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Nitrogen in silicon: Transport and mechanical properties

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Abstract

A novel dislocation locking technique is applied to nitrogen-doped float-zone silicon. Specimens containing well-defined arrays of dislocation half-loops are subjected to isothermal anneals of controlled duration, during which nitrogen diffuses to the dislocations. The stress required to bring about dislocation motion is then measured, generally at 550 °C. The segregation of nitrogen to dislocations is found to be stable to at least 1200 °C, and the dislocation unlocking stress measured at 550 °C is of similar magnitude to that for oxygen in Czochralski silicon. At all annealing temperatures studied, the measured unlocking stress as a function of annealing time initially rises linearly before taking a constant value. The rate of the initial rise is found to be strongly dependent on temperature, with an activation energy of 1.5 eV. In a separate set of experiments, the magnitude of the dislocation unlocking stress measured is also found to depend upon the temperature at which the unlocking process takes place in the 500–700 °C temperature range. The dislocation locking technique is also used to give some measure of nitrogen out-diffusion, by measuring the unlocking stress as a function of material etched away after annealing. For specimens annealed at 750 °C for 15 h, the dislocation unlocking stress is found to rise with increasing depth away from the specimen's surface, before it takes an approximately constant value. By fitting an error function to these data, the diffusion coefficient of nitrogen in silicon is deduced to be approximately 4×10^{-11} cm^2 s^{-1} at 750 °C. This value is consistent with a SIMS investigation by Itoh and Abe.

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1. Introduction

Manufacturers of silicon wafers have recently become interested in intentionally adding nitrogen to wafers as it allows flexibility in controlling oxygen precipitation in Czochralski silicon (Cz-Si) [1–5], controls vacancy concentration [6] and improves mechanical strength [7–11]. In spite of its utility, many of the fundamental properties of nitrogen in silicon, such as its diffusivity, transport mechanism and binding energy to dislocations, remain a matter of debate.

The dominant nitrogen species in silicon is known to be the nitrogen dimer [12] and it has been established that it is an interstitial defect [13]. Numerical simulations generally suggest that the nitrogen atoms in the dimer are strongly bound with an energy of 3.67–4.30 eV [14–16] and that the dimer is practically immobile with an activation energy for diffusion of 2.38–2.69 eV [17,18]. Experimental data obtained by SIMS give an activation energy for nitrogen transport as 2.8 eV in the 800–1200 °C temperature range [19]. However, nitrogen diffusion in nitrogen-implanted silicon has been shown to exhibit anomalous behaviour [20], indicating that the transport of nitrogen is not a simple problem. Recently, it has been proposed that nitrogen is transported by a dissociative mechanism, whereby a practically immobile nitrogen dimer splits into two monomers which diffuse with an activation energy of 1.38 eV and then recombine [21]. However, because of the insensitivity of SIMS to nitrogen in silicon, measurements of nitrogen

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transport are limited to date and so alternative methods of measuring transport should be considered.

Dislocations in materials can be pinned by impurity atoms and the critical resolved shear stress necessary to move these locked dislocations is known as the *unlocking stress*. By studying the variation in the dislocation unlocking stress as a function of annealing time at different temperatures, it is possible to deduce information on impurity transport and impurity-dislocation interactions [22]. Such a dislocation locking technique has been used to study oxygen in Cz-Si, for which it reproduced existing values obtained by SIMS for the diffusivity of oxygen in the 700–850 °C temperature range [22] and provided new evidence for enhanced oxygen transport due to dimer diffusion in the 350–650 °C temperature range [23,24].

Float-zone silicon (FZ-Si), which is virtually free of impurities such as oxygen, acts as a model system for the study of other impurities in silicon. In this work, the dislocation locking technique is applied to nitrogen-doped FZ-Si containing different concentrations of nitrogen. Data are presented which show the variation of the dislocation unlocking stress with annealing time at annealing temperatures from 500 to 1200 °C. Data are also presented which show, for given annealing conditions, the dependence of dislocation unlocking stress on unlocking temperature in the 500–700 °C temperature range. By making a small change to the standard dislocation locking technique [9,22–24], it is possible to obtain a measurement of impurity out-diffusion. Results using this new method are presented which show out-diffusion of nitrogen from FZ-Si annealed for 15 h at 750 °C.

