ELSEVIER

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Physica B 340–342 (2003) 996–1000

PHYSICA B

www.elsevier.com/locate/physb

Dislocation locking by nitrogen impurities in FZ-silicon

A. Giannattasio[a,*], S. Senkader[a], R.J. Falster[b], P.R. Wilshaw[a]

[a] *Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK*
[b] *MEMC Electronic Materials SpA, viale Gherzi 31, 28100 Novara, Novara, Italy*

Abstract

The locking of dislocations by nitrogen impurities in nitrogen-doped FZ-grown (NFZ) silicon crystals was investigated as a function of time in the temperature range 550–830°C. It was found that nitrogen impurities induce a strong locking effect on stationary dislocations after a sufficiently long anneal. The locking is similar in magnitude to that observed for oxygen atoms in Czochralski-grown crystals (Cz), although the nitrogen concentration in the NFZ samples ($2.2 \times 10^{15}\,\mathrm{cm}^{-3}$) is two orders of magnitude lower than the usual oxygen concentration in Cz silicon. The unlocking stress initially increases with annealing time and then saturates to a value of approximately 50 MPa for all the temperatures investigated. Information concerning nitrogen diffusion is deduced and by making certain physically realistic assumptions, data is inferred regarding the binding energy of nitrogen and the dislocation pinning force per nitrogen atom at the dislocation core.
© 2003 Elsevier B.V. All rights reserved.

PACS: 61.72.Ff; 66.30.Jt; 61.72.Lk; 61.72.Yx; 62.20.Fe

Keywords: Silicon; Nitrogen; Dislocation; Diffusion

1. Introduction

Float-Zone-grown (FZ) silicon wafers are more susceptible to warpage than Czochralski-grown (Cz) silicon wafers when subjected to high temperature treatments [1]. Wafer warpage is a consequence of the generation and multiplication of glide dislocations in the crystal. In Cz silicon, the agglomeration of oxygen impurities to the dislocation core during annealing at high temperatures produces the immobilisation of dislocations, an effect called dislocation "locking" [2,3]. A controlled use of this effect can reduce the occurrence of plastic deformation of wafers during device processing [4]. However, in the case of high purity FZ silicon the content of oxygen is usually below the detection limit and no appreciable locking of dislocations can be measured in pure FZ crystals for any temperature and any time of annealing [5]. The mechanical strength of FZ silicon wafers can be improved by doping the FZ crystals with other chemical species like nitrogen [6–8]. It is thought that nitrogen is incorporated in silicon in the form of stable N–N pairs (dimers) that can dissociate into nitrogen interstitials (monomers) upon increasing temperature, although it is believed that, in the temperature range considered here, nearly all of nitrogen in silicon is present as dimers [9–11]. Unfortunately,

*Corresponding author. Tel.: +44-(0)-1865-283214; fax: +44-(0)-1865-273789.
E-mail address: armando.giannattasio@materials.ox.ac.uk (A. Giannattasio).

0921-4526/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2003.09.191

data available in the literature are still not complete nor sufficient for a full understanding of the interaction between nitrogen and dislocations in silicon. Furthermore, there is an open debate concerning the nitrogen species which is responsible for atomic transport at different temperatures [12–14].

In this work, quantitative data about the mechanical strength of nitrogen-doped-FZ-grown (NFZ) silicon crystals have been collected as a function of temperature and time of annealing. In particular, we have investigated the critical shear stress needed to start dislocation motion at high temperatures after dislocation decoration by nitrogen impurities. This critical shear stress is usually known as the *unlocking stress*.

Since the unlocking stress depends on the number of nitrogen atoms that segregate to the dislocation core during annealing, some important information about the diffusion coefficient of nitrogen and its binding energy to the dislocations can be deduced from an analysis of the unlocking stress measurements.

2. Experimental

This investigation was carried out using NFZ wafers (n-type, 220 Ω cm) provided by Topsil Semiconductor Materials. The nitrogen concentration in the wafers was $2.2 \times 10^{15}\,\mathrm{cm}^{-3}$ as measured by FTIR. Control samples consisting of pure FZ silicon without any intentional nitrogen doping were also used as a reference. The experimental method employed was almost identical to that previously used to study Cz silicon (1 0 0) wafers, full details of which can be found in Ref. [5]. The only difference in this work is that the NFZ silicon wafers had (1 1 1) orientation and were cut from the tail-end of a FZ silicon ingot grown in the presence of nitrogen gas. All unlocking stress measurements in this work were made using 3-point bending at 550°C.

