UNCLASSIFIED

Defense Technical Information Center Compilation Part Notice

ADP011883

TITLE: Investigation of System Si-O [SiOx] Behavior in DAC at Submegabar Pressure

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: International Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals Held in Zakopane, Poland on 9-12 October 2000

To order the complete compilation report, use: ADA399287

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP011865 thru ADP011937

UNCLASSIFIED

Investigation of system Si – O (SiO_x) behavior in DAC at submegabar pressure

Borys M. Efros[a*], Natalya V. Shishkova[a], Anatolii Prudnikov[a], Andrzej Misiuk[b], J. Bąk-Misiuk[c], Juergen. Härtwig[d]

[a]Phys.& Tech. Institute, NASc, 72, R.Luxemburg, 83114, Donetsk, Ukraine
[b]Institute of Electron Technology, Warsaw, Poland
[c]Institute of Physics, PASc, Warsaw, Poland
[d]European Synchrotron Radiation Facility, Grenoble, France

ABSTRACT

Extensive experiment studies of the IV elements have been made in resent years. Motivations have included the rich variety of phase and structural transitions.

Different SiO_{2-x} defects can be created in Czochralski grown silicon, Cz-Si, by appropriate pre-annealing at atmospheric pressure (10^5 Pa). Some date concerning the effect of enhanced hydrostatic pressure on creation of defects in the Si- SiO_{2-x} system have been reported for defects-containing Cz-Si subjected to cyclic hydrostatic pressure treatment.

An attempt to observe the mentioned hydrostatic pressure-induced effect of massive creation of "new" defects in Cz-Si with oxygen-related defects was undertaken in this work.

The increase of defect concentration in the hydrostatic pressure-treated Cz-Si samples with initially present SiO_{2-x} precipitates can be considered as a proof of hydrostatic pressure-induced massive creation of defects on before-created oxygen-related defects. However, in the case of some DAC-treated samples, a misfit dislocation network was not directly proved to be created because of too small sample in comparison to the resolution of the spectroscopy and X-ray methods.

Keywords: diamond anvil cell, Czochralski sample, submegabar pressure.

1.INTRODUCTION

The fundamental nature and technological importance of elemental and binary semiconductors have made their high-pressure properties one of the most active areas of research, especially since the advent of the diamond-anvil cell (DAC) technique about 30 year ago. In spite of considerable effort done in above area, the structural systematic of the group-IV and related semiconductors still demands to be clarified. Moreover, practically nothing is known about possible effects of dopants or impurities on pressure-induced phase transitions, even in the case of the best-investigated material, silicon.

An effect of defect creation in the misfitting particle/matrix system has been investigated for about 25 years. Because of importance of silicon as the model semiconductor and basic material for microelectronics, the case of SiO_2 precipitates in Si bulk is of special interest.

Different $Si0_{2-x}$ defects can be created in Czochralski grows silicon (Cz-Si) by appropriate pre-annealing at atmospheric pressure (10^5 Pa). Some data concerning the effect of enhanced hydrostatic pressure (HP) on creation of defects in the Si-SiO_{2-x} system have been reported[1] for defects-containing Cz-Si subjected to the cyclic HP treatment at ≤ 2.5 GPa, much below the pressure of the diamond – to β-tin phase transition (at about 11 GPa).

An attempt to observe the mentioned HP-induced effect of massive creation of "new" defects in Cz-Si with oxygen-related defects was undertaken in this work. An effect of short-time HP-treatment (at HP up to 1.35 GPa) of the OPs-containing Cz-Si samples at temperatures just below the melting point of silicon (≈ 1680 K) was also investigated.

*Futher author information
B.M.E.(correspondence): Email efros@hpress.dipt.donetsk.ua
N.V.Sh.: Email: shishkov@kinetic.ac.donetsk.ua
A.M.:Email:misiuk@ite.waw.pl

Intl. Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals, Antoni Rogaski, Krzysztof Adamiec, Pawel Madejczyk, Editors, Proceedings of SPIE Vol. 4412 (2001) © 2001 SPIE · 0277-786X/01/$15.00

2.EXPERIMENTAL

Cz-Si samples were cut from commercially available Cz-Si *p*-type wafers of about 600μm thickness. The oxygen interstitial concentration (c_0) determined by Fourier Transform Infrared Spectrometry (FTIR) was ≤ 11 10^{17} cm^{-3}. One sample, designated as *S*, with c_0 = 11 10^{17} cm^{-3} was pre-annealed at 1000 K for 20 h to create small oxygen clusters with a total density of 1.3 10^6 cm^{-2} – sample *S1*. In effect of pre-annealing, the c_0 value decreased to 8.5 10^{17} cm^{-3}.

