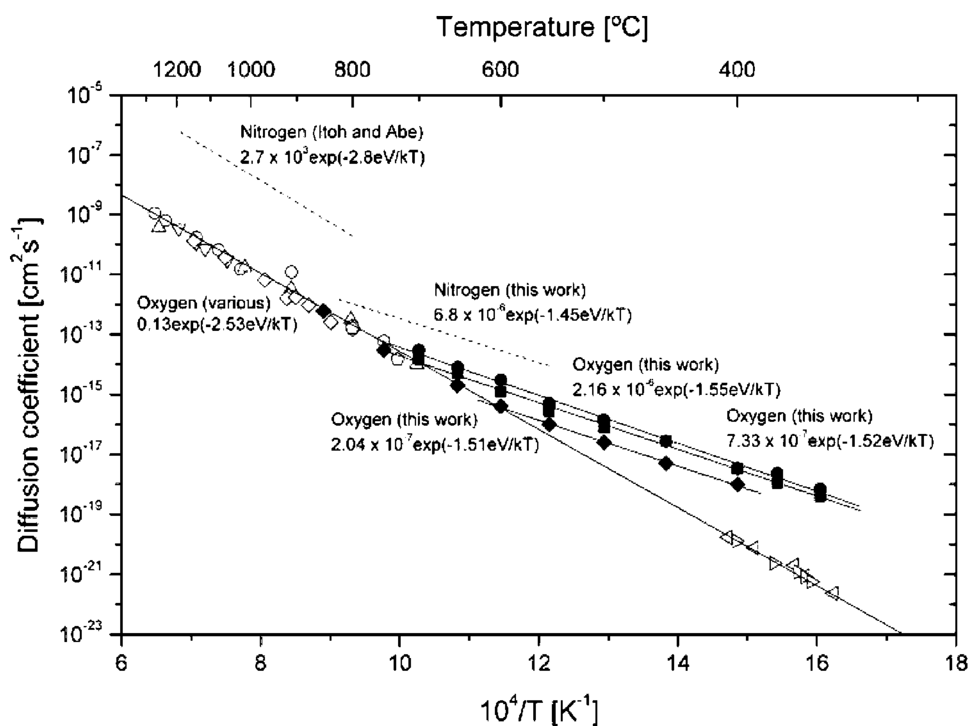

Figure 4. Diffusivity of oxygen and nitrogen in silicon as a function of reciprocal temperature. For oxygen, closed symbols are data in this work. (○, ●) High oxygen (10.4×10^{17} cm^{-3}), (□, ■) medium oxygen (6.3×10^{17} cm^{-3}), and (◇, ◆) low oxygen (2.6×10^{17} cm^{-3}). Open symbols are data from the literature.[12,13] The nitrogen data are from Itoh and Abe[16] and this work.

Figure 4 shows the results for the oxygen diffusivity as measured in this work compared to results in the literature.[13,14] There is excellent agreement for anneals at temperatures greater than ~700°C, giving an activation energy of ~2.5 eV. However, below this temperature the effective diffusivity is controlled by another activation energy of approximately 1.5 eV and its magnitude was found to become dependent on the oxygen concentration. Different expressions for the effective diffusivity were found for the three different oxygen concentrations studied

$$D_{\text{low}} = 2.04 \times 10^{-7} \exp\left(-\frac{1.51 \text{ eV}}{kT}\right) \text{cm}^2 \text{ s}^{-1} \quad [5]$$

$$D_{\text{medium}} = 7.33 \times 10^{-7} \exp\left(-\frac{1.52 \text{ eV}}{kT}\right) \text{cm}^2 \text{ s}^{-1} \quad [6]$$

$$D_{\text{high}} = 2.16 \times 10^{-6} \exp\left(-\frac{1.55 \text{ eV}}{kT}\right) \text{cm}^2 \text{ s}^{-1} \quad [7]$$

Comparison of the binding enthalpy data from Fig. 3 with the diffusivity data suggests that below approximately 650°C the movement of oxygen in CZ-Si is dominated by a species other than single oxygen atoms.

