# Generation and motion of dislocations in nitrogen-doped silicon single crystals



2002 J. Phys.: Condens. Matter 14 12903

(http://iopscience.iop.org/0953-8984/14/48/331)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 12903–12908 PII: S0953-8984(02)54002-9

# Generation and motion of dislocations in nitrogen-doped silicon single crystals

**M V Mezhennyi**[1], **M G Milvidski**[1], **V Ya Reznik**[1] **and R J Falster**[2]

[1] Institute of Rare Metals, Moscow, Russia
[2] MEMC Electronic Materials SpA, Novara, Italy

E-mail: icpm@mail.girmet.ru (M V Mezhennyi)

Received 27 September 2002
Published 22 November 2002
Online at stacks.iop.org/JPhysCM/14/12903

**Abstract**
Characteristic peculiarities of the generation and propagation of dislocations in nitrogen-doped silicon wafers (grown by the Czochralski method) were investigated by the four-point bending method. The critical stresses for the dislocation generation and dislocation velocity in nitrogen crystals are less than in non-doped crystals for equal loads. It was proposed that the strengthening of nitrogen-doped crystals is caused by the influence of nitrogen on the decomposition of the supersaturated oxygen solid solution during the cooling of the growing single crystals. As a result, many dispersed oxygen precipitates are generated in the crystal volume and harden it by hindering dislocation generation and propagation.

## 1. Introduction

In early papers on mechanical properties of silicon single crystals [1–5] it was shown that nitrogen doping caused material strengthening and, particularly, an increase of the upper limit of the plasticity. The earlier authors paid no attention to the nature of this effect and did not investigate the characteristic peculiarities of the generation and propagation of dislocations in nitrogen-doped silicon crystals. The purpose of this report is the investigation of characteristic properties of generation and propagation of dislocations in nitrogen-doped 'vacancy-type' silicon wafers by the four-point bending method in the temperature interval 500–800 °C.

## 2. Investigation technique

The wafers investigated were cut from nitrogen-doped, 150 mm diameter 'vacancy-type' single crystals. The boron-controlled resistivity of the nitrogen-doped samples was about 5 Ω cm. For comparison, we investigated 'control' non-nitrogen-doped samples prepared from crystal grown in the same conditions. The oxygen concentration was (7–8) $\times$ $10^{17}$ $cm^{-3}$ in all wafers. The list of the particular wafers used in the present study (all in the as-grown state) is as follows:

  

- sample series 1: nitrogen concentration in the melt $C_N = 1.6 \times 10^{14}$ cm$^{-3}$ (labelled NM—nitrogen medium);
- sample series 2: nitrogen concentration in the melt $C_N = 1.6 \times 10^{15}$ cm$^{-3}$ (labelled NH—nitrogen high)
- sample series 3: non-nitrogen-doped (labelled N0—nitrogen zero).

Samples for mechanical testing had the form of parallelepipeds with dimensions $25 \times 4 \times 0.6$ mm$^3$. The plane of the large side was $\{100\}$; the long edge of the sample was orientated along the $\langle 110 \rangle$ direction. Samples were etched in a mixture of hydrofluoric and nitric acids ($HF:HNO_3 = 1:6$) for 5 min. Layers of thickness $\sim$40 $\mu$m were removed from each surface during the etching. Subsequently, the $\{100\}$ surfaces of the samples were marked with 5–6 imprints from an indenter (Knupp) with a load of 0.25 N and an exposure time of about 15 s. The distance between imprints along the sample was 100 $\mu$m. After this, the samples were subjected to four-point bending [7]. The sample side with the imprints was stretched. The sample was placed into the furnace (already heated up to the desired temperature). In these conditions, the time taken to heat the sample to the loading temperature did not exceed 5 min. The time of exposure to the load was 20 min. After this, the sample was removed from the furnace and quenched in air. The dislocation pattern produced after loading was inspected with an optical microscope, after etching in a 1.5 M $CrO_3:HF = 1:1$ mixture for 5 min. Indentation produced dislocation half-loops; each half-loop consists of two 60° segments and one screw segment lying parallel to the surface of the sample. We concentrated on the movements of the 60° segments.

## 3. Results

The dislocation velocity, as a function of the applied shear stress $\tau$, is shown in figure 1, for loading at 500 and 600 °C. At higher loading temperatures, 700 and 800 °C, we could not plot the $V(\tau)$ function, because of the easy plastic flow: the unlocking stress was close to the plasticity limit. The numerous slip bands originating from the bulk sources masked the dislocations introduced by the indenter prints. The dislocation velocity could thus be measured only within a narrow interval of stress.