3. Results and numerical analysis

No appreciable locking effect was measured in high purity FZ silicon specimens (control samples) which were not intentionally doped with nitrogen. However in NFZ silicon, despite the low concentration, nitrogen was found to have a strong locking effect on dislocations. Data in Fig. 1 show the unlocking stress measured at 550°C in NFZ silicon samples previously subjected to different annealing conditions. The stress necessary to unlock the dislocations was found to increase with annealing time, with a slope strongly dependent on the annealing temperature. Fig. 1 shows that after an initial approximately linear increase (regime 1), the unlocking stress saturates to a value (regime 2) roughly equal to 50 MPa for all the temperatures investigated.

Since the locking effect is due to the segregation of nitrogen to the dislocation core, the unlocking stress τ_u can be written as $\tau_u = n\tau_0$, where n is the number of nitrogen monomers or dimers (depending on the active species) accumulated at the dislocation and τ_0 is the unlocking stress for a dislocation pinned by a single monomer or dimer per unit length. The amount of nitrogen at the core is in turn controlled by the diffusion of nitrogen impurities during annealing at a certain temperature and the number of sites at the core available for occupation. The segregation of nitrogen to the dislocation is described by the following equation which can be solved numerically to simulate the diffusion of impurities to a dislocation [5,15]:

$$\frac{\partial C_i}{\partial t} = D_i \nabla \left[\nabla C_i + \frac{C_i \nabla(\Delta G_i)}{kT} \right], \tag{1}$$

where C_i is the concentration of the active nitrogen species, D_i is its diffusivity, k is Boltzmann's constant, T is the absolute temperature, ΔG_i is the Gibbs free energy (binding energy) of the interaction between a nitrogen impurity and a dislocation and t is the annealing time. However, for most of regime 1 the unlocking stress τ_u increases linearly with time and, under these conditions, the rate of increase in τ_u is proportional to the transport of nitrogen to the dislocation $D_N = D_{0N} \exp(-E/kT)$, where D_{0N} and E are the prefactor and the activation energy for nitrogen transport. Thus:

$$\frac{\mathrm{d}\tau_u}{\mathrm{d}t} \propto \frac{\mathrm{d}n}{\mathrm{d}t} \propto D_{0N} \exp\left(-\frac{E}{kT}\right) \tag{2}$$

and the activation energy for transport of the nitrogen species can be obtained by an Arrhenius plot of $\ln(\tau_u/t)$ against $1/T$, as shown in Fig. 2. In the temperature range 550–830°C we deduce the activation energy for transport of nitrogen to the dislocations to be $E = 1.45\,\mathrm{eV}$. In general, the transport of nitrogen in silicon is described by $D_N = \sum_i C_i D_i$, where C_i and D_i are the concentration and diffusivity of the ith nitrogen species present in the material. Therefore, for transport dominated by a species whose concentration is temperature dependent, the measured activation energy E will be the sum of the activation energy for diffusion and the activation energy determining its concentration. Whereas, if the concentration of the nitrogen species responsible for transport is effectively constant, then the measured activation energy will simply be equal to that for the diffusion of the active species.

In order to perform the full numerical simulation of the experimental data using Eq. (1), it is necessary to know the bulk concentration of the nitrogen diffusing species and the concentration of sites available for occupation by the locking species at the dislocation core. In the following, we assume that it is the nitrogen dimer (whose concentration is approximately temperature independent [9,10]) which diffuses to the dislocation and then locks it. With this assumption, we use in the simulation a dimer concentration of $1.1 \times 10^{15}\,\mathrm{cm}^{-3}$, that is half the total nitrogen concentration, and a density of available sites for dimers along the dislocation of $1.3 \times 10^{7}\,\mathrm{cm}^{-1}$, which is equivalent to nitrogen atoms lying along a perfect