Furthermore, the results presented here indicate a 3 orders of magnitude enhancement in the oxygen transport at 350°C compared to previous measurements using stress-induced dichroism.[14] The stress-induced dichroism measurements follow the same relation, $D = 0.13 \exp(-2.5 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$, as found at temperatures above ~700°C; however, the stress-induced dichroism technique is sensitive only to the hopping of single atoms from one site in the crystal to another and is not sensitive to longer range transport of oxygen such as that required to lock dislocations. Thus, the values measured in this work indicate that much faster transport of oxygen is possible in the temperature range below ~650°C by an oxygen-containing species which is not a single monomer. It is expected that it will be this fast transport of oxygen which is relevant to many of the defect processes in silicon, such as the formation of thermal donors[15] and the early stages of precipitation, as well as the locking of dislocations by oxygen. The measurements made using different oxygen concentration wafers show that the effective diffusivity of oxygen in this low-temperature range varies approximately linearly with the oxygen concentration, and this indicates that the likely candidate for the fast diffusing species is the oxygen dimer as is shown in the following.

Assuming that oxygen can be incorporated in silicon in the form of monomers and dimers, the total flux of oxygen atoms can be written as

$$J = -D_1\frac{dC_1}{dx} - 2D_2\frac{dC_2}{dx} \quad [8]$$

where D_1, C_1 and D_2, C_2 are the diffusivity and concentration of the monomer and dimer species, respectively.

An approximate expression for the total flux is given by

$$J = -D_{\text{eff}}\frac{dC}{dx} \quad [9]$$

where C is the total oxygen concentration and D_{eff} is the "effective" oxygen diffusivity defined as

$$D_{\text{eff}} = \frac{C_1D_1 + 2C_2D_2}{C_1 + 2C_2} \quad [10]$$

For the case of the oxygen dimer, C_2 is not known but is assumed to be much smaller than the concentration of the dominant monomer, C_1, and hence

$$D_{\text{eff}} \approx D_1 + 2\frac{C_2}{C_1}D_2 \quad [11]$$

If oxygen dimers are in equilibrium with the monomers, then their concentration is described by

$$C_2 = C_1^2 \exp\left(\frac{|\Delta G_2|}{kT}\right) \quad [12]$$

where ΔG_2 represents the oxygen dimer binding energy and C_1 and C_2 represent the fraction of available sites in the lattice occupied by each oxygen species. Thus, from Eq. 11 and 12, the effective diffusivity can be written as

$$D_{\text{eff}} \approx D_1 + 2C_1D_2 \exp\left(\frac{|\Delta G_2|}{kT}\right) \quad [13]$$

From our data, and for the oxygen concentrations studied, it appears that the effective diffusivity is dominated by the first term of Eq. 13 at high temperatures and the second term of the equation below ~650°C. This implies that the small proportion of oxygen which is present as dimers at low temperatures diffuses sufficiently quickly that it dominates overall transport of oxygen. Moreover, when dimer transport dominates ($D_2 \gg D_1$) and if the dimer and monomer concentrations are in equilibrium, Eq. 13 becomes

$$D_{\text{eff}} \approx 2C_1D_{02} \exp\left(\frac{|\Delta G_2| - E_2}{kT}\right) \quad [14]$$

where E_2 and D_{02} are the activation energy and prefactor for dimer diffusion, respectively, such that

$$D_2 = D_{02} \exp\left(-\frac{E_2}{kT}\right) \quad [15]$$

From Eq. 14

$$D_{\text{eff}} \propto C_1 \exp\left(\frac{|\Delta H_2| - E_2}{kT}\right) \quad [16]$$

where ΔH_2 is the formation enthalpy of an oxygen dimer.