The temperature dependence of the dislocation velocity, for some characteristic values of stress, is shown in figure 2. Here results for only two values of $T$ (500 and 600 °C) are presented, for the reason mentioned above.

Figures 3(a), (b) show histograms of the nitrogen effect on the unlocking stress, $\tau_{cr}$, for indenter-induced dislocations, and on the stress $\tau_{pl}$ inducing a plastic flow (dislocation generation at numerous bulk sources). The two stresses are represented by a lower and upper column, respectively. In figure 3(a) the effect of the temperature, at specified nitrogen content, is shown, while in figure 3(b) the same data are presented in a form showing the effect of nitrogen at specified $T$.

The elements of the histograms at 500 °C contain black and white regions. The boundary between the shaded regions corresponds to the stress of brittle damage. The upper boundary of the shaded regions corresponds to the upper limit of plasticity at 500 °C.

The dependence on the nitrogen content of the unlocking stress is shown in figure 4, for the whole temperature range. There is a considerable—by a factor of 2—increase in the unlocking stress due to nitrogen doping. The nitrogen effect is already strong at the medium doping level (NM), and further increase in $C_N$ does not add much to the material strength.

In figure 5 the temperature dependences of the characteristic stresses are presented. Nitrogen doping increases not only the unlocking stress ($\tau_{cr}$) but also the critical stress ($\tau_{pl}$) for plastic flow caused by internal dislocation sources. The latter effect is most pronounced at temperature higher than 600 °C.

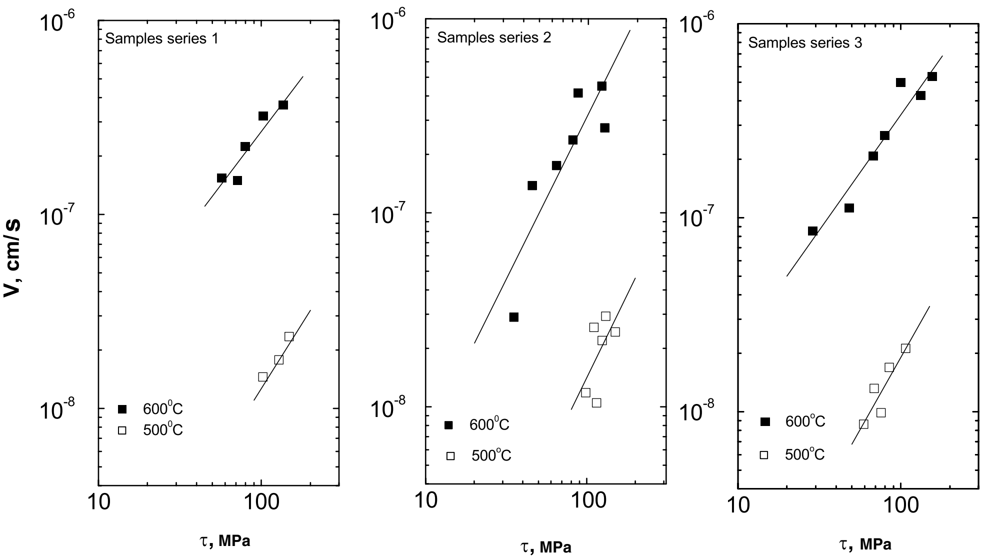


**Figure 1.** The dependence of the dislocation velocity on the applied shear stress, at $T = 500$ and 600 °C, in nitrogen-doped and reference crystals.

