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Dislocation luminescence in nitrogen-doped Czochralski and float zone silicon

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Abstract

This paper reports the results of a study of the effect of nitrogen on the optical properties of dislocations in nitrogen-doped Czochralski and nitrogen-doped float zone silicon samples where the nitrogen doping was carried out by adding Si₃N₄ in the molten silicon charge or by nitrogen gas dissolution. Dislocations were introduced by plastic deformation at 650 °C.

In nitrogen-doped plastically deformed samples, emissions in the range of the D1–D4 bands of dislocations are present with a significant shifting from the energies and intensities of the corresponding bands in nitrogen-free samples. It has been shown that the main effect of nitrogen could be the enhancement of the oxygen precipitation. The results confirm the suggestion of some of the present authors that luminescence at 0.830 eV is associated with some intrinsic properties of oxygen precipitates.

1. Introduction

Even before dislocation luminescence was suggested to be of possible interest for optoelectronic applications [1, 2], photoluminescence (PL) studies of dislocations were extensively carried out for years and correlated with the results of DLTS and EPR measurements [3–5], in efforts to achieve a better understanding of their electronic properties. In spite of the wide set of studies on the optical properties of dislocations, there are still many open questions, which mostly relate to the intrinsic or extrinsic origin of the dislocation luminescence and, therefore, to the effect of impurities on the dislocation luminescence.

We have already shown that oxygen interacts with dislocations in plastically deformed Czochralski silicon, leading to the setting up of characteristic broad PL emissions in the same range of energy (0.8–1.0 eV) typical of the D1–D4 bands of dislocations [6, 7]. The oxygen-related component of the D1 band at 0.830 eV is particularly significant and could be easily extracted from the main band by suitable deconvolution procedures. We have also shown

Table 1. Summary of the main properties of the samples analysed. The nitrogen concentration was measured by FTIR or SIMS analysis by the suppliers.

Sample	Source	Orientation	[O] (cm ⁻³)	[N] (cm ⁻³)	Resistivity (Ω cm)
Cz 1	MEMC	⟨100⟩	10 ¹⁸	N-free	250 p-type
Cz 1 N	MEMC	⟨100⟩	10 ¹⁸	10 ¹⁵	60 p-type
Cz 2	MEMC	⟨111⟩	10 ¹⁸	N-free	4.4 n-type
FZ	Wacker	⟨111⟩	<10 ¹⁶	N-free	2000 p-type
FZ N	Wacker	⟨111⟩	<10 ¹⁶	1.2×10 ¹⁵	1.5 p-type

that oxygen precipitates and their nuclei emit in the same range of energy, with at least two characteristic emissions at 0.817 and 0.830 eV and a broad band centred at 0.850 eV [8].

On the other hand, it is already well known that nitrogen affects the silicon material properties considerably. As an example, it could suppress the formation of voids [9] and thermal donors [10, 11] and also enhance the oxygen precipitation [12]. This last effect was confirmed by gold diffusion experiments which show that nitrogen and nitrogen-related complexes stimulate oxygen precipitation [13, 14].

It is also well known that nitrogen reacts with oxygen giving rise to the formation of N–O complexes [15] which are stable up to 900 °C [16].

In addition, it has also been shown that extended defects affect the nitrogen–oxygen equilibria [17], as well as the kinetics of formation of N–O complexes.

All of these effects can be explained, at least qualitatively, by supposing that nitrogen affects the point defect equilibria and the oxygen agglomeration kinetics in silicon with an appreciable enhancement of the oxygen precipitation.

Having in mind that any interaction of nitrogen, oxygen and point defects with dislocation should affect the features of the luminescence, this work was addressed to obtaining a better understanding of the physics of these processes by PL spectroscopy.

2. Experimental details

Two different sets of samples were examined.

The first one originated from ⟨100⟩-oriented p-type Cz crystals grown at the MEMC Electronic Materials factory, where the nitrogen doping was carried out by adding Si₃N₄ to the melt (Cz 1 N). The second set consisted of ⟨111⟩-oriented float zone (FZ) Wacker Siltronic wafers, cut from p-type crystals grown in a nitrogen atmosphere (FZ N).