2. Experimental method

For the standard dislocation locking experiments, FZ-Si wafers produced by Topsil Semiconductor Materials A/S were used. Bars measuring 2 mm by 1 mm by 30 mm were cleaved from a (1 1 1) wafer (220 Ω cm n-type) with a nitrogen concentration of 2.2×10^{15} cm^{-3} and bars measuring 0.5 mm by 3.5 mm by 30 mm were cleaved from a (1 0 0) wafer (>10,000 Ω cm p-type) with a nitrogen concentration of 3×10^{14} cm^{-3}. The nitrogen concentrations were determined using FTIR carried out by the manufacturer. For the out-diffusion experiments, a (1 0 0) nitrogen-doped FZ-Si wafer (>100 Ω cm) produced by Wacker was cleaved into bars measuring 0.55 mm by 3.5 mm by 30 mm. The nitrogen concentration in the wafer was measured to be 2.5×10^{15} cm^{-3} by FTIR carried out by the manufacturer. It should be noted that since there is no generally accepted calibration standard for nitrogen concentrations in silicon, the nitrogen concentrations measured by the different manufacturers cannot be directly compared.

A Vickers diamond tip was used with a 0.1 N load and a 5 s dwell time to place indents at 250 μm intervals along the length of each bar. The bars were then subjected to a four-point bend at temperatures between 400 and 600 °C to grow the punched-out dislocation half-loops to a diameter of 100–200 μm. Specimens with the lower nitrogen concentration and those used in the out-diffusion experiments were cooled to below 400 °C before the load was removed.

For the standard dislocation locking experiments, the bars were then annealed at constant temperatures (from 500 to 1200 °C) for various times (from 0 to 4345 h). Specimens annealed at temperatures of 1000 °C and lower were annealed in argon atmosphere. Specimens annealed at 1100 °C and 1200 °C were sealed in evacuated silica ampules and were quenched after annealing by placing the ampule directly into water. In this way it is thought that no significant dislocation locking occurred during cooling. A planar etch comprising HF (40%), HNO_3 (69%) and CH_3COOH (glacial) in the ratio 8:75:17, which was found to etch silicon at the rate of approximately 0.8 μm/min at room temperature, was used to remove a controlled amount of material from each bar after annealing. For the standard dislocation locking experiments, the amount of material removed was 30 μm for specimens annealed below 1000 °C and 50 μm for specimens annealed at 1000 °C and above. This was done to remove the damage associated with the indents and to negate the effects of nitrogen out-diffusion.

A three-point bend at elevated temperature was then applied to each specimen. The stress in a three-point bending configuration varies linearly from the outer to the central knife-edges. Thus, dislocation half-loops at different points along the bar were subjected to different stresses [22]. A preferential etch comprising CrO_3 (0.3 M) and HF (40%) mixed in the ratio 5:4 was then used to reveal the dislocation half-loops. Optical microscopy was used to locate the dislocation half-loop that moved under the least resolved shear stress (i.e. the unlocking stress).

For most measurements the temperature of the three-point bending process was carefully controlled to be 550 °C. However, for one set of experiments the temperature dependence of the unlocking process was also investigated. Sets of specimens with a nitrogen concentration of 3×10^{14} cm^{-3} were annealed at the same temperature for a fixed time (640 °C for 150 h and 700 °C for 50 h). These specimens were then subjected to a three-point bend at different temperatures in the 500–700 °C temperature range.

To measure nitrogen out-diffusion, a small modification to the standard dislocation locking technique was made. A set of dislocation-containing nitrogen-doped FZ-Si specimens was produced using the methods described above. The specimens were all then annealed at 750 °C for 15 h. After this annealing stage, a different amount of material was removed from each specimen by the planar etch; from 5 to 55 μm. This was instead of the 30 or 50 μm of material removed in the standard process. The dislocation unlocking process was carried out by three-point bending at 550 °C.

3. Experimental results

The dislocation unlocking stress measured at 550 °C as a function of annealing time at different annealing temperatures is shown in Fig. 1. Data at other temperatures for high nitrogen-containing specimens have been published

