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Nitrogen transport in float-zone and Czochralski silicon investigated by dislocation locking experiments

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Dislocation locking experiments have been used to investigate nitrogen-doped float-zone silicon (NFZ-Si). Experiments on NFZ-Si with a nitrogen concentration of 2.2×10^{15} cm^{-3} were carried out at different annealing temperatures (550–830 °C) for different annealing times (0–1500 hours) and experiments on NFZ-Si with a nitrogen concentration of 3×10^{14} cm^{-3} were carried out at 600 °C for 0–1200 hours. After an initial rise, the unlocking stress was found to saturate for all combinations of conditions investigated. The rate of the initial rise was found to be consistent with diffusion by a dimeric nitrogen species. The saturation value of the unlocking stress was found to be dependent on the nitrogen concentration. Experiments were also carried out on nitrogen-doped Czochralski silicon (NCz-Si) with an oxygen concentration of 5.74×10^{17} cm^{-3} and a nitrogen concentration of 2.10×10^{15} cm^{-3} at 600 °C from 0–5 hours. The dislocation locking due to oxygen appeared to be unaffected by the presence of nitrogen for the conditions investigated.

1 Introduction

The intentional addition of nitrogen to silicon is of considerable interest since it can control vacancy concentration [1], affect oxygen precipitation [2–5] and improve mechanical strength by immobilising dislocations [6]. It has long been thought that nitrogen is incorporated into silicon as a dimer [7] and it has been established that dimeric nitrogen is an interstitial defect [8]. However, there is an open debate as to which species is responsible for nitrogen transport in different temperature ranges [9–12].

Wafers of float-zone silicon (FZ-Si) are more susceptible to warpage than Czochralski silicon (Cz-Si) wafers during high temperature treatments [13]. This is attributed to the locking of dislocations by oxygen in Cz-Si. The concentration of oxygen in FZ-Si is below the detection limit, and no appreciable locking of dislocations has been measured in pure FZ-Si crystals over a range of temperatures and annealing times [14]. It is thought that adding other chemical species, such as nitrogen, will improve the mechanical strength of FZ-Si [6, 15, 16] and it has been shown that the locking effect in nitrogen-doped FZ-Si (NFZ-Si) [6, 17] is comparable in magnitude to that in Cz-Si [6, 14, 18], despite the nitrogen concentration being more than two orders of magnitude lower than the oxygen concentration.

In this work, quantitative data on the mechanical strength of NFZ-Si crystals are presented. In particular, the critical shear stress necessary for dislocation motion at elevated temperature has been measured as a function of annealing time. Dislocations in silicon crystals can be pinned by impurity atoms during annealing, and the critical shear stress for movement of these locked dislocations is usually referred to as the *unlocking stress*. A comparison is made between unlocking stresses in NFZ-Si with different nitrogen concentrations.

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Nitrogen-doped Cz-Si (NCz-Si) is of considerable interest to silicon manufacturers, as it has been found that the presence of nitrogen can enhance oxygen precipitation after heat treatment [2–5], reduce the size of vacancy aggregates [1] and increase mechanical strength [6]. In this work, a direct measurement of dislocation locking in NCz-Si is made. This, besides giving quantitative values for the unlocking stress, gives information on the diffusivity of the species responsible for the immobilisation of the dislocations when both oxygen and nitrogen are present in a silicon crystal.

2 Experimental method

Wafers of NFZ-Si with different nitrogen concentrations (as determined by FTIR) were provided by Topsil Semiconductor Materials A/S. Bars measuring 2 mm × 1 mm × 30 mm were cleaved from a NFZ-Si wafer with a nitrogen concentration of 2.2×10^{15} cm^{-3} and bars measuring 0.5 mm × 3.5 mm × 30 mm were cleaved from a NFZ-Si wafer with a nitrogen concentration of 3×10^{14} cm^{-3}. Specimens with dimensions 0.65 mm × 3.5 mm × 30 mm were also cleaved from an NCz-Si wafer with an oxygen concentration of 5.74×10^{17} cm^{-3} (DIN 50438/I) and a nitrogen concentration of 2.10×10^{15} cm^{-3}. An overview of the experimental method is presented here; full details are given in Ref. [19].

