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Defect Structure of Nitrogen Doped Czochralski Silicon Annealed under Enhanced Pressure

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Defect structure of Czochralski grown silicon (Cz-Si) with nitrogen admixture, $c_N \le 5 \times 10^{14}$ cm^{-3} (Cz-Si:N), annealed for up to 10 h at 1270–1400 K under hydrostatic Ar pressure $\le$ 1.1 GPa, was investigated by synchrotron diffraction topography (HASYLAB, Germany), X-ray reciprocal space mapping, and infrared spectroscopy. Extended defects were not detected in Cz-Si:N processed at up to 1270 K. Such defects were created, however, in Cz-Si:N pre-annealed at 923 K and next processed at 1270 K or in as-grown Cz-Si:N processed at 1400 K. Investigation of temperature–pressure effects in nitrogen-doped silicon contributes to the understanding of defect formation in Cz-Si:N.

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1. Introduction

As grown Czochralski grown silicon single crystals (Cz-Si) contain oxygen up to about 2×10^{18} cm^{-3} concentration (c_O), mostly in the form of interstitials (O_i's). Doping of Cz-Si with nitrogen in a low concentration (to produce Cz-Si:N) results in improved mechanical properties of Cz-Si:N wafers and in specific gettering properties of this material in respect of non-desired impurities [1]. At the annealing of Cz-Si and of Cz-Si:N, O_i's tend to form small clusters, larger SiO_{2-x} precipitates and other extended defects.

The presence of nitrogen affects strongly the kind and distribution of such oxygen-containing microdefects; only small oxygen-containing clusters are formed at processing of Cz-Si:N [2]. Similarly as in the case of nitrogen-lean Cz-Si, clustering/precipitation of O_i's in Cz-Si:N at enhanced temperatures (HT) depends also on hydrostatic pressure (HP) applied at processing [3].

Defect structure of the Cz-Si:N samples with nitrogen concentration $c_N \le 5 \times 10^{14}$ cm^{-3} is investigated in present work after subjecting the samples to the HT–HP treatment at 1270–1400 K. Investigation of the temperature–pressure effects in nitrogen-doped Cz-Si contributes to the understanding of the role of nitrogen in Cz-Si:N widely applied in microelectronics [1].

2. Experimental

The (001) oriented 2 mm thick Cz-Si:N samples with $c_N \le 5 \times 10^{14}$ cm^{-3} and $c_O \approx 9 \times 10^{17}$ cm^{-3} were treated for up to 10 h at HT within the 1270–1400 K range under HP $\le$ 1.1 GPa exerted by Ar gas [4, 5]. Some samples were pre-annealed for 10 h at 923 K under 10^5 Pa/1.1 GPa to create nucleation centers (NC's) for subsequent oxygen precipitation. About 150 μm thick near-surface layer was removed after processing from the Cz-Si:N surface by chemical polishing.

The defect structure of Cz-Si:N was investigated by synchrotron diffraction topography at the F1 and E2 experimental stations of the DORIS III synchrotron in HASYLAB (Germany). White and monochromatic (λ = 0.1115 nm) beam topographic methods in the Bragg geometry were used. Section topography (with the application of a fine 5 μm slit and glancing angle of 5°) enabled indication of volume character of the defect distribution. High sensitivity to strains associated with small inclusions and dislocation loops was provided by monochromatic beam topography.

Also high resolution X-ray diffraction (to record reciprocal space maps, XRRSM's) and IR absorption methods were used for characterization of the samples.

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3. Results and discussion

The synchrotron topographic investigation, applied in present research, enables to visualize large precipitates in the HT–HP treated Cz-Si:N ($c_N \approx 5 \times 10^{14}$ cm^{-3}) samples. It was possible to follow the formation of individual precipitates, better visible in the section and projection white beam topographs than in the monochromatic beam ones (not reported here). The use of white beam section topographs in the investigation of variously treated samples makes it possible to confirm the volume distribution of the large precipitates as they appear at a large area behind the black stripe corresponding to the intersection of the beam with the sample surface.

