Andrzej MISIUK[1], Jadwiga BAK-MISIUK[2], Marek PRUJSZCZYK[1], Przemyslaw ROMANOWSKI[2]

Institute of Electron Technology, Warszawa (1), Institute of Physics, PAS, Warszawa (2)

Pressure-assisted generation of thermal donors in doped Cz-Si

Abstract. *Generation of thermal donors (TD's) in oxygen-containing Cz-Si, also admixed with N or Ge, annealed at about 720 K for up to 20 h, also under Ar hydrostatic pressure (HP) up to 1.4 GPa, was investigated by electrical and X-ray methods. Contrary to annealing at 723 K - 10^5 Pa, processing under HP leads to TD's concentration peaking at the wider temperature range, it is also dependent on dopants present in Cz-Si. HP processing results also in other hitherto not known effects.*

Streszczenie. *Zbadano, przy zastosowaniu metod elektrycznych i rentgenowskich, generację donorów termicznych (TD's) w zawierającym tlen Cz-Si, w tym domieszkowanym N lub Ge i wygrzanym w ok. 720 K przez czas do 20 godzin w warunkach wysokiego ciśnienia hydrostatycznego Ar (HP), do 1,4 GPa. W przeciwieństwie do efektu wygrzania Cz-Si w 723 K pod ciśnieniem 10^5 Pa, wygrzanie w warunkach HP prowadzi do zwiększonej koncentracji TD's w szerszym zakresie temperatur i innych nieznanych dotąd efektów. (**Uwarunkowana zwiększonym ciśnieniem generacja donorów termicznych w domieszkowanym Cz-Si**).*

Keywords: Cz-Si, thermal donors, high hydrostatic pressure, annealing.
Słowa kluczowe: Cz-Si, donory termiczne, wysokie ciśnienie hydrostatyczne, wygrzewanie.

Introduction

In spite of extended investigations [1], some aspects of generation of thermal donors (TD's) in oxygen-containing Czochralski grown silicon (Cz-Si) remain to be mysterious, hydrostatic pressure (*HP*)-induced enhancement of the TD's formation [2] among them. The effect of *HP* on the TD's generation in Cz-Si doped with B, N, P and Ge and processed at 673–873 K (*HT*) under *HP*≤1.4 GPa is now investigated in more details by four points probe; the structure of some samples has been controlled by X-ray diffractometry.

Experimental

Boron- or phosphorus doped n- and p-type Cz-Si samples, about 0.6 mm thick and (001) oriented, were investigated in present study. Some samples were additionally doped with nitrogen (Si-N) or germanium (Si-Ge). The content of interstital oxygen (the main component of TD's), concentration of N and Ge dopants, conductivity type and carrier concentration of as-grown (initial) samples are presented in Table 1. Interstitial oxygen (O_i) content (c_o) determined by Fourier Infrared Spectroscopy, FTIR, was practically the same in the Si-B, Si-P and Si-N samples and equal to about $9.2x10^{17}$ cm^{-3}. This content was about 30% lower in Si-Ge than that in other investigated samples.

The samples were annealed for up to 20 h within the 673–873 K temperature range under hydrostatic pressure (*HP*, up to 1.4 GPa) exerted by inert Ar atmosphere. Some samples were subjected to 2-steps sequential annealing procedure (the last step at 723 K) to produce TD's in a higher concentration.

The sample structure was controlled by X-ray recording reciprocal space maps, XRRSM's, sensitive to the presence of defects. The carrier concentration was determined by electrical four points probe method.

Table 1. Characteristics of investigated samples: interstitial oxygen concentration, c_o, additional dopant (N or Ge) concentration, c_{dop}, conductivity type and carrier concentration, *N*

Sample	$c_O x10^{-17}$ [cm^{-3}]	$c_{dop,}x10^{-14}$ [cm^{-3}]	Conductivity type	$N x10^{-14}$ [cm^{-3}]
Si-B	9.4	-	p	6.5
Si-P	9.1	-	n	12.1
Si-N	9	2	n	8
Si-Ge	6.5	7000	p	1.9

Results and discussion

As follows from X-ray measurements (not presented), processing of Si-B and Si-P at 698-748 K, both under 10^5 Pa and *HP*, does not produce the defects revealed by XRRSM.