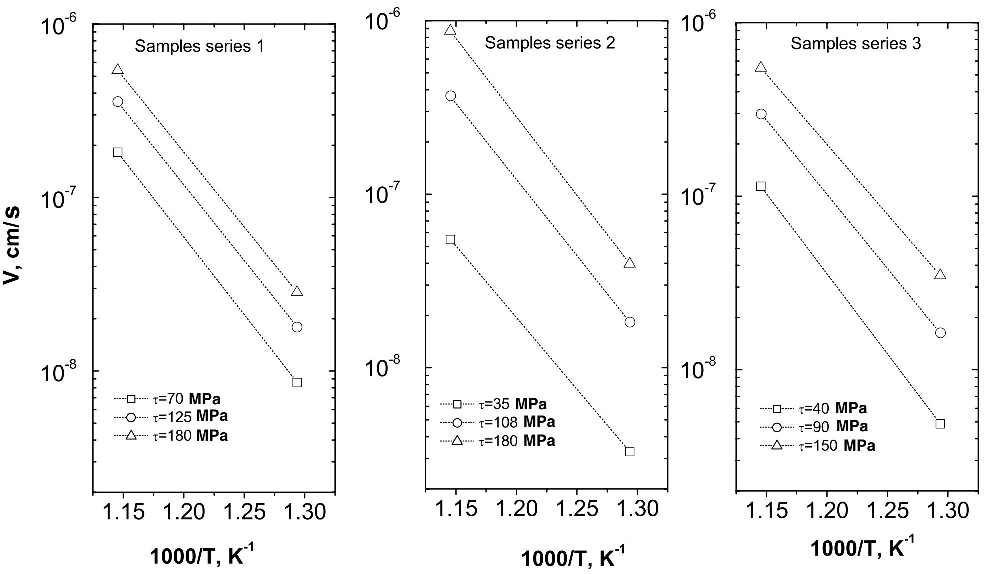


**Figure 2.** The temperature dependence of the dislocation velocity (in a limited temperature range 500–600 °C).

## 4. Discussion

The nature of the deformation is fundamentally changed within the temperature range 500–800 °C, at the stress level employed. The generation and motion of dislocations induced by the surface sources can be reliably monitored only at 500 and 600 °C, in the stress range 30–130 MPa. Higher stress results in brittle damage (at 500 °C) or combined plastic bending and

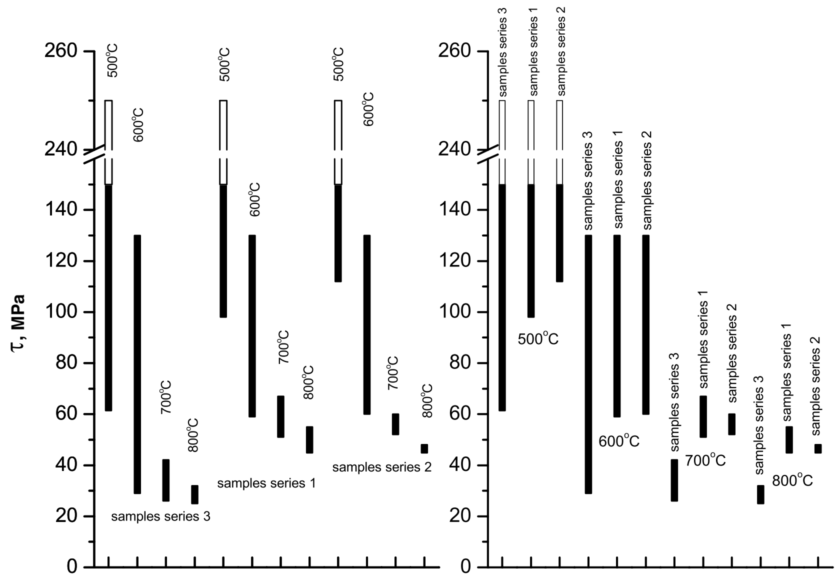


**Figure 3.** Histograms of the unlocking stress, $\tau_{cr}$, and the critical stress for plastic flow caused by bulk sources, $\tau_{pl}$: (a) presentation of data at various temperature $T$; (b) presentation of data at various nitrogen contents, $C_N$.

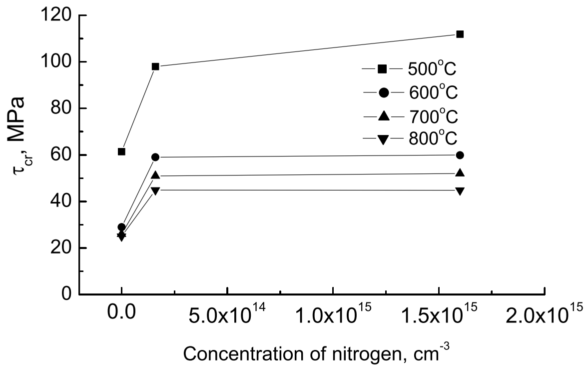


**Figure 4.** The dependence on the nitrogen concentration of the unlocking stress, $\tau_{cr}$, for $T = 500$–$800\,°\mathrm{C}$.

brittle damage (at 600 °C). At 700 °C—and to a greater extent at 800 °C—a drastic activation of bulk dislocation sources takes place. Accordingly, the unlocking stress and the plastic flow stress become comparable. The dislocation density in the sample bulk was strongly increased, the distinct slip bands were formed, and at stress more than 50 MPa a plastic bending—without any features of brittle damage—was observed. Therefore, it was practically impossible to measure the dynamic properties of dislocations at elevated loading temperatures. In short, it can be said that there is a well pronounced transition from the brittle damage (at lower $T$) to plastic deformation (at higher $T$). The transition is at about 600 °C.

Doping with nitrogen results in the material strengthening which is manifested in an increase in both the unlocking stress and the critical stress for plastic flow, and also in a decreased dislocation velocity (and increased activation energy).