Thus, the effective diffusivity has an activation energy equal to $|\Delta H_2| - E_2$, and from our data we find this to have a value of approximately -1.5 eV. Equation 14 suggests that if oxygen transport at low temperatures is dominated by oxygen dimers, then the effective diffusivity should scale with the atomic oxygen concentration (or monomer concentration C_1) as indeed observed in our experiments (Fig. 4). Because it is difficult to make measurements at temperatures below about 400°C, due to the small amount of transport occurring, it is possible that at these very low temperatures other, more complex, species such as oxygen trimers contribute significantly to the overall transport of oxygen in silicon.

Temperature dependence of the unlocking.— The dislocation locking by oxygen during annealing and the unlocking of dislocations by applying stress are two separate processes. Previous results presented in this work used a constant unlocking temperature of 550°C with specimens annealed for a variety of different times at different temperatures.

To investigate the temperature dependence of the unlocking, two sets of samples were annealed at 730°C, one set for 15 min and the other for 90 min. From previous work[5] it is known that the specimens annealed for 15 min would be in the first regime of oxygen locking and specimens annealed for 90 min would be in the second regime. The unlocking procedure was then performed at temperatures between 450 and 700°C. The unlocking stresses measured as a function of unlocking temperature are shown in Fig. 5.

The unlocking stress was found to decrease with increasing unlocking temperature in an approximately linear way between 450 and 600°C, although the trend at temperatures above 600°C is less clear. The unlocking stress, τ_u, is proportional to the number of oxygen atoms at the dislocation core, N_c

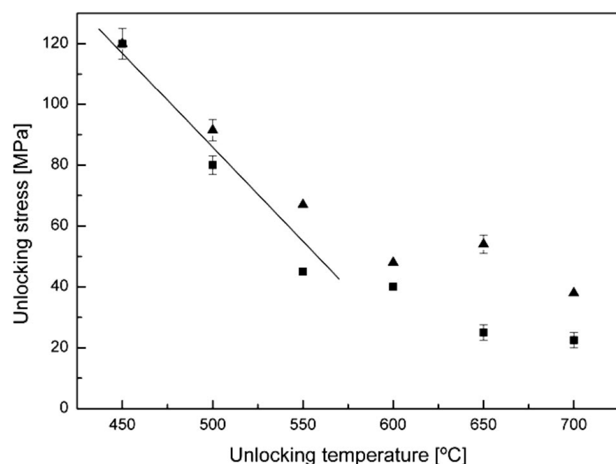

Figure 5. Unlocking stress as a function of three-point bend (unlocking) temperature. Specimens of medium oxygen concentration (6.3×10^{17} cm^{-3}) were annealed for (■) 15 and (▲) 90 min at 730°C.

$$\tau_u(T) = \tau_0(T) \cdot N_c \quad [17]$$

where τ_0 is the unlocking stress for unit concentration of oxygen atoms at the dislocation core. Using the previously deduced relation[5] that, at 550°C, the unlocking stress per atom per unit length along the dislocation core is 7 Pa cm, the results in Fig. 6 give an empirical expression for τ_0 as

$$\tau_0(T) = -0.07T + 64.61 \text{ Pa cm} \quad [18]$$

in the temperature range up to 600°C. The linear variation of the unlocking stress with increasing unlocking temperature is predicted by a simple theory of thermally activated release of dislocations from impurities.[17,18] According to this theory, the expression for the unlocking stress for a pinned dislocation segment is

$$\tau_u = \frac{N}{b^2}\left[\Delta G - kT \ln\left(\frac{LN\nu}{\Gamma}\right)\right] \quad [19]$$

where L is the dislocation length, N is the number of impurity (locking points) along a unit length of dislocation, ΔG is the maximum interaction energy between an impurity and the dislocation, ν is the vibration frequency of the dislocation, Γ is the release rate of the locked dislocation, k is the Boltzmann constant, T is the absolute temperature, and b is the magnitude of the Burgers vector of the dislocation. There are several parameters in Eq. 18 for which it is not possible to estimate accurate values. However, at absolute zero temperature the equation predicts