As references, nitrogen-free ⟨100⟩, ⟨111⟩ Cz MEMC silicon wafers (Cz 1, Cz 2) and ⟨111⟩ FZ silicon wafers were used (FZ).

Details of the resistivity and oxygen and nitrogen concentrations of all samples are reported in table 1.

Dislocation sources were nucleated first by scratching the sample surface with a diamond tip loaded with a 0.3 N weight and then the samples were elastically bent in the cantilever mode. Finally the samples were heated under stress for 1 h at $T = 650$ °C using a quartz and ultrapure graphite deformation apparatus in a pure argon atmosphere. A getter trap was used to

Table 2. Variation of the interstitial oxygen concentration in the Cz samples after deformation and post-deformation annealing.

Sample	Orientation	Process	$\Delta[\text{O}_i]$ (ppma)
Cz 1	$\langle 100 \rangle$	Deformed for 1 h at 650 °C	<0.1
Cz 1 N	$\langle 100 \rangle$	Deformed for 1 h at 650 °C	2
Cz 2	$\langle 111 \rangle$	Deformed for 1 h at 650 °C	<0.1
Cz 2 TT	$\langle 111 \rangle$	Deformed for 1 h at 650 °C and annealed for 24 h at 800 °C	3

remove residual water and oxygen from the argon stream to less than 1 ppba. After scratching and before deformation and thermal annealing procedures, the samples were subjected to the standard RCA cleaning procedure to remove traces of metallic contaminants, which, otherwise, would preferentially segregate in correspondence to the scratch.

A single dislocated sample of the Cz 2 type, nitrogen-free (labelled Cz 2 TT), was subjected to an annealing at 800 °C for 24 h in order to induce segregation of oxygen at dislocations.

The PL spectra were recorded at 12 K with a spectral resolution of 4 meV, using standard lock-in techniques in conjunction with a grating monochromator and an InGaAs detector. For the excitation, a GaAs laser ($\lambda = 808$ nm) with a power density of 6 W cm⁻² was used.

3. Results and discussion

3.1. Effect of nitrogen on oxygen segregation in dislocated samples

The variation of oxygen concentration in the Cz samples, detected by IR analysis [18], after deformation and post-deformation annealing is reported in table 2.

It should be remarked that oxygen does not segregate in the absence of nitrogen doping during the dislocation generation procedure and that a post-deformation annealing at 800 °C on a nitrogen-free sample has the same effect as nitrogen doping on the oxygen segregation process during deformation.

3.2. Plastically deformed Cz samples

As expected, by selective etching with Schimmel etch [19] and optical examination, etch pits and slip lines nucleated in correspondence to the scratch could be detected in Cz $\langle 100 \rangle$ samples, as shown in figure 1. It should be noted that the distribution of the slip lines is affected by the applied stress and it takes a maximum corresponding to the region of maximum deformation.

The PL spectra of the dislocated nitrogen-free and nitrogen-doped Czochralski (NCz) samples, collected in three selected regions of the samples, are displayed in figures 2 and 3. It is clearly seen that the N-free sample exhibits the well known set of D1–D4 broad lines, peaking at their literature energy values (0.807, 0.874, 0.944 and 1.01 eV), and an intense excitonic emission at 1.1 eV (see the inset in figure 2). In the N-doped sample a substantial quenching of the excitonic luminescence is observed, with an increase of all of the dislocation luminescence intensities, but the energy positions of the emissions are different, as they occur