Another sample was pre-annealed at 1000 K for 20 h and, additionally, at 1320 K for 20 h – to create larger defects (OPs with a density 2.1 10^4 cm^{-2} and stacking faults) – sample *S2*. In effect of such pre-annealing the c_0 value decreased to 6.1 10^{17} cm^{-3}.

By chemical etching, foils with thickness of 50 μm were prepared from the S1 and *S2* samples. The foils were pressurized for 20-36 hours at 8.5-10.5 GPa at room temperature in DAC, using an H_2O - methanol solution.

The DAC design and the pressure measuring device are described in work [2]. In the DAC, a sample hole of radius a_0 is formed in the centre of the gasket, and contains a pressure-transmitting fluid, ideally with shear strength k = 0. While increasing pressure (Fig. 1), the cell seals by virtue of the normal pressure between the gasket and anvil being greater than the hydrostatic pressure by an amount equal to the shear strength in a thick gasket, and greater still in a thin gasket (Fig. 2). For each experiment to be carried out in a DAC, the gasket may be selected differently according to the pressure range required, the sample size, and the number of pressure cycles required. A thick gasket may be chosen to give a larger sample space, or a more linear force Q-pressure *P* curve, and less hysteresis between increasing and decreasing pressure. A thin gasket, on the other hand, will allow higher pressures to be reached, and can give better control at low pressure since the gasket seals at forces much below those necessary to give any pressure in the fluid. However, in either case, the run should be stopped if the gasket hole shows signs of enlarging, or the force-pressure plot becomes sub-linear.

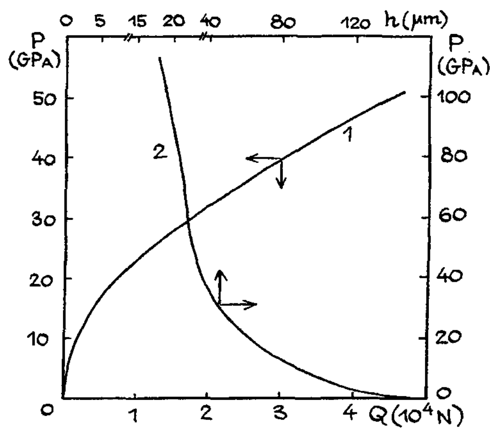

Fig.1.

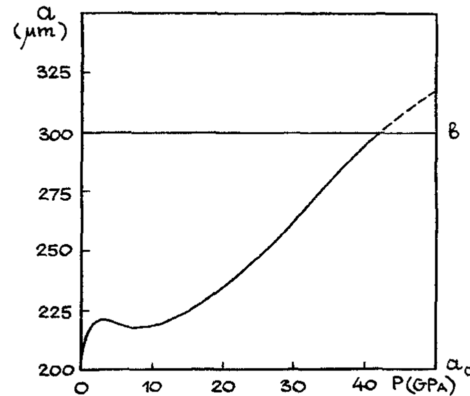

Fig.2

Fig. 1. Pressure P -force Q (1) and pressure P – thickness h (2) plots for value of stress yielding $YS_{0.2}$ =500MPa andradius of gasket hole a_0 =200μm (initial thickness of gasket h_0 = 150 μm and radius of diamond anvil b = 300 μm)

Fig. 2. Radius of gasket hole a - pressure P plot for value of yielding stress $YS_{0.2}$ =500Mpa and initial thickness of gasket h_0 = 150μm (initial radius of gasket hole a_0 = 200 μm and radius of diamond anvil b = 300 μm)

The deformable gasket material was 301 stainless steel; the disk-shaped gaskets (diameter D = 4 mm, thickness h_0 = 150 μm) after pre-strengthening treatment were tested in screw-lever DAC at pressures P up to 15 GPa. Pressure was determined with the help of the shift of R_1 and R_2 ruby luminescence lines using the relation given in work [3]:

$$P = 380.8 \cdot \left[\left(\Delta\lambda / 694.2 + 1^5\right) - 1\right] \quad (1)$$

where $\Delta\lambda = \lambda_p - \lambda_0$ is the difference in position between R-ruby luminescence lines at pressure P (GPa) and at atmospheric pressure (nm).

Other 600 μm thick, S2 and S3 samples (for S3 initial c_0 was $8\ 10^{17}$ cm^{-3}, S3 was pre-annealed at 720 K for 96 h) were HP-treated for 5 min at 1550-1620 K in a high-pressure furnace.