In the presently investigated Cz-Si:N samples we observed large individual inclusions, of a concentration dependent on the processing condition, providing intense isolated contrasts. The section topographs confirmed the volume distribution of these defects, as they appeared in a relatively wide area behind the stripe corresponding to the intersection of the beam with the surface — the region where the beam enters the crystal.

In the case of Cz-Si:N samples processed at 1270 K such large inclusions are evidently related to oxygen precipitated on some crystal non-homogeneities within the sample volume (Fig. 1). Nitrogen may be also involved in such precipitation but clarification of this issue needs further investigation.

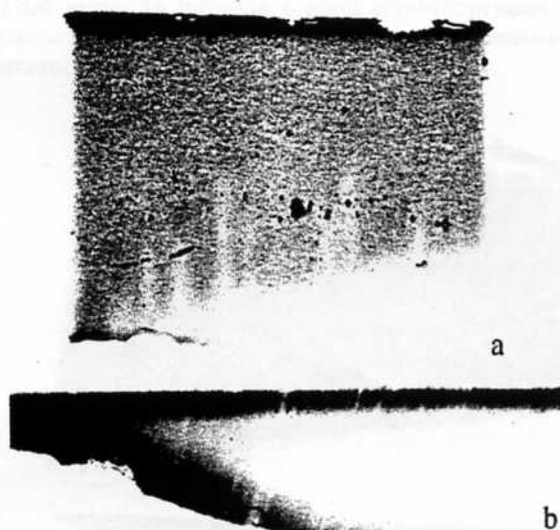

Fig. 1. White beam projection (a) and section (b) topographs of Cz-Si:N sample processed for 5 h at 1270 K under 1.2 GPa. Width of reproduced areas is equal to 8 mm, similarly as in topographs presented in Figs. 5–7.

In the case of samples subjected to pre-annealing at 923 K and subsequently processed at 1270 K, XRRSM's patterns can be interpreted as evidencing the presence of numerous defects distributed within the sample volume (Fig. 2). The sample defect structure is dependent also on HP applied at pre-annealing (compare Figs. 2A and 2B). The X-ray diffuse scattering intensity, evidencing the presence of microdefects, was a little more pronounced for the sample pre-annealed under atmospheric pressure (Fig. 2A). This intensity is related to an increase of the defects concentration and/or to their dimensions.

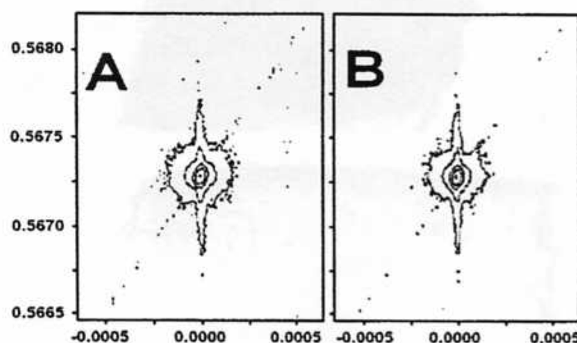

Fig. 2. XRRSM's of Cz-Si:N samples pre-annealed for 10 h at 923 K under 10^5 Pa (A) or 1.1 GPa (B) and finally processed for 5 h at 1270 K under 1.1 GPa. Axes are marked in $\lambda/2d$ units (λ — wavelength, d — interplanar distance).

Processing of as grown Cz-Si:N at 1270 K for 5 h, both under 10^5 Pa and 1.1 GPa, practically does not affect the concentration of interstitial oxygen, remaining within 10% the same as in the as grown samples. Similar treatments of Cz-Si:N pre-annealed at 923 K result in precipitation of about 40% of initially present O_i's (IR measurements, see also Fig. 2).

From deconvolution of the non-symmetrical IR peak at 1107 cm^{-1} one can judge on the effect of the pre-annealing conditions on the formation of different oxygen-containing precipitates [6–8] (Figs. 3 and 4).