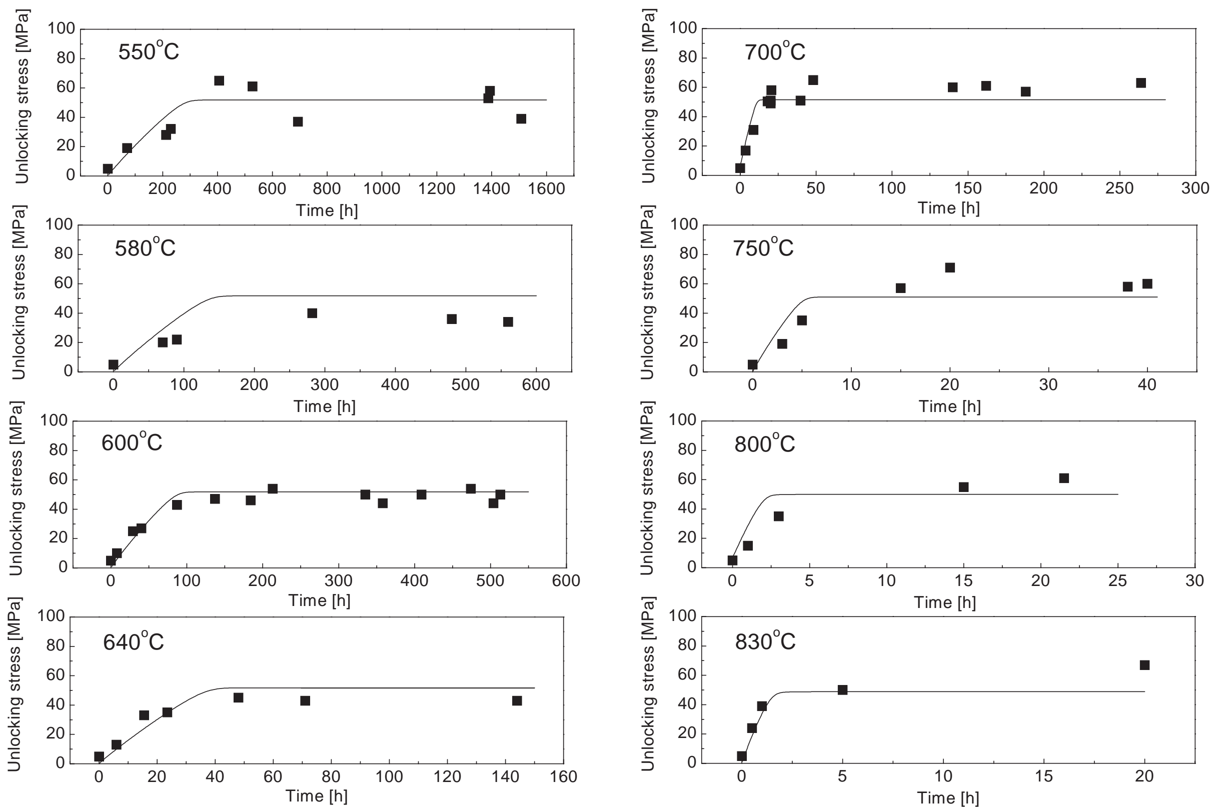

Fig. 1. Data points (squares) represent the unlocking stress measured at 550°C in N-doped FZ silicon samples subjected to different annealing durations (0–1500 h) and annealing temperatures (550–830°C). Values obtained by using a numerical simulation with fit parameters as described in the text are also shown in the figure (lines).

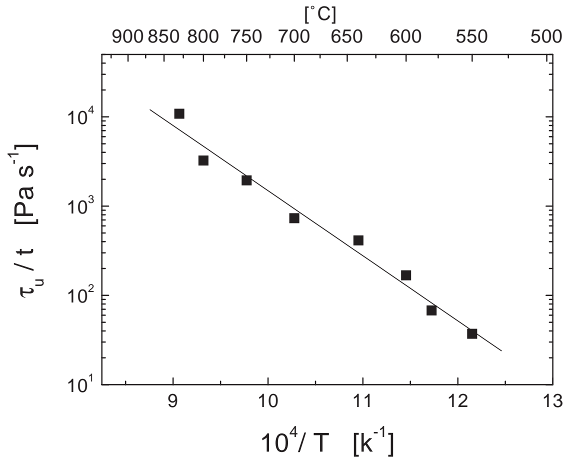

Fig. 2. An Arrhenius plot of the ratio τ_u/t at different temperatures. The best linear fit to the data gives an activation energy for nitrogen transport of 1.45 eV.

dislocation and accommodated in interstitial sites separated by 3.8 Å each from the other. The numerical simulation can then be used to fit all the experimental data of Fig. 1 using $\tau_0, D_{0\text{dimer}}$, ΔS and ΔH as fit parameters, where ΔS and ΔH are the entropy and enthalpy change after the interaction between a nitrogen dimer and the dislocation.