Indents separated by 250 μm were made in a line along the centre of each bar. The bars were then subjected to a four point bend at approximately 550 °C to grow the dislocation loops to a diameter of approximately 200 μm. The specimens were then annealed at a range of temperatures and for a range of times. A planar etch was then used to remove approximately 30 μm of material from each bar.

A three-point bend at 550 °C was then applied to each bar. This subjected the dislocations arising from a particular indent to a unique stress; varying linearly from the outer to the central knife-edges. A preferential etch was used to reveal the dislocations and optical microscopy was then used to identify the dislocations that had moved under the applied stress. The minimum stress required for dislocation motion is a measurement of the dislocation unlocking stress.

3 Results and discussion

3.1 Nitrogen-doped FZ-Si

No appreciable locking effect was measured in high purity FZ-Si specimens, which were not intentionally doped with nitrogen. In NFZ-Si, a strong dislocation locking effect was observed. Data in Fig. 1 show the dislocation unlocking stress as a function of annealing time for NFZ-Si with a nitrogen concentration of 2.2×10^{15} cm^{-3}. The stress necessary to cause dislocation motion was found to increase roughly linearly with annealing time, with a rate strongly dependent on the annealing temperature (regime 1). The unlocking stress was then found to saturate (regime 2) to approximately 50 MPa for all annealing temperatures investigated.

If the locking of the dislocations is initially limited by diffusion of nitrogen to the dislocation core, the rate of increase in the unlocking stress, τ_u, would be proportional to the rate of transport of nitrogen to the dislocation. Thus, from an Arrhenius plot of $\ln(d\tau_u/dt)$ against $1/T$, the activation energy for transport of the locking species to the dislocation can be deduced. The data presented in Fig. 1, together with other values presented elsewhere [17], give a value of 1.45 eV for the activation energy for nitrogen transport to, and locking of, the dislocations.

A numerical model has been developed to describe the transport of nitrogen to the dislocation core [17]. This requires the concentration of the locking species, the diffusivity of the locking species, the number of available sites for occupation at the dislocation core and the binding energy of the locking species to the dislocation core as fitting parameters. By assuming that the nitrogen dimer is responsible for dislocation locking, numerical simulations of the diffusion process have been run and give the solid curves in Fig. 1.

The model was then used to predict the unlocking stress profile as a function of annealing time for NFZ-Si with a nitrogen concentration of 3×10^{14} cm^{-3}. The same fitting parameters were used to do this,