After HP-treatment, the X-ray topographs were obtained at the Topography Beamline (ID19) of the ESRF. White beam topography was used for the DAC-treated thin S1 and S2 samples, and double crystal topography – for the furnace-treated "thick" S2 and S3 samples. Complementary X-ray and FTIR measurements were performed to check structure perfection of the samples.

3.RESULTS AND DISCUSSION

The description of defect formation model at the particle/matrix boundary at HP has been presented e.g. in work .[4] For a precipitate completely embedded in a matrix, it is necessary to exploit the concept of a misfit (ε) between the matrix and precipitate material. A misfitting precipitate may lose part of its elastic energy when a dislocation is emitted from an interface between the precipitate and the matrix. There are two criteria for estimation of ε and of precipitate size (d) for which dislocation loops can be generated. The first criterion (A) defines the smallest misfit for which the local shear stress at a precipitate boundary can exceed the theoretical shear strength of the matrix. In this case the stress at a precipitate surface and, hence, the critical misfit (ε_{cr}) does not depend on d. The ε_{cr} value for criterion A would be close to $5 \cdot 10^{-2}$ according to paper .[4]

The second criterion (B) defines the critical misfit from the energy of the system decreases if a dislocation loop is generated at a precipitate boundary, the ε_{cr} value decreases for higher *d*. Its value would be closed to 10^{-3} for $d \approx 1$ μm, and to about 10^{-2} for $d \approx 100$ nm.[5]. The criterion *B* applies for generation of dislocations at incoherent precipitates.

"Initial" misfit (ε_0) is present usually at the Si matrix/oxygen precipitate (*OP*) boundary because of much larger *OP* volume as compared to that of Si as well as of different thermal expansion of Si and SiO_{2-x}.

HP would influence on ε at the mentioned boundary because of much higher compressibility γ ($\gamma = 1/K$, where K – the bulk modulus) of SiO_2 as compared to that of Si ($K_{SiO2} = 40$ GPa, $K_{Si} = 98$ GPa). For a spherical embedded particle, the misfit can be estimated from Eq. 2 [5,6]:

$$\varepsilon = \varepsilon_0 + \frac{K_p}{3K_p + 4G_{Si}} \cdot \left[\Delta T \cdot \left(\beta_p - \beta_{Si}\right) + HP \cdot \left(\frac{1}{K_{Si}} - \frac{1}{K_p}\right)\right] \quad (2)$$

where:
K – bulk modulus,
G – shear modulus,
β - volume thermal expansion coefficient,
$\Delta T = T_{exp} - 300$ K, T_{exp} – temperature for which ε is calculated.
The bottom indexes in Eq. 2 denote the precipitate/matrix.

An estimation (Eq. 2) gives, for SiO_2 – Si system at 10 GPa, the misfit value equals to about $1.3 \cdot 10^{-2}$ (close to the value for criterion *A*, may be even reaching it under assumption that *OPs* are composed of stoichiometric SiO_2).

So, at sufficiently high *HP* one can expect massive creation of dislocations and other defects on each, even coherent, particle. Of course, nonstoichiometry of the *OP* composition (in comparison to stoichiometric SiO_2) must be taken into account.

White beam topographs of the *DAC*-treated samples showed elongated, very weak Laue spots (Fig. 3).

This can be considered as a sign of asterism which has its origin in the *HP*-induced transformation of Si single crystals to crystals with grains. From this effect it was possible to estimate the mosaic spread of the single grains and orientational

distribution of the grains. It appears that these mosaic spreads were of the order of 2-6 arc min for individual grains and of 12-30 arc min for the grain distribution (Table 1).

In the case of *S1* sample (with high density of small oxygen clusters), a strong sample fragmentation after the *DAC* treatment at 10.5 GPa was observed. The treatment of the *S1* sample at 8.5 GPa caused much minor structure changes (Fig.3 and Table 1).

In the case of *S2* sample with larger *OPs*, such fragmentation was observed just after the treatment at 9 GPa. This can be considered as some kind of proof that, at sufficiently high pressure (dependent on *d*), the presence of defects in Cz-Si resulted in massive *HP*-induced creation of additional defects because of reaching the "criterion *B* value" of ε_{cr}, or, possibly, even the ε_{cr} value according to the criterion *A*.

Table 1. Estimation of mosaic spread half-width within individual grain and those of grains within whole crystal

Sample	*DAC* treatment, GPa	Mosaic spreads, arc min	
		Individual grain	Grain distribution
S1	8.5	2	12
	10.5	4-8	25-30
S2	9.0	2-6	20-30

It must be stressed, however, that it would be impossible to investigate Cz-Si in this respect at higher *HP* because at about 11 GPa a phase transition occurs in Si .[6] Possibility of some kind of phase transformation at about 10 GPa in amorphous SiO_2 must also be accounted for paper.[7]. In this last case the Si matrix would be untouched, whereas the mentioned phase transformation in SiO_2 (in fact SiO_{2-x}, because *OPs* are typically of substoichiometric composition) would contribute to structural changes at the *OP*/Si boundary.