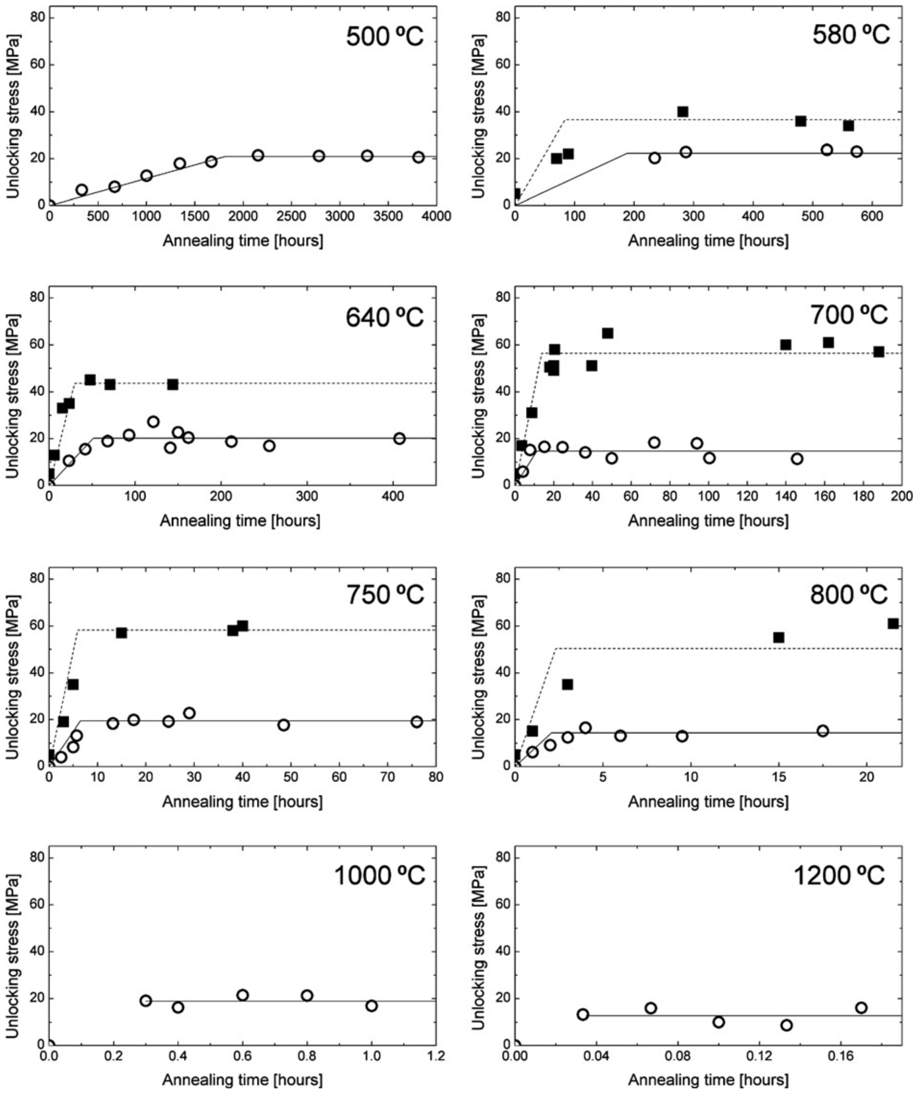

Fig. 1. The dislocation unlocking stress measured at 550 °C as a function of annealing time at selected annealing temperatures. The closed squares are for nitrogen-doped FZ-Si with a nitrogen concentration of 2.2×10^{15} cm^{-3} and the open circles are for nitrogen-doped FZ-Si with a nitrogen concentration of 3×10^{14} cm^{-3}.

elsewhere [9]. Nitrogen is found to provide a strong locking effect on dislocations in FZ-Si for annealing temperatures from 500 to 1200 °C.

The unlocking stress as a function of annealing time exhibits two distinct regimes for both nitrogen concentrations investigated. In the first regime the unlocking stress rises approximately linearly with annealing time, at a rate which is dependent on the annealing temperature and on the specimen's nitrogen concentration. In the second regime the unlocking stress takes a constant value, which is dependent on the nitrogen concentration and is approximately independent of the annealing temperature. For annealing temperatures of 1000 °C and above, data were only obtained in the second regime. This is because with the present experimental configuration the duration of the first regime is too short to allow accurate measurements to be made.

The gradient of the initial rise in unlocking stress, τ_u, with annealing time, t, in the first regime can be used to deduce the activation energy for the dislocation locking process. The rate of the initial rise in unlocking stress, $\frac{d\tau_u}{dt}$, is plotted as a function of reciprocal temperature in Fig. 2. This Arrhenius plot gives the activation energy of the dislocation locking process to be 1.5 ± 0.1 eV for both concentrations of nitrogen.

The unlocking stress measured as a function of unlocking temperature in the 500–700 °C temperature range for specimens subjected to certain annealing conditions is shown in Fig. 3. It can be seen that the unlocking stress decreases approximately linearly with increasing unlocking temperature.