Annealing for 10 h at 698-748 K of all investigated samples (Table 1) leads to their n-type conductivity. This effect is related to the creation of so called double thermal donors composed of supersaturated oxygen aggregated on Si core [3]. Processing of Si-P and Si-B samples at about 723 K leads to non-linear increase of electron concentration with *HP*. Similarly to the case reported earlier [2], the N_e value reaches saturation after processing under *HP* exceeding 1 GPa. At even higher *HP*, the N_e value tends to decrease slightly. This effect is independent of the initial conductivity type and related first of all to the content of interstitial oxygen [3] (Table 1, Fig. 1).

Contrary to the usually reported maximum electron concentration reached in Cz-Si after processing under atmospheric pressure (10^5 Pa) just at 723 K [1, 3], processing under *HP* leads to a shift of this characteristic temperature (*HT_{TD}*), to the higher value (in the case of B-doped sample) or to the existence of wider temperature range, (ΔHT_{TD}) within which the TD's species are most intensively created (Fig. 1, the case of Si-P samples).

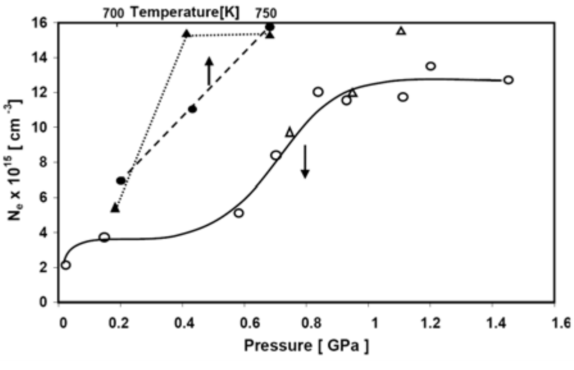

Fig.1. Electron concentration, N_e, versus pressure (○,Δ) and temperature (●,▲) for initially n-type, P-doped Si-P (Δ,▲) and for initially p-type, B-doped, Si-B (○,●) samples processed for 10 h at *HT-HP*: ○, Δ – after processing at 723 K versus *HP*; ●,▲ – after processing under 1.2 GPa versus *HT*

Light doping of the n-type Cz-Si samples with nitrogen (Si-N, Table 1) leads to similar increase (compare [4]) of characteristic *HT_{TD}* as that observed for the B-doped samples processed under *HP* (Fig. 2, compare Fig. 1).

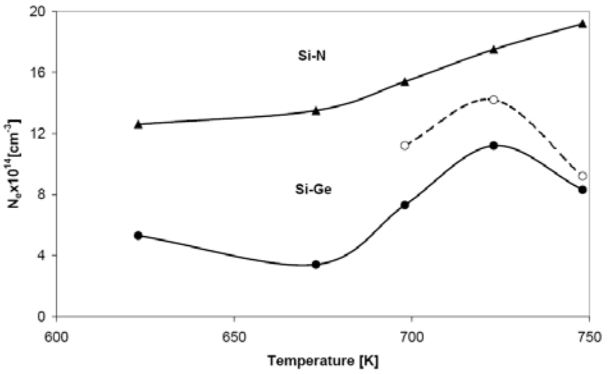

Fig.2. Electron concentration versus processing temperature for N-doped, Si-N (▲) and Ge-doped, Si-Ge (○,●) samples processed for 10 h: ○ – processing under 1.1 GPa at *HT*; ●,▲ – processing under 1.1 GPa at *HT* and, subsequently, for 10 h at 723 K under 10^5 Pa

In the case of heavily Ge-doped Si-Ge samples ([5], Table 1) rather sharp maximum of HT_{TD} has been observed, both after one-step processing under 1.1 GPa as well as after subsequent annealing of the one-step treated samples for 10 h at 723 K under 10^5 Pa (Figs 2 and 3). Processing of the SI-Ge samples at 723 K leads to detectable increase with *HP* of the electron carriers concentration. Accounting for the known strong dependence of new-created TD's concentration on c_o, an increase of TD's concentration with *HP* after processing at 723 K for 10 h (Fig. 3) can be considered as analogous with that detected for the Ge-lean Cz-Si samples (Fig. 1, [2, 6]).