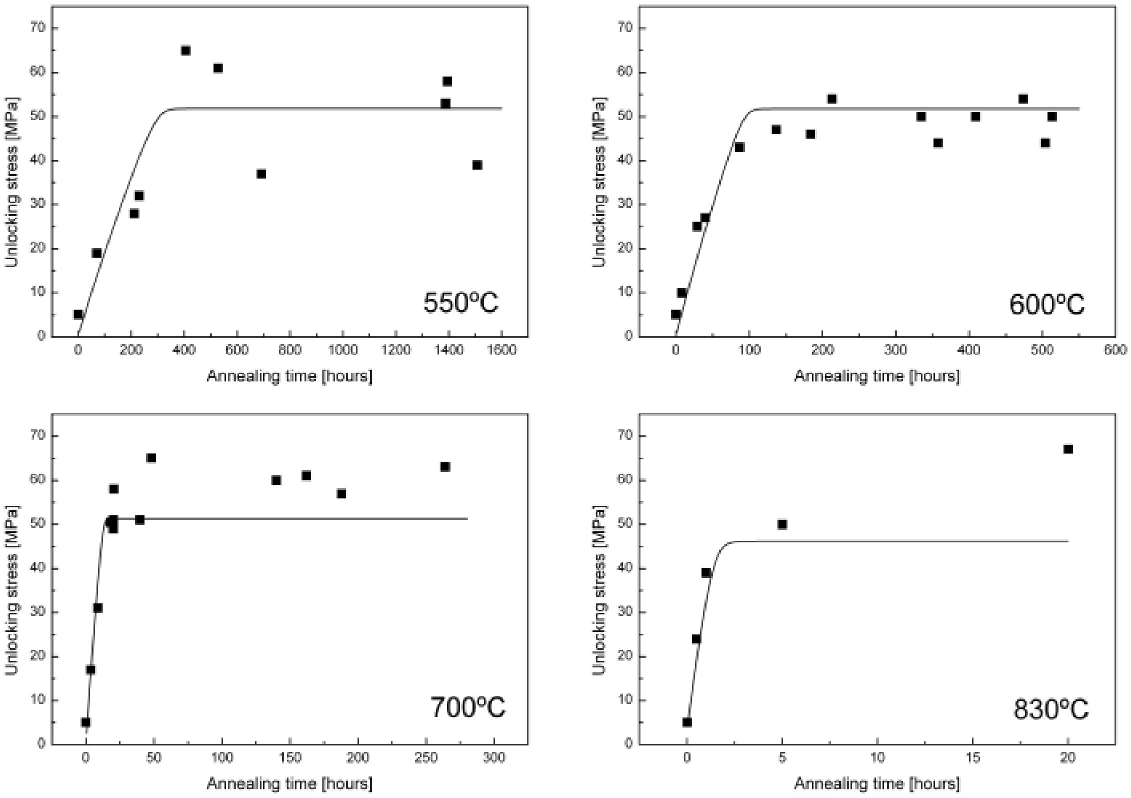

Fig. 1 Unlocking stress as a function of annealing time at various temperatures for NFZ-Si with a nitrogen concentration of 2.2×10^{15} cm^{-3}. The solid curves are from a numerical simulation.

as were the assumptions that the locking was due to the nitrogen dimer and that saturation was due to all the available sites at the dislocation core being full.

Figure 2 shows unlocking stress measurements as a function of annealing time at 600 °C for NFZ-Si with a concentration of 3×10^{14} cm^{-3}. The unlocking stress again rises approximately linearly with time (regime 1) before saturating to a value of approximately 20 MPa (regime 2). A comparison of the actual data is made with the prediction from the model, which is shown by a dashed line. Also shown on Fig. 2 are the unlocking measurements for NFZ-Si also at 600 °C with a nitrogen concentration of 2.2×10^{15} cm^{-3} and its associated numerical simulation.

The rate of the initial rise scales with nitrogen concentration as expected if the transport to the dislocations were due to a dimeric nitrogen species. If transport to the dislocation were due to a monomeric nitrogen species, the initial rise would scale as the square root of the ratio of the two nitrogen concentrations rather than as the simple ratio. However, the assumption that all the sites on the dislocation core are full is not justified by the experimental data. If this were the case then the saturation value of unlocking stress would be independent of nitrogen concentration. Additionally, it is noted from Fig. 1 that the value of the saturation unlocking stress is temperature independent and, because of this, it is not the case that the saturation is due to a local equilibrium between the nitrogen at the dislocation core and the nitrogen in the bulk being established.

3.2 Nitrogen-doped Cz-Si

The unlocking stress as a function of annealing time at 600 °C for NCz-Si is shown in Fig. 3. The unlocking stress is seen to rise approximately linearly with annealing time. As with the nitrogen results