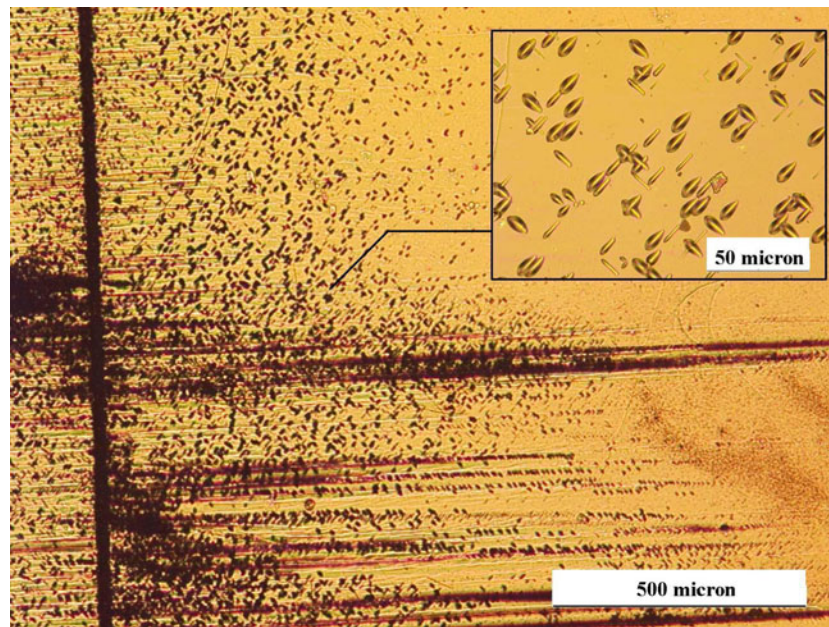


Figure 1. An optical micrograph of the dislocated Cz 1 N silicon sample after Schimmel etching. (This figure is in colour only in the electronic version)

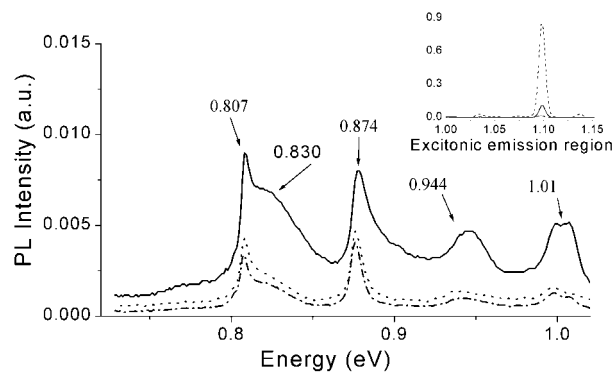


Figure 2. PL spectra in the D band region ($T = 12$ K, $P = 6$ W cm⁻², $dE = 4$ meV) of a plastically deformed nitrogen-free Cz (100) sample (Cz 1) at different densities of dislocations. (—: high density; - - -: medium density; ·····: low density). In the inset the excitonic emission region is displayed.

at 0.825, 0.882, 0.936, 0.993 eV. In addition, an emission at 0.773 eV, of intensity comparable with that of the D3/D4 bands, sets up.

The PL emission features of the N-doped samples suggest that nitrogen favours the interaction of oxygen with dislocations or/and the heterogeneous segregation of oxygen at dislocations.

In fact the emission at about 0.820–0.830 eV has already been shown to be associated with oxygen precipitates [7, 8].

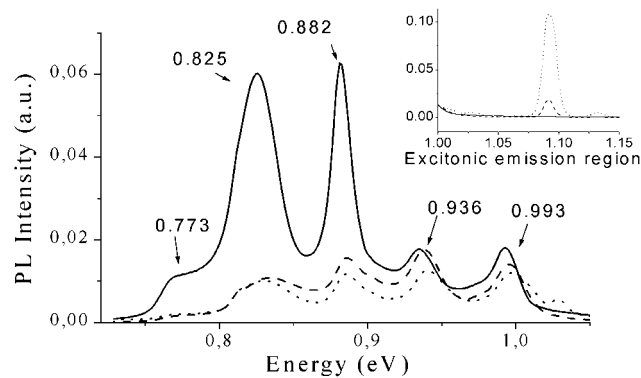


Figure 3. PL spectra in the D band region ($T = 12$ K, $P = 6$ W cm $^{-2}$, $dE = 4$ meV) of a plastically deformed NCz (100) sample (Cz 1 N) at different densities of dislocations. (—: high density; - - -: medium density; ·····: low density). In the inset the excitonic emission region is displayed.