As follows from X-ray measurements and contrary to the case of *HP*-processed Si-B and Si-P samples, the treatment of Si-Ge, especially under *HP*, produces some defects revealed by XRRSM (Fig. 4). Because the strain fields caused by the presence of TD's may be considered to be small, the defects can originate also from transformed (clustered ?) Ge dopant under *HT-HP*.

Dependencies of the TD's-related electron concentration on processing time at 723 K are presented in Figs 5 and 6. The data for processing at other temperatures are given for reference reasons. Processing of the Si-P as well as of Si-B samples for up to 20 h at 723 K under 1.2 GPa does not lead to the saturated values of N_e (Figs 5 and 6).

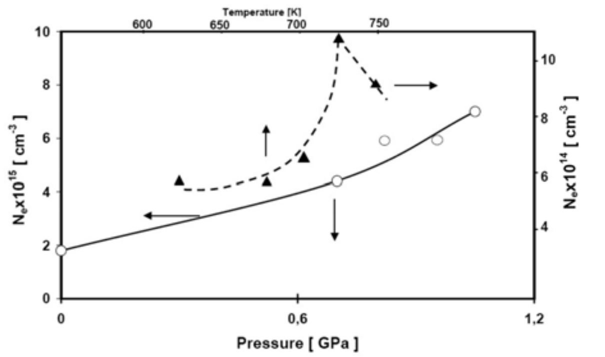

Fig.3. Electron concentration versus *HP* (○) and *HT* (▲) for Si-Ge samples (Table 1) processed for 10 h: ○ – at 723 K; ▲ – processing under 1.2 GPa at *HT* and subsequent annealing at 723 K for 10 h under 10^5 Pa

As also seen in Fig. 5, processing at 723 K within the 1.2-1.4 GPa range leads to practically identical concentration of carriers. Processing of the samples under *HP* for up to 10 h at distinctly lower (673 K) or higher (873 K) temperatures does not produce carriers in distinctly enhanced concentrations (Fig. 5).

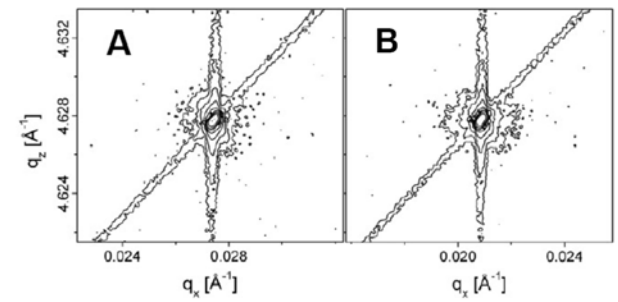

Fig.4. XRRSM's (004 reflection) of Si-Ge samples: A-as grown; B-processed for 10 h at 623 K under 1 GPa and for 10 h at 723 K under 10^5 Pa. Axes are presented in reciprocal lattice space units (rlu)

Subsequent processing at 723 K of the Si-B samples pre-annealed at 833 K under 10^5 Pa leads to definitely decreased carrier concentration in comparison to that observed for the case of processed as grown samples. The same while less pronounced effect is observed for the Si-B samples pre-annealed sequentially at 723 K (to create TD's) and at 833 K (to annihilate them [8]) and finally annealed at 723 K under 10^5 Pa (Fig. 6). It is important to mention that such pre-anneals do not result in marked change of the interstitial oxygen concentration as detected by FTIR (this change does not exceed 5% of the value detected for the as grown samples). This means that the effects of annealing of the Cz-Si samples at about 723 K reflects to some extent their thermal history in respect of annealing or other processing (compare [7]).

While some *HP*-induced effects in doped Cz-Si processed at about 723 K have been reported earlier [2, 4-6, 8], we found now some new effects seemingly as so far not detected. Most interesting among them are:

- broadened temperature range or shifted temperature position of the most intensive TD's creation under *HP* (Fig. 1), and
- clear dependence of the TD's creation rate on thermal treatment history of the investigated samples with the same interstitial oxygen concentration (Fig. 6).