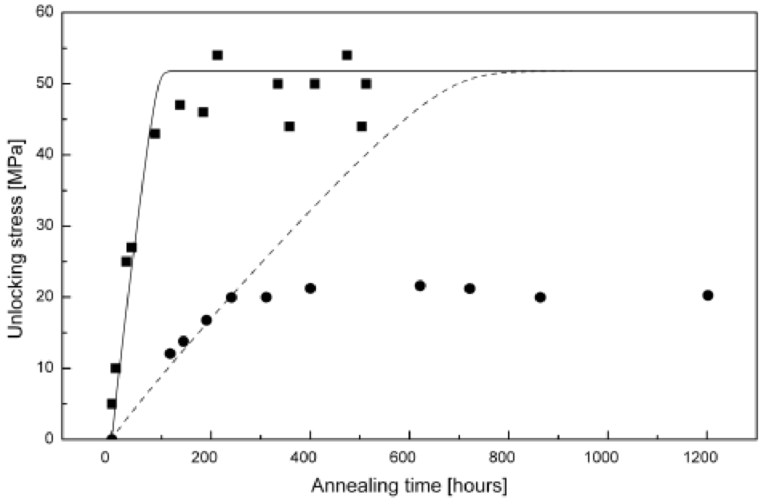

Fig. 2 Dislocation unlocking stress for NFZ-Si with nitrogen concentrations of 2.2 × 10^{15} cm^{-3} (squares) and 3 × 10^{14} cm^{-3} (circles) annealed at 600 °C. The numerical simulation (dashed line) is the expected unlocking stress if the locking species were dimeric nitrogen and if the saturation regime was caused by saturation of the dislocation core.

presented above and with other work on oxygen locking of dislocations [14, 18], this is due to locking being limited by the diffusion of the locking species to the dislocation core. Also shown in Fig. 3 are data for nitrogen-free Cz-Si with a similar, but slightly higher, oxygen concentration. Within experimental error this shows that the locking of dislocations in NCz-Si in regime 1 behaves the same as that for dislocations in standard Cz-Si with a similar oxygen concentration. In standard Cz-Si it has been shown that the locking is due to the transport of oxygen to the dislocation core [14, 18]. Thus, it is inferred from this work that the presence of nitrogen in NCz-Si has no significant effect on the transport of oxygen to dislocations at 600 °C for the annealing times investigated.

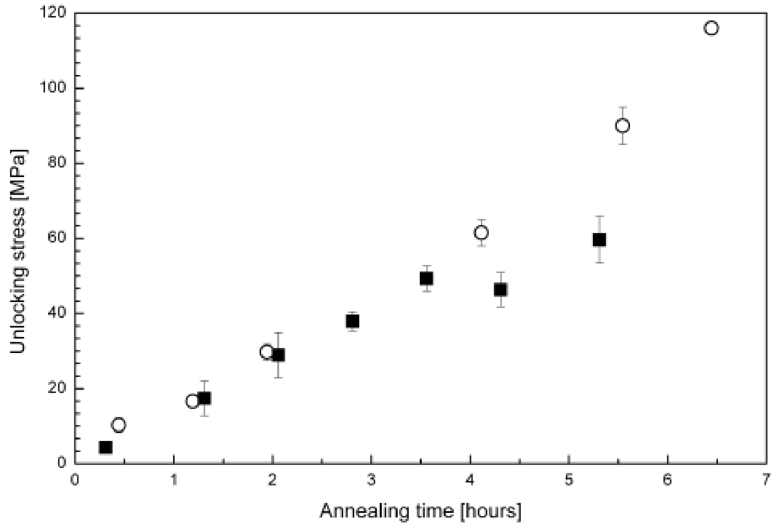

Fig. 3 Unlocking stress as a function of annealing time at 600 °C for NCz-Si with an oxygen concentration of 5.74 × 10^{17} cm^{-3} and a nitrogen concentration of 2.1 × 10^{15} cm^{-3} (filled squares). Also shown is data for Cz-Si with an oxygen concentration of 6.3 × 10^{17} cm^{-3} (open circles).

4 Conclusions

This experimental investigation provided quantitative data on the locking of dislocations in nitrogen-doped float-zone silicon due to annealing at temperatures between 550 and 830 °C. The unlocking stress as a function of annealing time showed two distinct regimes for all temperatures investigated. By varying the nitrogen concentration in the wafer, it was possible to show that the scaling in the gradient of the initial rise in the unlocking stress was consistent with dislocation locking by a dimeric nitrogen species. The activation energy for locking by this species was found to be 1.45 eV and the saturation value of the unlocking stress was found to be dependent on the nitrogen concentration. Additionally, the locking of dislocations in nitrogen-doped Czochralski silicon was investigated at 600 °C. The locking effect due to oxygen appeared to be unaffected by the presence of nitrogen for the conditions investigated.

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