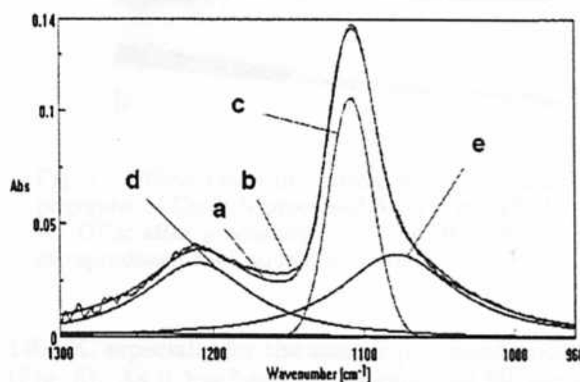

Fig. 3. Deconvolution of IR absorption bands at 1107 cm^{-1} (**a**, **b**) on different sub-bands (**c**, **d**, **e**) for Cz-Si:N sample pre-annealed for 10 h at 923 K under 10^5 Pa and finally processed for 5 h at 1270 K under 1.1 GPa. **c** — IR band at 1107 cm^{-1} after deconvolution; **d** — IR band peaking at about 1210 cm^{-1}, most probably related to spheroidal SiO_x precipitates [7, 8]; **e** — IR band peaking at about 1080 cm^{-1}, related to needle-like oxygen precipitates [6–8].

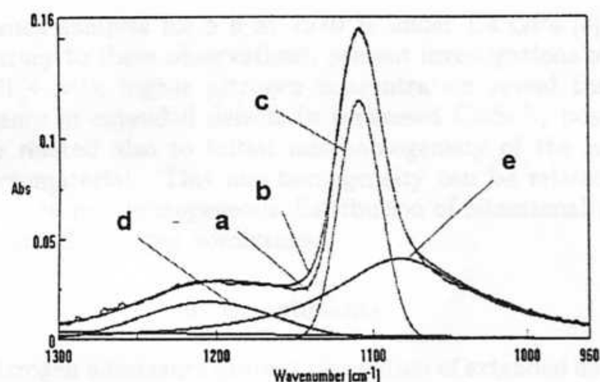

Fig. 4. Deconvolution of IR absorption band at 1107 cm^{-1} (**a**, **b**) on different sub-bands (**c**, **d**, **e**) for Cz-Si:N sample pre-annealed for 10 h at 923 K under 1.1 GPa and finally processed for 5 h at 1270 K under 1.1 GPa. See Fig. 3 caption for explanation of deconvoluted sub-bands.

Comparing Figs. 3 and 4 one can state that HP applied at pre-annealing of Cz-Si:N at 923 K affects strongly the content of spheroidal-like SiO_x precipitates; this is manifested by the changed intensity of the 1210 cm^{-1} band. The intensities of other IR sub-bands were not affected markedly by the pre-annealing conditions.

One can notice a weak Uragami interference fringe close to the strongest stripe in white beam section topographs of the samples processed at 1400 K (Figs. 5–7). That seems to indicate a good crystallographic quality, particularly the absence of any larger concentration of irresolvable inclusions.

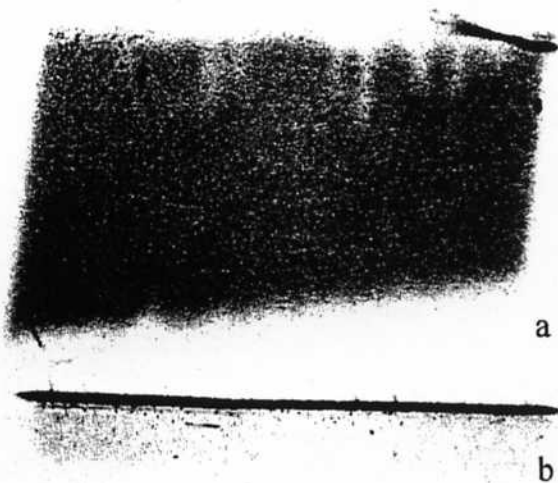

Fig. 5. White beam projection (a) and section (b) topographs of Cz-Si:N processed for 5 h at 1400 K under 10^7 Pa; after processing $c_O = 8.5 \times 10^{17}$ cm^{-3}. Width of reproduced area equals to 8 mm.