In the case of experiments at enhanced temperatures (*HT*) (at which ε_{cr} is expected to be achieved at lower *HP* than that at about 300 K), there exists some uncertainty in interpretation of results. It follows, between others, from stress-enhanced oxygen precipitation[8], dissolution of *OPs* at the *HT* [9] and from structural transformations during sample cooling. So, only short-time *HP-HT* experiments can lead to conclusive results.

Indications of *HP*-induced creation of additional defects were found for the samples treated at parameters: > 1550 K – 1 GPa for 5 min (Fig. 4).

The *A* and *B* topographs (of the sample *S2*) are quite similar. However, as it follows from supplementary measurements, the *S2* sample structure was more "disturbed" when annealed at higher *HP* (Table 2).

Table 2. Effect of *HP* on c_0, on static Debye-Waller factor, L_{660} [10] and on anomalous *X*-ray transmission (*Ia*) for *S* (as-grown) and *S2* samples treated at 1580 K for 5 min

Sample	*HP*, Pa	$c_o \cdot 10^{17}$, cm^{-3}	$L \cdot 10^3$	*Ia*[arb. units]
S	10^5	8.6		110
S	10^9	8.6		120
S2	10^5	8.6	26	78
S2	10^9	7.9	33	67

It can be explained as an effect of "fulfillment" of the conditions for creation of additional defects at the largest defects/matrix boundary (*OPs* with different sizes were present in the Si matrix).

In the case of *S3* samples with small oxygen clusters (created by pre-annealing at 720 K), the effect of *HP* was even stronger. The treatment at 10^5 Pa resulted in creation of individual large dislocation loops (probably an effect of oxygen

precipitation on some structural irregularities during sample cooling), whereas in the samples treated at 1.35 GPa, numerous "additional" defects were observed.

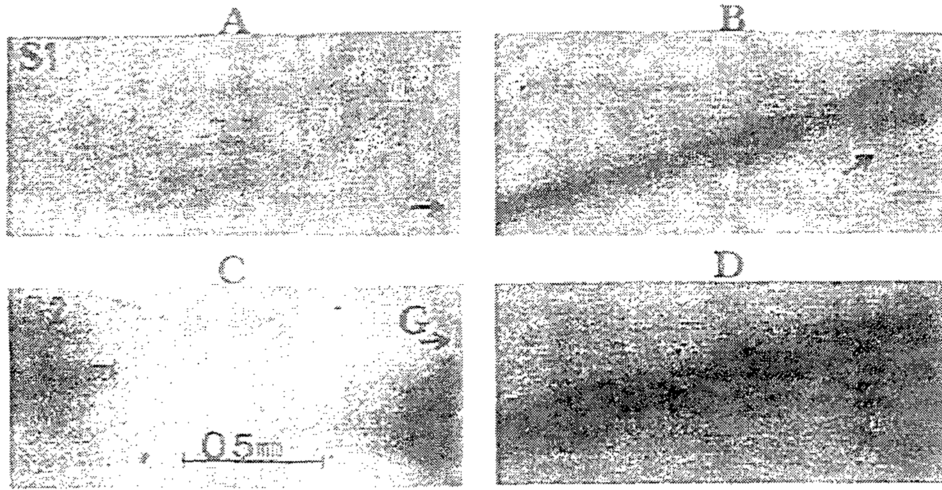

Fig. 3. White beam Laue topographs of 50 μm thick *S1* and *S2* samples:*A* – *S1* sample *DAC*-treated at 8.5 GPa; *B* – *S1* sample *DAC*-treated at 10.5 GPa;*C* – non-treated *S2* sample;*D* – *S2* sample *DAC*-treated at 9 GPa;*G* – diffraction vector