$$\tau_u = \frac{N\Delta G}{b^2} \quad [20]$$

whereas extrapolation of the experimental data yields a value of τ_u at absolute zero of ~65 Pa cm per atom per cm. From this value and using $b = 0.38$ nm for the dislocations studied, we infer that $\Delta G \approx 0.6$ eV. This value for the interaction energy between an oxygen atom and dislocation deduced from the temperature dependence of the unlocking stress is rather approximate given the errors involved in extrapolating the experimental data to absolute zero, but even so is in good agreement with the binding energy, 0.74 eV, deduced for dislocations annealed at the same temperatures by considering the equilibrium concentration of oxygen atoms at the core (Fig. 3).

Application of the numerical model to device processing.— The stress necessary to unlock dislocations varies with duration of thermal treatments and with temperature depending on the amount of oxygen atoms segregated to the dislocation core. In practice, time-temperature profiles during semiconductor device processing are often modified to minimize spatial temperature profiles and thus the thermo-mechanical stresses in wafers being processed. If external stresses are kept below the unlocking stress, then plastic deformation of wafers can be prevented.

The experimental results obtained from the dislocation locking experiments have provided quantitative values for oxygen transport over a wide range of temperatures and oxygen concentrations. These together with the value for the oxygen binding energy to a dislocation can be used in the numerical model used to solve the diffusion equation to predict the concentration of oxygen atoms at the dislocation core during any series of annealing treatments.[19] This data, together with the temperature dependence of the dislocation unlocking stress, can then be used to predict the stress required to move dislocations in a silicon wafer during device processing. Such predictions are only indicative because in a real wafer dislocations may be produced at precipitates or near the surface where the oxygen concentration is not equal to that in the bulk. In addition, our data for the unlocking stress above 600°C contains significant scatter and for the purposes of this analysis is assumed at these temperatures to be constant. Nonetheless, this approach does give an indication of how the strength of wafers will behave during device processing and the following example shows how a small heat-treatment modification can be used to increase the strength of a wafer during a particular processing step.

The graphs in Fig. 6 show a simple example of different heat-treatments, although the model could easily be applied to the more complicated treatments used in real device fabrication. Figure 6a shows an increasing temperature ramp (20°C/min up to 950°C)

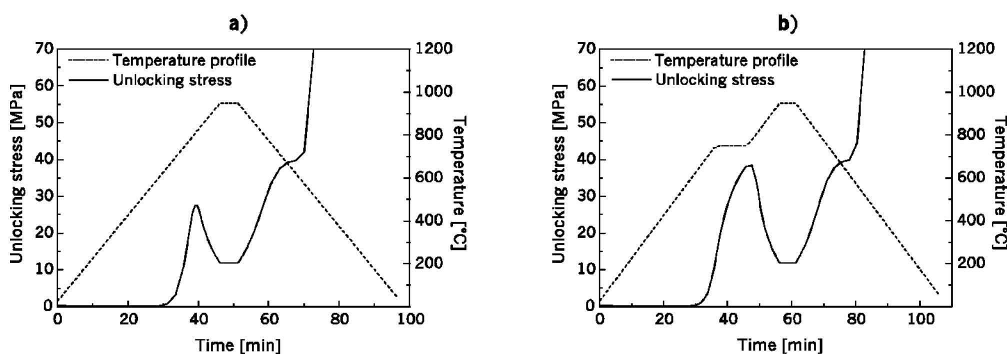

Figure 6. Unlocking stress and temperature profiles as a function time during multistep annealing treatments in CZ-Si with an oxygen concentration of 6.3×10^{17} cm^{-3}.