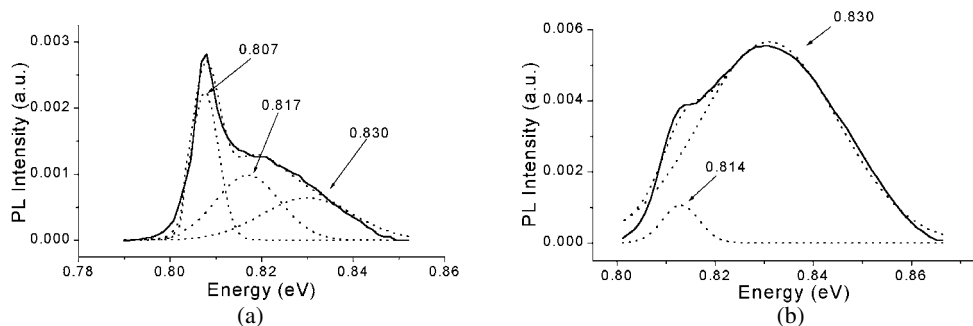


Figure 4. (a) Deconvolution into Gaussian curves of the D1 band for the plastically deformed nitrogen-free Cz (100) sample (Cz 1); (b) deconvolution into Gaussian curves of the D1 band for the plastically deformed NCz (100) sample (Cz 1 N). The full curve is the experimental spectrum ($T = 12$ K, $P = 6$ W cm $^{-2}$, $dE = 4$ meV).

Moreover, as can be observed in figure 4(a), the D1 band of the N-free sample presents the same features as were observed and discussed in our previous paper [8] for the case of dislocated Cz samples. In fact, it is the Gaussian convolution of a band peaked at 0.807 eV, typical of dislocations, and two bands at 0.817 and 0.830 eV which were observed for Cz samples subjected to a classical high–low–high oxygen precipitation process. The D1 band of the N-doped sample presents (see figure 4(b)), instead, only the spectral components associated with oxygen precipitates at 0.814 and 0.830 eV, with that at 0.830 eV being the dominant one.

This result is confirmed by the PL spectrum (see figure 5(a)) of the samples Cz 2 TT subjected to a thermal treatment at 800 °C for 24 h, after the deformation procedure, which shows only an intense broad band peaked at 0.818 eV with a shoulder at 0.773 eV. Moreover, an additional effect of the heat treatments is the quenching of the dislocation luminescence; the emission typical of dislocations, present in the samples before the annealing (see figure 5(b)), is now absent.

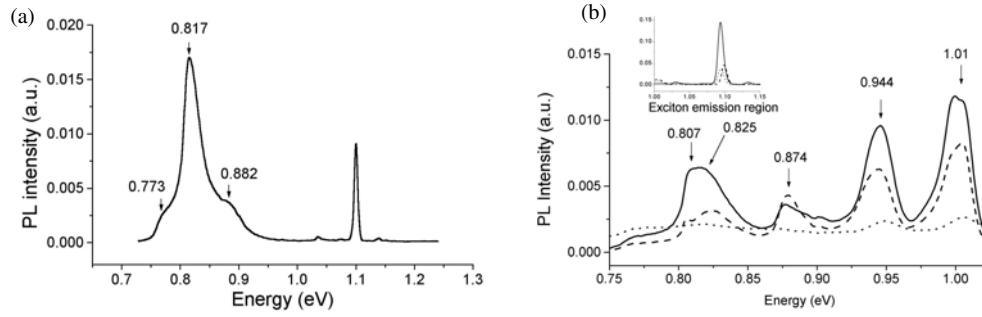


Figure 5. (a) The PL spectrum of sample Cz 2TT, dislocated and subjected to a post-deformation annealing at 800 °C for 24 h; (b) the PL spectrum of sample Cz 2TT after deformation and before post-deformation annealing ($T = 12$ K, $P = 6$ W cm⁻², $dE = 4$ meV). In the inset the excitonic emission region is displayed.