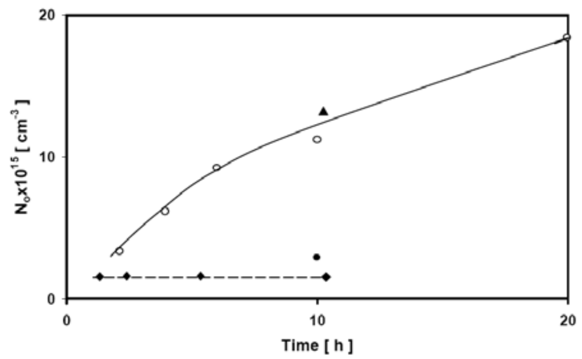

Fig.5. Electron concentration versus time of annealing for Si-P samples: ○ – processed at 723 K under 1.2 GPa; ● – processed at 673 K under 1.2 GPa; ▲ – processed at 723 K under 1.4 GPa. Data for reference Si-P samples processed at 873 K under 1.2 GPa are depicted as ♦

Traditional explanation [9] of the abnormally high rate of TD's creation at 723 K (the case of annealing under 10^5 Pa) is most usually delivered by an assumption that isolated (interstitial) oxygen atoms are converted to a fast diffusing species (such as oxygen dimers [10]) just near this temperature. On the other hand, our earlier works [2, 6] as well as the papers of other authors [11-13] suggest other explanation. This other one accounts for the effect of the internal elastic stresses created by the effect of microfluctuation of oxygen and thermal donors concentrations in the Cz-Si lattice on the effective diffusion coefficient of oxygen. An estimation of the dimension of such fluctuations gives a value within a few tens of micrometers [11, 12]. The presence of clusters (clouds) of TD's has been confirmed experimentally [13]. This confirms our idea concerning a pressure-induced activation of such irregularities to act as the cores of newly (additionally) created TD's. Their presence contributes to qualitative explanation of the *HP*-induced effects on TD's generation.

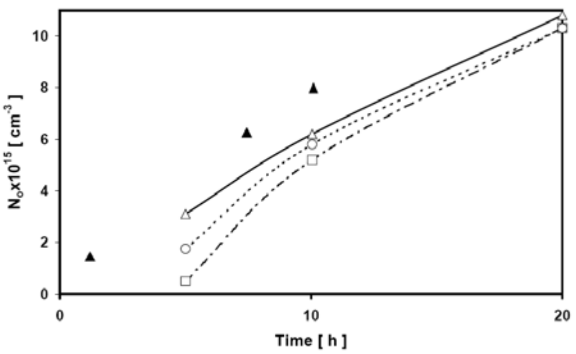

Fig.6. Electron concentration versus time of annealing at 723 K under 10^5 Pa for Si-B samples: ∆ – as grown (Table 1), □ – pre-annealed for 20 h at 833 K under 10^5 Pa, ○ – sequentially pre-annealed for 20 h at 723 K and for 20 h at 833 K under 10^5 Pa. ▲ – as grown samples, processed at 723 K under 1.1 GPa

HP-induced activation would be related [2, 6] to a *HP*-affected misfit at the interstitials cluster/Si matrix boundary, dependent, among others, on the dimension and kind of O_i's clouds. This would mean that both the temperature range of TD's creation and dependence of this creation on thermal history (and so on the presence of different microdefects) can be influenced strongly by *HP*. Still further work on recognition of the effect of *HP* on diffusivity of oxygen dimers is needed to understand the complexity of high hydrostatic pressure effects on thermal donors creation in doped oxygen-containing Czochralski grown silicon.

Conclusions

HP-stimulated (for up to an order of magnitude) generation of TD's has been confirmed for Cz-Si samples doped with boron, phosphorus, nitrogen or germanium. This generation increases with interstitial oxygen concentration (c_o) and, sometimes, with *HT* while is less dependent on the concentration of the investigated dopants.

It has been confirmed that the presence of local clouds of oxygen interstitials seems to be the important factor responsible for the *HP*-induced increase of TD's concentration in doped oxygen-containing Czochralski grown silicon.