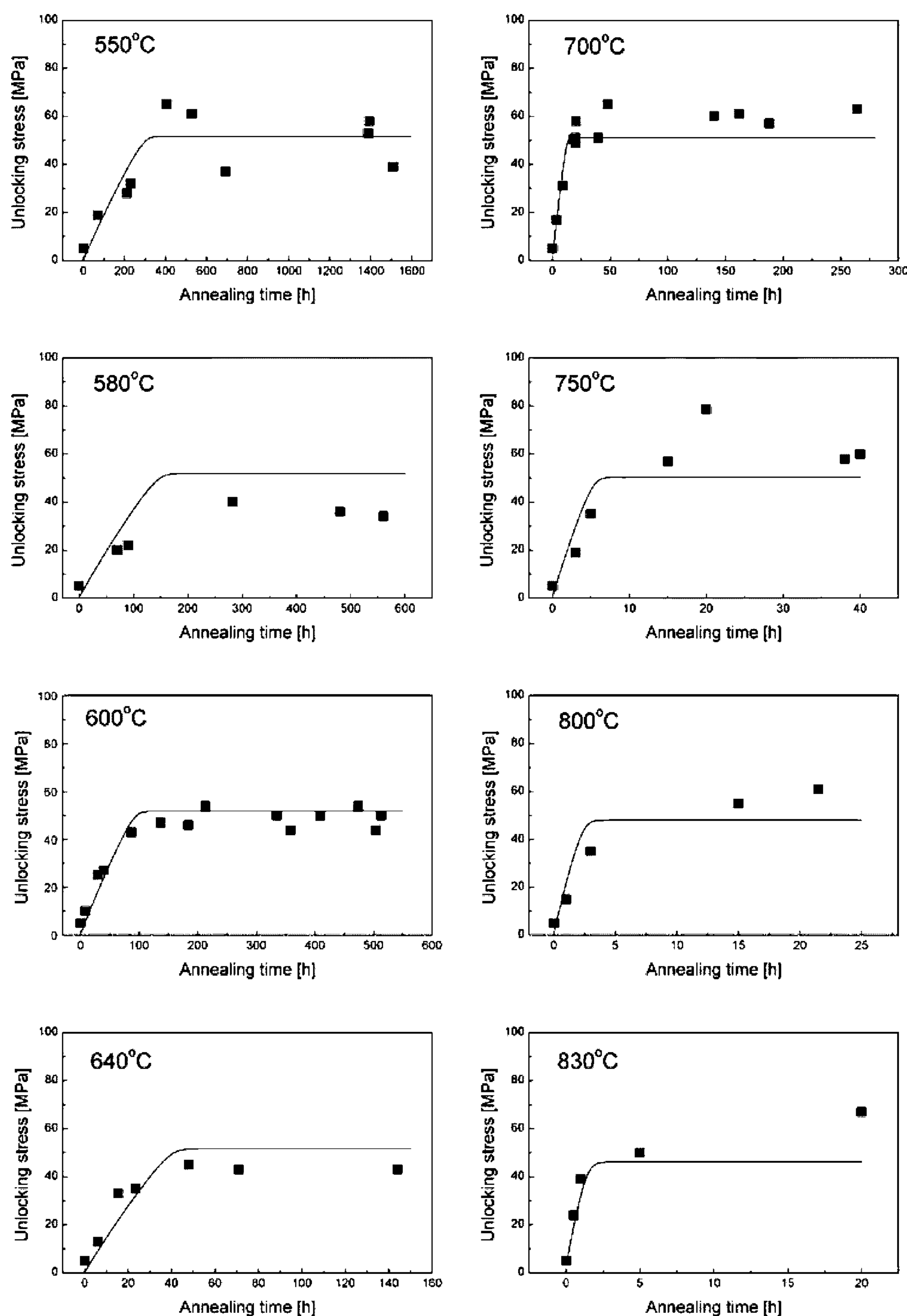

Figure 7. Data points represent the unlocking stress at 550°C in N-doped FZ-Si subjected to different annealing durations (0-1500 h) and different annealing temperatures (550-830°C). The lines represent values obtained by a numerical simulation.