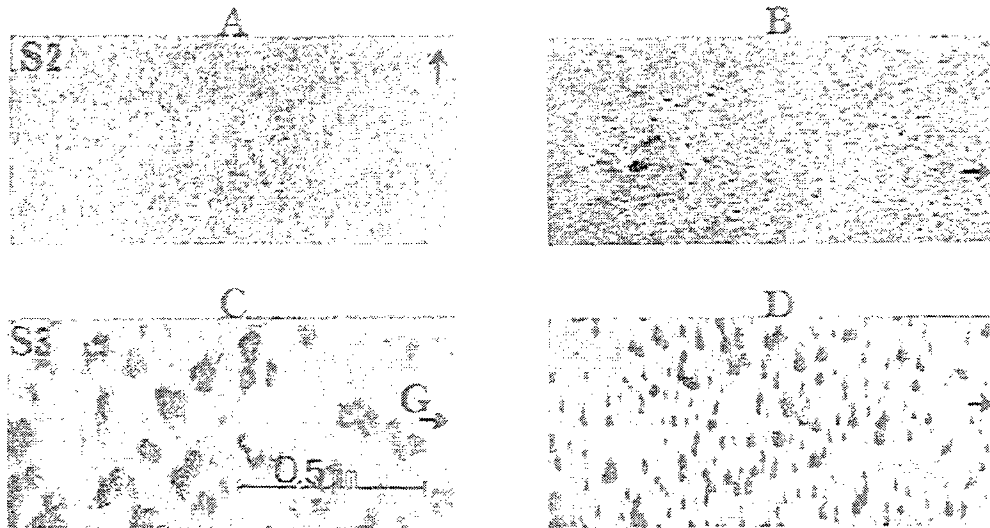

Fig. 4. 111 topographs ($\lambda \approx 0.04$ nm) of 600 μm thick *S2* and *S3* samples subjected to *HP* treatment for 5 min. Treatment conditions: *S2* sample was annealed at 1580 K - 10^7 Pa (*A*) and at 1580 K – 1 GPa (*B*); *S3* sample – at 1550 K - 10^5 Pa (*C*) and at 1550 K – 1.35 GPa (*D*)

4.CONCLUSIONS

The increase of defect concentration in the *HP* – (*HT*) treated Cz-Si samples with initially present SiO_{2-x} precipitates can be considered as a proof of *HP*-induced massive creation of defects on before-created oxygen-related defects. However, in the case of *DAC*-treated *S1* and *S2* samples, a misfit dislocation network was not directly proven to be created because of too small sample dimension (all dimensions of about 50 μm) in comparison to the resolution (of the order of a micrometer) of the applied X-ray (synchrotron) method.

Also results obtained at *HP – HT* experiments must be considered with caution, because part of structural transformations can occur during sample cooling (the cooling rate of about 2 Ks^{-1}). For this reason, it would be desirable to perform "direct" observations of the *HP*-induced phenomena by further *in situ* experiments, using *DAC* mounted directly on the *ESRF* beam line.

ACKNOWLEDGEMENTS

The authors are grateful to Dr J.Jun from the High Pressure Research Centre, PAS, Warsaw and m.sc. A.Panas from the Institute of Electron Technology, Warsaw for their help during preparation of investigated samples.

This work was supported in part at 1999 - 2000 by Polish Committee for Scientific Research, grant no. 7T08A 057 17.

REFERENCES

1. Misiuk A., Wolf J., Datsenko L., Adamczewska J., Bak-Misiuk J., "Microscopic model of phenomena at SiOx/Si boundary in strained Cz-Si single crystals", *Nukleonika, 39*, 281-286, 1994.
2. Beresnev B.I., Efros B.M., *Physica **139&140***,pp 910-915,1986.
3. Mao H., Bell P.," High pressure Physics: Sustained static generation of 1.36 to 1,72 megabars" *Science* **200**, pp.1145-147,1978.
4. Jung J. "High-pressure-induced defect formation in silicon singlecrystals.II.Mechanism of stress-field formation at precipitates", *Phil. Mag. A,* **50**, 257-274,1984.
5. Bak-Misiuk J., Misiuk A., Klima K., Kucharski K., Skibska M., in *Proc. 8th Intern. School "Defects in Crystals"*, ed.E.Mizera,, SzcZyrk, Poland, Publ. World Scientific, pp. 359-367, 1988
6. Olijnyk H., Holzapfel W.B., "Phase transitions in Si, Ge and Sn under pressure", *J. Phys.*, 45, C8-153-159,1984.
7. Polian A., Grimsditch M., "Room-temperature densification of α-SiO_2 versus pressure", *Phys. Rev. B, **41**,* pp.6086-87, 1990.
8. Misiuk A., Surma B., Hartwig J., " Stress induced oxygen precipitation in Cz-Si", Mater.Sci. Eng., *Mater. Sci. Eng., **B36**, pp.* 30-32, 1996.
9. Datsenko L., Khrupa V., Krasulya S., Misiuk A., Hartwig J., Surma "Structural perfection of Czochralski grown silicon crystals annealed above 1500 K under hydrostatic pressure", *Acta Phys. Pol. A, **91**,* pp. 929-933, 1997.