The authors are obliged for Dr W. Jung and M. Remiszewska from the Institute of Electron Technology, Warsaw, as well as for m. sc. B. Surma from the Institute of Electronic Materials Technology, Warsaw for some electrical and FTIR data

REFERENCES

[1] Voronkov V.V., Voronkova G.I., Batunina A.V., Golovina V.N., Falster R., Cornara M., Tiurina N.B., Guliaeva A.S., Properties of fast-diffusing oxygen species in silicon deduced from the generation kinetics of thermal donors, *Solid State Phen.,* 156-158 (2010), 115-122

[2] Misiuk A., Jung W., Surma B., Jun J., Rozental M., Effect of stress induced defects on electrical properties of Czochralski grown silicon, *Solid State Phen.*, 57-58 (1997), 393-398

[3] Young Joo Lee, von Boehm J., Nieminen R.M., Interstitial oxygen loss and the formation of thermal double donors in Si, *Appl. Phys. Lett.*, 79 (2001), 1453-1455

[4] Misiuk A., Surma B., Deren Yang, Prujszczyk M., Stress dependent structure of annealed nitrogen-doped Cz-Si, *Materials Sci. Engng B.*, 134 (2006), 218-221

[5] Misiuk A., Deren Yang, Surma B., Londos C.A, Bak-Misiuk J., Andrianakis A., Defects in Ge-doped Cz-Si annealed under high stress, *Mater. Sci. Semicond. Process.*, 9 (2006), 82-87

[6] Misiuk A., Effect of silicon microstructure on stress-stimulated creation of thermal donors, in International Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals, A. Rogalski, K. Adamiec, P. Madejczyk, Eds, Proceed. SPIE 4412 (2001), 85-90

[7] Misiuk A., Jung W., Prujszczyk K., Bak-Misiuk J., Felba J., Ujawnienie historii radiacyjnej napromieniowanego elektronami krzemu otrzymanego metodą Czochralskiego poprzez po-radiacyjną obróbkę termiczną, *Przegląd Elektrotechniczny*, 7 (2010), 29-31

[8] Misiuk A., Annihilation of Thermal Donors in Silicon Annealed under High Hydrostatic Pressure, in Solid State Crystals 2002: Crystalline Materials for Optoelectronics, J. Rutkowski, A. Rogalski, Eds, Proceed. SPIE 5136 (2002), 47-52

[9] McQuaid S.A., Johnson B.K., Gambaro D., Falster R., Ashwin M.J., Tucker J.H., The conversion of isolated oxygen atoms to a fast diffusing species in Czochralski silicon at low temperatures, *J. Appl. Phys.*, 86 (1999),1878-1887

[10] Yarykin N., Weber J., DLTS study of the dimer formation kinetics in silicon, *Physica B*, 404 (2009), 4576-4579

[11] Neimash V.B., Puzenko E.A., Kabaldin A.N., Kraichinhii A.N., Kras'ko N.N., Nature of the nuclei for thermal donor formation in silicon (or another variant of accelerated oxygen diffusion), *Semiconductors*, 33 (1999) 1279-1283

[12] Neimash V.B., Kraichinhii A.N., Kras'ko N.N., Puzenko E.A., Claeys C., Simoen E., Svensson B., Kuznetsov A., Influence of Tin Impurities on the Generation and Annealing of Thermal Oxygen Donors in Czochralski Silicon at 450°C, *J. Electrochem. Soc.*, 147 (2000), 2727-2733

[13] Kraitchinkii A., Kras'ko M., Neimash V., Shpinar L., Tishchenko V., Voitovich V., Goushcha A.O., Metzler R.A., Small angle light scattering and clusters of thermal donors in Si, *J. Appl. Phys.*, 96 (2004), 7235-7238

Autorzy: *dr hab. inż. Andrzej Misiuk, Marek Prujszczyk, Instytut Technologii Elektronowej, Al. Lotników 46, 02-668 Warszawa, Polska, E-mail: misiuk@ite.waw.pl.*

Prof. dr hab. Jadwiga Bak-Misiuk, mgr Przemyslaw Romanowski, Instytut Fizyki PAN, Al. Lotników 32/46, 02-668 Warszawa, Polska, E-mail: bakmi@ifpan.edu.pl.