followed by a constant temperature step (5 min at 950°C) and a final cooling step (20°C/min down to 25°C). During the increasing temperature ramp the value of the unlocking stress is initially negligible because the oxygen atoms at low temperatures move very slowly and do not have time to reach the dislocation core in significant numbers. The unlocking stress then increases sharply as the wafer temperature is raised from 700 to 800°C and diffusion becomes much more rapid; it subsequently decreases with almost the same slope until the constant temperature step at 950°C takes place. The decrease is due to the enhancement at higher temperatures of the emission of oxygen atoms from the dislocation core that dominates over the absorption process. In the final temperature step, during wafer cooling, the unlocking stress starts increasing again. Initially this is mainly due to increasing capture of oxygen atoms to the dislocation, but for temperatures below 600°C, when diffusion is relatively slow, the increase in unlocking stress is predominantly due to the thermally activated temperature dependence of the unlocking stress as described by the empirical expression.[18]

In another sequence shown in Fig. 6b, a pause in the heating ramp has been introduced at 750°C. In this case the calculation shows that the additional annealing treatment at 750°C for 10 min allows the unlocking stress to reach a maximum value during the heating that is approximately 11 MPa higher than the previous value. This increase is significant given that thermal stresses encountered during device processing are generally not very high and shows how a knowledge of oxygen transport and its interaction with dislocations may be exploited to improve the resistance to warpage of a silicon wafer.

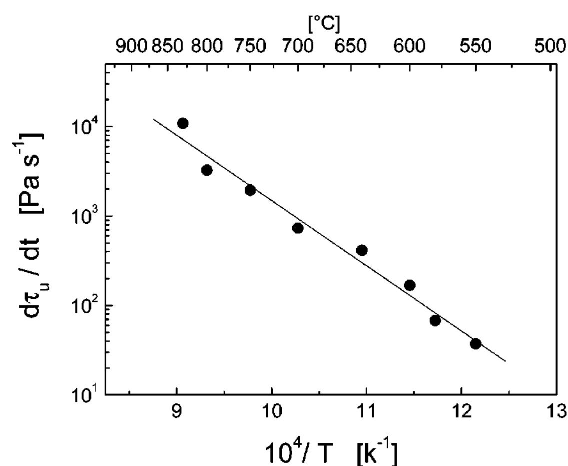

Figure 8. An Arrhenius plot of the gradient of the initial rate of increase in unlocking stress due to nitrogen in NFZ-Si as a function of the reciprocal of the annealing temperature.

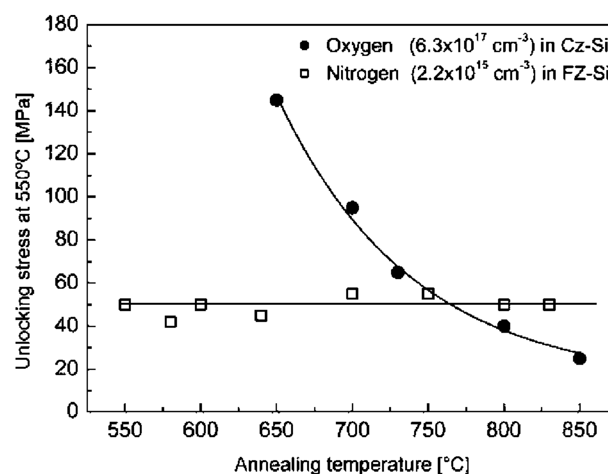

Figure 9. The saturation unlocking stress (regime 2), measured at 550°C, plotted as a function of the annealing temperature for dislocations in CZ-Si and NFZ-Si.