Significantly great concentration of the individual inclusions was observed in the case of Cz-Si:N annealed at 1400 K, especially for the sample processed under 10^7 Pa (Fig. 5). As it has been earlier reported [9], oxygen precipitation and the formation of defects in annealed Cz-Si are dependent on HP in a very complicated manner and, while increasing with HP, indicate specific irregularities.

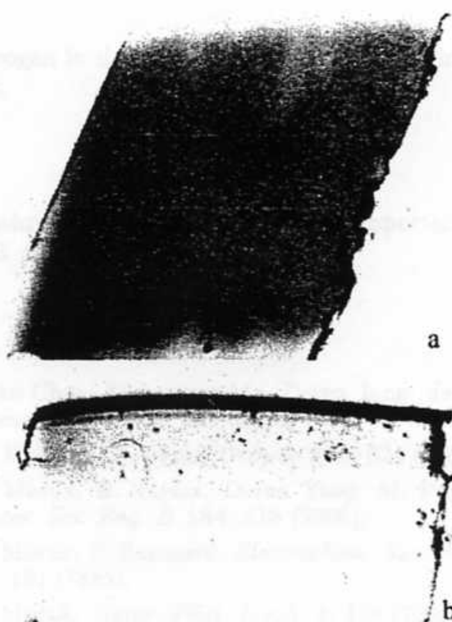

Fig. 6. White beam projection (a) and section (b) topographs of Cz-Si:N processed for 5 h at 1400 K under 0.3 GPa. Width of reproduced area equals to 8 mm.

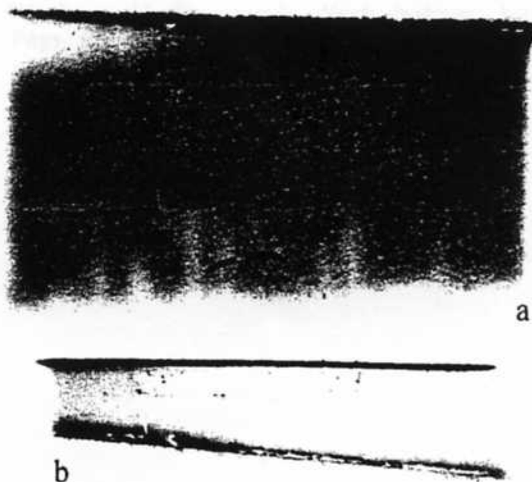

Fig. 7. White beam projection (a) and section (b) topographs of Cz-Si:N processed for 5 h at 1400 K under 1.1 GPa; after processing $c_O = 5 \times 10^{17}$ cm^{-3}. Width of reproduced area equals to 8 mm.

Annealing the nitrogen doped Cz-Si:N samples ($c_N \approx 2 \times 10^{14}$ cm^{-3}) at $T \geq 1070$ K, both under 10^5 Pa and HP, has been reported earlier to result in negligible precipitation of O_i's [3]. The formation of dislocations and of other extended defects was negligible also after process-

ing such samples for 5 h at 1270 K under 1.4 GPa [3]. Contrary to these observations, present investigations of Cz-Si:N with higher nitrogen concentration reveal the presence of extended defects in processed Cz-Si:N, possibly related also to initial non-homogeneity of the as grown material. This non-homogeneity can be related in part to non-homogeneous distribution of intentionally introduced nitrogen admixture.

4. Conclusions

Nitrogen admixture prevents formation of extended defects in Cz-Si:N ($c_N \approx 5 \times 10^{14}$ cm^{-3}) at processing done under 10^5 Pa at $T \leq 1270$ K. Such defects were formed, however, in Cz-Si:N pre-annealed at 923 K under 10^5 Pa/1.1 GPa (to create nucleation centres for oxygen precipitation) and next processed at 1270 K. Numerous large oxygen-related defects were observed in Cz-Si:N processed for 5 h at 1400 K under HP.

Annealing of nitrogen doped Czochralski grown silicon at 1270–1400 K under HP results in the formation of specific microstructure: oxygen–containing clusters and precipitates are created. Nitrogen may also be present within such clusters but this issue would demand further studies.

Investigation of the temperature–pressure effects in nitrogen-doped Cz-Si contributes to understanding the role of nitrogen in doped silicon presently used in microelectronics.

Acknowledgments

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