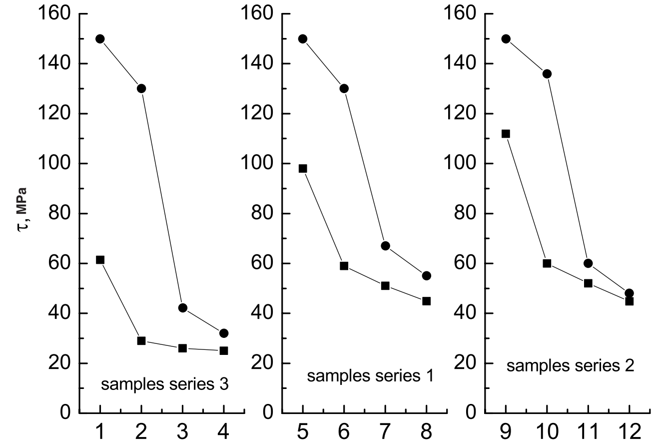


**Figure 5.** The temperature dependence of the unlocking stress, $\tau_{cr}$ (■), and the critical stress of plastic flow caused by bulk sources, $\tau_{pl}$ (●).

A medium doping level ($10^{14}$ $cm^{-3}$) is already enough to produce the strengthening effect. The unlocking stress becomes twice as large as that in non-doped material. The activation energy of dislocation motion is reduced by a factor of 1.15. The critical stress for plastic flow is increased significantly at 700 and 800 °C.

A higher doping level does not add much to the nitrogen-induced strengthening of silicon. On the contrary, the critical plastic stress is even reduced at higher $C_N$.

The multi-step annealing reduces the nitrogen-induced strengthening effect but does not eliminate it completely.

At the moment, it is hard to interpret, in a unique way, the nitrogen effect on the mechanical properties of silicon. It starts at surprisingly low concentration—only $10^{14}$ $cm^{-3}$. For comparison, the conventional dopants affect the strength at concentrations higher by 3–4 orders of magnitude [8]. Therefore one could think that the nitrogen effect does not occur by direct interaction with the dislocation core but rather by the effect of nitrogen on the intrinsic point defects, in the course of crystal growth. We already pointed out that the nitrogen effect can be attributed to an enhanced oxygen precipitation at low $T$ (below 800 °C). As a result, a high density of tiny oxygen clusters may be formed, and these clusters are obstacles for dislocation motion. This hypothesis is considered as crucial for the interpretation of the nitrogen-induced strengthening. At the same time, the absence of further strengthening on increasing $C_N$ to $10^{15}$ $cm^{-3}$ may indicate a direct effect of nitrogen on the dislocation generation and motion. The nitrogen solid solution is highly supersaturated, due to the limited solubility, and nitrogen can precipitate into very small clusters. This process may occur both in the course of crystal cooling and during subsequent anneals.

## 5. Conclusions

We have investigated the characteristic property generation and propagation of dislocations in nitrogen-doped silicon wafers (grown by the Czochralski method) by applying four-point bending. It is shown that the presence of nitrogen both increases the resolved shear stress and increases the stress formation in dislocations from internal sources. The dislocation velocities in nitrogen-doped crystals are higher than in non-doped crystals, for equal loads. It has been proposed that the process of strengthening by oxygen in the crystal occurs while cooling the ingot and, as a result, there is an increase in volume of the finely dispersed crystalline oxygen precipitates. The precipitates hinder the generation and propagation of dislocations.

## References


[1] Alexander H 1986 *Dislocation in Solids* vol 7, ed F R N Nabarro (Amsterdam: Elsevier) ch 35, p 113

[2] Sumino K 1985 *Proc. 1st Int. Autumn School on Gettering and Defect Engineering in Semiconductor Technology (Garzau)* ed H Richter p 41

[3] Senkader S, Jurkschat K, Gambaro D, Falster R J and Wilshaw P R 2001 *Phil. Mag.* A **81** 759

[4] Peidous I V and Loiko K V 2000 *Proc. Electrochem. Soc.* **17** 145

[5] Peidous I V, Loiko K V, Balasubramaniam N and Schuelke T 2000 *Proc. Electrochem. Soc.* **17** 180

[6] Milvidski M G 1998 *Proc. Higher Educ. Inst., Ser. Mater. Electron. Eng.* **3** 4

[7] Koncevoi Yu A, Litvinov Yu M and Fattahov E A 1982 *Plasticity and Durability of Semiconductor Materials and Structures* (Moscow: Radio and Communication)

[8] Imai M and Sumino K 1983 *Phil. Mag.* **4** 599