In Fig. 4, the unlocking stress measured at 550 °C is plotted as a function of the material removed from specimens subjected to anneals at 750 °C for 15 h. The unlocking stress increases with the amount of material removed, before reaching an approximately constant value of 65 MPa.

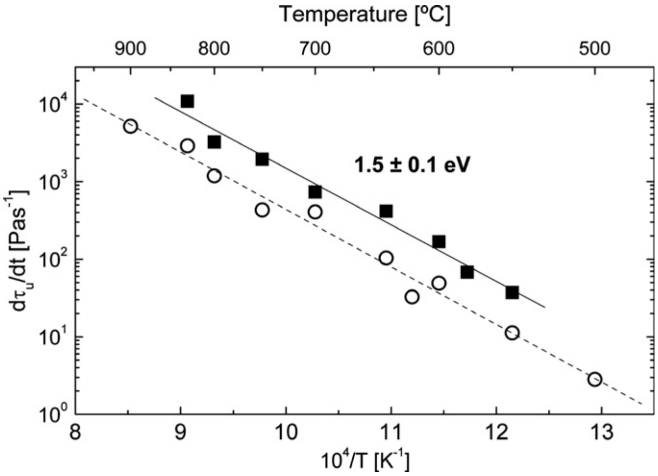

Fig. 2. An Arrhenius plot of the gradient of the initial rise in unlocking stress (regime 1), $\frac{d\tau_u}{dt}$, for specimens annealed at temperatures from 500 °C and 900 °C. The symbols used are the same as in Fig. 1. The closed squares are for nitrogen-doped FZ-Si with a nitrogen concentration of $2.2 \times 10^{15}\ \text{cm}^{-3}$ and the open circles are for nitrogen-doped FZ-Si with a nitrogen concentration of $3 \times 10^{14}\ \text{cm}^{-3}$. Best-fit lines to each set of data points are shown, both of which correspond to an activation energy of 1.5 ± 0.1 eV.

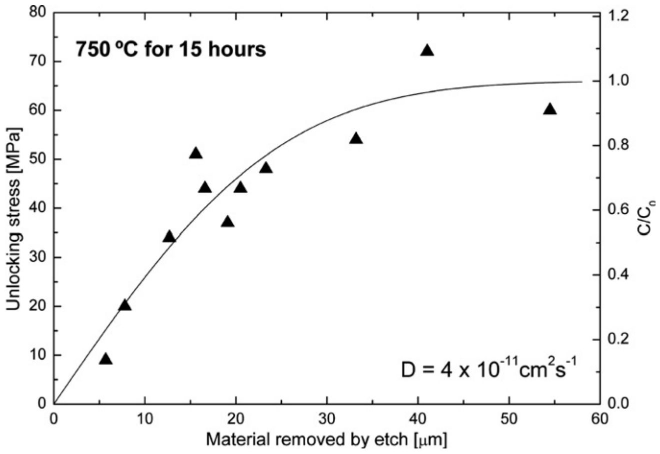

Fig. 4. The dislocation unlocking stress in nitrogen doped FZ-Si with a nitrogen concentration of $2.5 \times 10^{15}\ \text{cm}^{-3}$ measured as a function of material etched away, x, after annealing at 750 °C for 15 h. The closed triangles represent unlocking stress measurements. The best-fit curve is an error function of the form $\frac{C}{C_0} = \text{erf}\left(\frac{x}{\sqrt{Dt}}\right)$, where $\frac{C}{C_0}$ is the nitrogen concentration as a proportion of the total nitrogen concentration, D is the effective diffusivity of nitrogen and t is the annealing time.

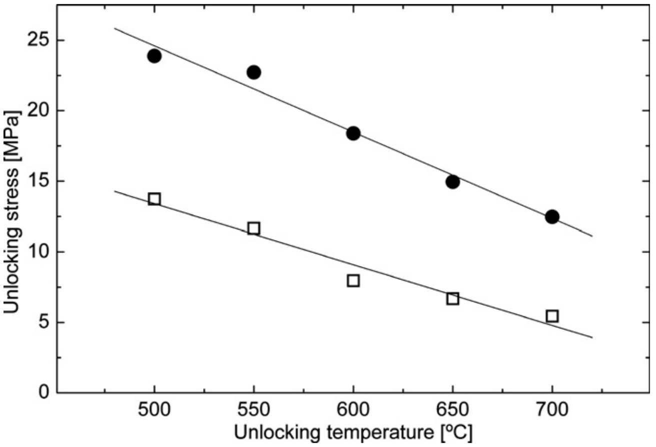

Fig. 3. The dependence of the dislocation unlocking stress on unlocking temperature for nitrogen-doped FZ-Si with a nitrogen concentration of $3 \times 10^{14}\ \text{cm}^{-3}$. The filled circles represent dislocation unlocking stresses in specimens annealed at 640 °C for 150 h. The open squares represent unlocking stresses measured for dislocations locked by annealing at 700 °C for 50 h.