Nitrogen in FZ-SI

Results and discussion.— Dislocation unlocking experiments were performed on NFZ-Si material containing 2.2×10^{15} cm^{-3} nitrogen atoms. A strong locking effect on dislocations was found and, as in CZ-Si, the unlocking stress was found to increase initially with annealing time (regime 1) and the rate of increase was found to depend on the annealing temperature (Fig. 7). However, unlike for CZ-Si, the unlocking stress was found to saturate to the same value (~50 MPa) for all temperatures investigated (regime 2).

In regime 1, the unlocking stress, τ_u, increases at a rate controlled by transport of nitrogen to the dislocation core. Thus, an Arrhenius plot of the rate of increase of τ_u *vs.* $1/T$ gives the activation energy for this process. Such a plot is shown in Fig. 8 and from this an activation energy of 1.45 eV is inferred for nitrogen transport to the dislocations in the temperature range 550-830°C.

Modeling and discussion.— The nitrogen locking data presented in Fig. 7 can be modeled in a similar manner to that used for oxygen in CZ-Si. In the present work it is not possible to be sure which nitrogen species is responsible for transport to, and locking of, the dislocation. However, it is known that nitrogen is present in silicon at room temperature in the form of dimers and their binding energy is thought to be sufficiently high that this is true up to high temperatures and possibly even up to the silicon melting point.[20-22] If this is so then it seems likely that the species responsible for locking the dislocations is indeed the dimers and then the experimental data can be fitted with an expression for nitrogen dimer diffusion given by

$$D_{\text{dimer}} = 6.8 \times 10^{-6} \exp\left(-\frac{1.45\ \text{eV}}{kT}\right)\ \text{cm}^2\ \text{s}^{-1} \qquad [21]$$

although the estimated error in the prefactor of Eq. 21 can be up to an order of magnitude.

However, in the temperature range investigated, if dislocation locking is due to segregation of dimers, this does not imply that all nitrogen transport is dominated by dimers in this range. In fact, it is possible that the concentration of monomers in the bulk is so small that the equilibrium concentration of monomers at the dislocation core would be insufficient to give a significant locking stress (the saturation stress in regime 2). Thus, even if the transport of monomers was faster than that of dimers, the dislocation unlocking experiments would only be sensitive to the behavior of the dimers. Figure 4 shows that the diffusivity values obtained in this work are much lower than those obtained by Itoh *et al.* at high temperatures. It is proposed that the results presented here are consistent with those of Itoh *et al.* being due to fast diffusing monomers (to which out-diffusion measurements are sensitive), and that any monomer segregation to dislocation cores is too small to produce significant locking. From this point of view, nitrogen and oxygen in silicon behave similarly in that dimer transport dominates at low temperatures, but monomers become important at higher temperatures.

Comparison Between CZ-Si and NFZ-Si

From the point of view of device processing, a key issue is wafer warpage at high temperatures. As has already been shown, the segregation of oxygen to dislocations at high temperatures can leave them immobile until a stress exceeding τ_u, the unlocking stress, is applied. However, the binding energy of oxygen to dislocations is found to be rather small (~0.74 eV for anneals at high temperatures) and thus, the maximum concentration at the core, reached during regime 2 of the locking behavior, decreases rapidly as the temperature is raised. The concentration of oxygen at the core due to an anneal at a given temperature can be measured by unlocking the dislocations at 550°C, as was shown by our previous measurements, and such data is presented in Fig. 9 for a CZ-Si wafer annealed at temperatures up to 850°C. Also shown on the same graph is data obtained from a NFZ-Si wafer. This indicates that for anneals at high temperatures the effect of nitrogen present of concentrations of 2.2×10^{15} cm^{-3} (measured by unlocking at 550°C) is actually greater than that of the oxygen in the CZ-Si wafer measured at the same temperature. This is thought to be because of the greater binding energy of nitrogen to a dislocation which enables the core to be saturated with nitrogen even up to the higher temperatures. These results indicate that nitrogen could be a useful addition to silicon with regard to reducing high-temperature wafer warpage.

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