The calculated curves that best fit the experimental data over the temperature range of interest can be seen in Fig. 1. The values used for the curves shown are $D_{\text{dimer}} = 6.8 \times 10^{-6} \exp(-1.45\,\text{eV}/kT)\,\text{cm}^2\,\text{s}^{-1}$, $\tau_0 = 4\,\text{Pa cm}$, $\Delta H = 1.7\,\text{eV}$ and $\Delta S = 8.6 \times 10^{-5}\,\text{eV K}^{-1}$, although the simulation is rather insensitive to the particular value chosen for ΔS.

4. Discussion

The curves shown in Fig. 1 demonstrate that the numerical simulation can provide a good fit to the experimental data. The observed behaviour can be understood in terms of regime 1 being due to an increasing concentration of nitrogen at the dislocation core, as the anneal progresses, with transport of nitrogen to the dislocation being faster at high temperatures. Regime 2 occurs when all (or nearly all) of the available sites at the dislocation core are full. Once this point is reached, no further increase in locking can be obtained because the concentration at the dislocation is independent of time and temperature. In order for nearly all of the available dislocation sites to be filled (after sufficient time), in the temperature range 550–830°C the binding enthalpy ΔH of the nitrogen dimers to the dislocations must be greater than approximately 1.7 eV. This value is physically reasonable being roughly double the binding enthalpy already deduced for oxygen monomers ($\Delta H = 0.74\,\text{eV}$) at dislocations [5]. The value of the unlocking stress per nitrogen dimer, $\tau_0 = 4\,\text{Pa cm}$, is also comparable, but less than that for oxygen monomers (7 Pa cm). Thus, if the active nitrogen species is assumed to be dimers, then the experimental data can be modelled using physically reasonable values for the different parameters involved and the diffusivity of the dimers is given by $D_{\text{dimer}} = 6.8 \times 10^{-6} \exp(-1.45\,\text{eV}/kT)$. It should be noted that the experimental data can also be fitted assuming that nitrogen monomers are responsible for the locking process, but in this case the fit parameters required are less physically reasonable and the activation energy for transport (1.45 eV) then represents the sum of the activation energy for monomer diffusion and the activation energy controlling the monomer concentration. A fuller analysis of dislocation locking by nitrogen in terms of monomer and dimer transport and segregation to the dislocation core will be published elsewhere.

References

[1] S.M. Hu, W.J. Patrick, J. Appl. Phys. 46 (1975) 1869.
[2] S.M. Hu, Appl. Phys. Lett. 31 (1977) 53.
[3] K. Sumino, M. Imai, Philos. Mag. A 47 (1983) 753.
[4] A. Giannattasio, S. Senkader, S. Azam, R.J. Falster, P.R. Wilshaw, Microelectron. Eng. 70 (2003) 125.
[5] S. Senkader, K. Jurkshat, D. Gambaro, R.J. Falster, P.R. Wilshaw, Philos. Mag. A 81 (2001) 795.
[6] K. Sumino, I. Yonenaga, M. Imai, T. Abe, J. Appl. Phys. 54 (1983) 5016.
[7] J. Vedde, P. Gravesen, Mater. Sci. Eng. B B36 (1996) 246.
[8] L. Jastrzebski, G.W. Cullen, R. Soydan, G. Harbeke, J. Lagowski, S. Vecrumba, W.N. Henry, J. Electrochem. Soc. 134 (1987) 466.

[9] R. Jones, S. Öberg, F. Berg Rasmussen, B. Bech Nielsen, Phys. Rev. Lett. 72 (1994) 1882.
[10] H. Sawada, K. Kawakami, Phys. Rev. B 62 (2000) 1851.
[11] V.V. Voronkov, R. Falster, Solid State Phenom. 95–96 (2004) 83.
[12] T. Ito, T. Abe, Appl. Phys. Lett. 53 (1988) 39.
[13] R.S. Hockett, Appl. Phys. Lett. 54 (1989) 1793.
[14] L.S. Adam, M.E. Law, K.S. Jones, O. Dokumaci, C.S. Murthy, S. Hegde, J. Appl. Phys. 87 (2000) 2282.
[15] F.S. Ham, J. Appl. Phys. 30 (1959) 915.