The absolute values presented here for the unlocking stresses measured using the standard dislocation locking technique in the material with a low concentration of nitrogen differ from those presented previously [25,26]. The reason for this discrepancy is that the stress calculations have been recalibrated to be consistent with the stress measured in the material with a high concentration of nitrogen.

4. Discussion

It has been shown in this work that nitrogen is capable of providing a strong locking effect on dislocations, even though it is present in a concentration of just $3 \times 10^{14}\ \text{cm}^{-3}$ in some specimens. The dislocation unlocking stress measured at 550 °C has been found to be significant for specimens annealed at temperatures up to at least 1200 °C. The previously highest annealing temperature at which nitrogen locking of dislocations has been reported was 830 °C [9], so it is now known that nitrogen is capable of locking dislocations over the entire device processing temperature range.

The fact that dislocation locking by nitrogen is stable up to 1200 °C suggests that nitrogen binds strongly to the dislocation core. In previous work it was shown that dislocation locking by oxygen in Cz-Si is strongly reduced at temperatures greater than approximately 800 °C [22], as above this temperature oxygen, which has a binding energy to the dislocation core of 0.74 eV, “boils off” the dislocation. Thus the present work shows that nitrogen impurities provide dislocation locking in FZ-Si at temperatures at which oxygen impurities in Cz-Si do not. It is suggested that the addition of nitrogen to Cz-Si would be beneficial for the mechanical properties of these wafers, as nitrogen may be able to immobilise dislocations at temperatures at which the locking due to oxygen is practically non-existent.

From the Arrhenius plot in Fig. 2, the activation energy for the dislocation locking process has been found to be approximately 1.5 eV for both concentrations of nitrogen. The stress required to unpin the dislocation from nitrogen is also thermally activated. For the particular sets of annealing conditions studied, the unlocking stress decreases approximately linearly with the temperature at which the unlocking process takes place. Previous work using the same technique for oxygen in Cz-Si also shows an approximately linear dependence of dislocation unlocking stress on unlocking temperature [24].

If it is assumed that nitrogen diffuses to the specimen's surface during the annealing process, then a nitrogen concentration profile will be produced. Therefore, upon annealing, the segments of the dislocations close to the specimen's surface experience a nitrogen concentration lower than those in the bulk and will consequently be less strongly locked. During the subsequent unlocking process, the dislocations will first unpin from the position at which they are locked least strongly and it is this value of the unlocking stress that is measured. Thus, by removing different thicknesses of material after the annealing stage, the strength of the dislocation pinning at different depths beneath the surface, which depends on the nitrogen concentration at that depth, can be measured. In this work, 5–55 μm of material was etched away from the surface of a set of dislocation-containing specimens annealed at 750 °C for 15 h. As shown in Fig. 4, the dislocation unlocking stress measured in these specimens was found to increase as more material was removed, before it reached an approximately constant value.

The data are only indicative of the nitrogen concentration profile in the specimen since the concentration profile evolves during the course of the anneal. However, they do give an indication of the distances over which nitrogen diffusion to the surface is occurring. Bearing in mind these limitations, an error function profile fitted to the data in Fig. 4 gives the diffusion coefficient of nitrogen in silicon at 750 °C to be approximately 4×10^{-11} cm^2 s^{-1}. The nitrogen out-diffusion measured by the dislocation locking technique is consistent with that expected from a SIMS investigation by Itoh and Abe, since extrapolation of their reported diffusion expression gives a value of 4.3×10^{-11} cm^2 s^{-1} at this temperature [19].

5. Conclusions

Dislocation locking by nitrogen in FZ-Si has been investigated in the 500–1200 °C temperature range. It has been shown that nitrogen, despite being present at a concentration of only 3×10^{14} cm^{-3} in some specimens, is effective at locking dislocations throughout this wide temperature range. It is noted that dislocation locking by nitrogen in FZ-Si is stronger than that due to oxygen in Cz-Si at high temperatures (>800 °C) and it is suggested that the addition of nitrogen to Cz-Si will improve its mechanical properties.