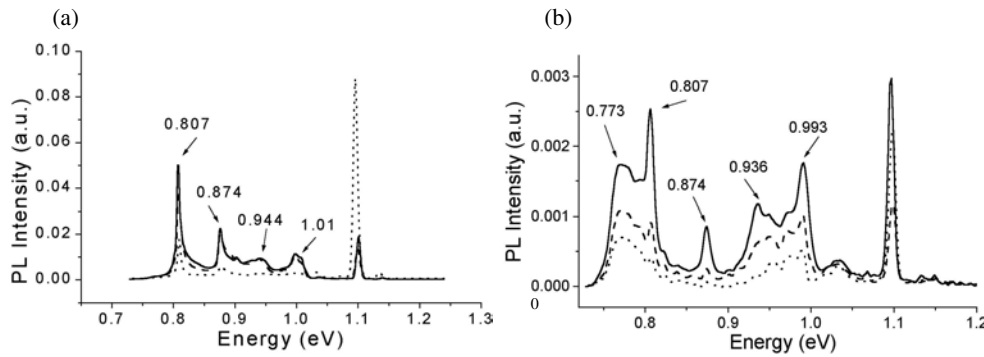


Figure 6. (a) PL spectra ($T = 12$ K, $P = 6$ W cm⁻², $dE = 4$ meV) of a plastically deformed NFZ (111) silicon sample (FZ N) at different densities of dislocations; (b) PL spectra in the D band region ($T = 12$ K, $P = 6$ W cm⁻², $dE = 4$ meV) of a plastically deformed nitrogen-free FZ silicon sample (FZ).

3.3. Photoluminescence features of plastically deformed FZ (111) samples

The PL spectra of N-free and nitrogen-doped FZ (NFZ) samples are displayed in figures 6(a) and (b) for different densities of dislocations. Here, while the spectral features and the PL emissions of the undoped FZ samples compare well with those reported in the literature, with the D1–D4 lines peaking at their literature values, for NFZ samples the spectral components of the D lines are strongly affected by nitrogen doping.

In fact, the emission in the range of the D1 band presents, in addition to the D1 band for dislocations at 0.807 eV, a well resolved peak at 0.773 eV observed in highly dislocated FZ samples [8]. Moreover, and unlike the case for dislocated nitrogen-free FZ samples, the presence of emissions typical of oxygen precipitates at 0.820 and at 0.835 eV is observed from the deconvolution of the main band at 0.807 eV, as shown in figure 7.

Also in this case, as for NCz samples, a red-shift of about 9 meV of the D3 and D4 bands is observed.

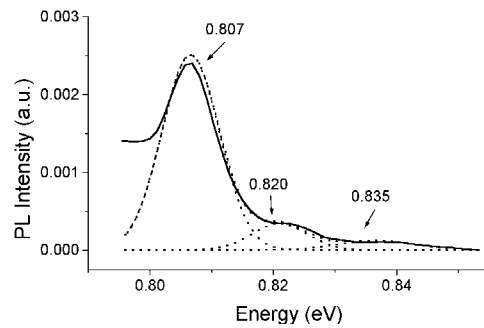


Figure 7. Deconvolution into Gaussian curves of the D1 band for plastically deformed NFZ $\langle 111 \rangle$ (FZ N). The full curve is the experimental spectrum ($T = 12$ K, $P = 6$ W cm $^{-2}$, $dE = 4$ meV).

Table 3. Summary of the PL emissions from dislocated and oxygen-precipitated samples.

Sample	Orientation	Energy band position (eV)				
		Other emissions	D1 region	D2 region	D3 region	D4 region
Cz 1	$\langle 100 \rangle$	—	0.807 0.830	0.874	0.944	1.01
Cz 1 N	$\langle 100 \rangle$	0.773	0.825	0.882	0.936	0.993
Cz 2	$\langle 111 \rangle$	—	0.807 0.825	0.874	0.944	1.01
Cz 2 TT	$\langle 111 \rangle$	0.773	0.817	0.882	—	—
FZ	$\langle 111 \rangle$	—	0.807	0.874	0.944	1.01
FZ N	$\langle 111 \rangle$	0.773	0.807	0.874	0.936	0.993

4. Conclusions

A summary of all the bands detected in the PL spectra taken is shown in table 3.

We have shown by means of PL measurements on dislocation-containing samples that the major effect of nitrogen in both Cz and FZ samples is to enhance the oxygen–dislocation interaction, and thus also the oxygen precipitation process, as can be inferred by the occurrence of the emissions at 0.773 and 0.825 eV in the PL spectra of the nitrogen-doped samples [8]. Whether this is a direct or an indirect catalytic effect is still an open question, which deserves further efforts to find a definite solution. Another open problem is the red-shift of D3 and D4 bands observed for the nitrogen-doped samples (Cz and FZ) and in Cz samples subjected to oxygen precipitation annealing procedures, as this is in conflict with the literature assumption that the D3 and D4 bands are found systematically at the same wavelengths, independently of the experimental conditions. The conclusion that this is an effect associated with the stress field of dislocations in the presence of oxygen precipitates demands further investigation.

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