The dislocation locking by nitrogen as a function of annealing time at a particular temperature is found to have two distinct regimes. By analysing the first regime, a linear rise, it is possible to deduce the activation energy for the dislocation locking process as 1.5 eV. The release of a dislocation from nitrogen impurities has also been shown to be a thermally activated process in the 500–700 °C temperature range.

The dislocation unlocking stress has been measured in a set of nitrogen-doped FZ-Si specimens annealed at 750 °C for 15 h, each of which has had a different amount of material removed from its surface after the annealing stage. The dislocation unlocking stress is found to increase with material removed, until it takes an approximately constant value. This variation in dislocation locking is due to nitrogen out-diffusion. From fitting an error function profile to the experimental data, the diffusion coefficient of nitrogen in silicon is estimated to be approximately 4×10^{-11} cm^2 s^{-1} at 750 °C.

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References

[1] F. Shimura, R.S. Hockett, Appl. Phys. Lett. 48 (1986) 224.
[2] Q. Sun, K.H. Yao, H.C. Gatos, J. Lagowski, J. Appl. Phys. 71 (1992) 3760.
[3] K. Aihara, H. Takeno, Y. Hayamizu, M. Tamatsuka, T. Masui, J. Appl. Phys. 88 (2000) 3705.
[4] K. Nakai, Y. Inoue, H. Yokota, A. Ikari, J. Takahashi, A. Tachikawa, K. Kitahara, Y. Ohta, W. Ohashi, J. Appl. Phys. 89 (2001) 4301.
[5] X.G. Yu, D.R. Yang, X.Y. Ma, J.S. Yang, L.B. Li, D.L. Que, J. Appl. Phys. 92 (2002) 188.
[6] D. Gräf, M. Suhren, U. Lambert, R. Schmolke, A. Ehlert, W.v. Ammon, P. Wagner, J. Electrochem. Soc. 145 (1998) 275.
[7] K. Sumino, I. Yonenaga, M. Imai, T. Abe, J. Appl. Phys. 54 (1983) 5016.
[8] G. Wang, D. Yang, D. Li, Q. Shui, J. Yang, D. Que, Physica B 308–310 (2001) 450.
[9] A. Giannattasio, S. Senkader, R.J. Falster, P.R. Wilshaw, Physica B 340–342 (2003) 996.
[10] V.I. Orlov, Y.L. Iunin, M.V. Badylevich, O. Lysytskiy, H. Richter, Solid State Phenom. 95–96 (2004) 465.
[11] I . Yonenaga, J. Appl. Phys. 98 (2005) 023517.
[12] H.J. Stein, Mater. Res. Soc. Symp. Proc. 59 (1986) 523.
[13] R. Jones, S. Öberg, F. Berg Rasmussen, B. Bech Nielsen, Phys. Rev. Lett. 72 (1994) 1882.
[14] H. Sawada, K. Kawakami, Phys. Rev. B 62 (2000) 1851.
[15] H. Kageshima, A. Taguchi, K. Wada, Appl. Phys. Lett. 76 (2000) 3718.
[16] J.P. Goss, I. Hahn, R. Jones, P.R. Briddon, S. Öberg, Phys. Rev. B 67 (2003) 045206.
[17] N. Stoddard, P. Pichler, G. Duscher, W. Windl, Phys. Rev. Lett. 95 (2005) 025901.
[18] N. Fujita, R. Jones, J.P. Goss, P.R. Briddon, T. Frauenheim, Appl. Phys. Lett. 87 (2005) 021902.
[19] T. Itoh, T. Abe, Appl. Phys. Lett. 53 (1988) 39.
[20] R.S. Hockett, Appl. Phys. Lett. 54 (1989) 1793.
[21] V.V. Voronkov, R. Falster, Solid State Phenom. 95–96 (2004) 83.
[22] S. Senkader, K. Jurkschat, D. Gambaro, R.J. Falster, P.R. Wilshaw, Philos. Mag. A 81 (2001) 795.
[23] S. Senkader, P.R. Wilshaw, R.J. Falster, J. Appl. Phys. 89 (2001) 4803.
[24] A. Giannattasio, J.D. Murphy, S. Senkader, R.J. Falster, P.R. Wilshaw, J. Electrochem. Soc. 152 (2005) G460.
[25] J.D. Murphy, A. Giannattasio, S. Senkader, R.J. Falster, P.R. Wilshaw, Phys. Status Solidi A 202 (2005) 926.
[26] J.D. Murphy, A. Giannattasio, C.R. Alpass, S. Senkader, R.J. Falster, P.R. Wilshaw, Solid State Phenom. 108–109 (2005) 139.