

The impact of Ge codoping on grown-in O precipitates in Ga-doped Czochralski-silicon

著者	Arivanandhan Mukannan, Gotoh Raira, Fujiwara Kozo, Ozawa Tetsuo, Hayakawa Yasuhiro, Uda Satoshi
journal or publication title	Journal of Crystal Growth
volume	321
number	1
page range	24-28
year	2011-04-15
出版者	Elsevier
権利	Copyright (C) 2011 Elsevier B.V. All rights reserved.
URL	http://hdl.handle.net/10297/5646

doi: 10.1016/j.jcrysgro.2011.02.028

The impact of Ge codoping on grown-in O precipitates in Ga-doped Czochralski-silicon

Mukannan Arivanandhan^{a*}, Raira Gotoh^b, Kozo Fujiwara^b, Tetsuo Ozawa^c, Yasuhiro Hayakawa^a,
Satoshi Uda^b

^aResearch Institute of Electronics, Shizuoka University, Johoku 3-5-1, Naka-Ku, Hamamatsu,
Shizuoka 432-8011, Japan

^bInstitute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku,
Sendai 980-8577, Japan

^cDepartment of Electrical Engineering, Shizuoka Institute of Science and Technology, Fukuroi,
Shizuoka 437-8555

Abstract:

The intensity of the infrared absorption band at 1107 cm^{-1} , related to interstitial oxygen (O_i) concentration, decreased as the Ge concentration increased in Ga and Ge codoped CZ-Si crystals. In contrast, the number of precipitates observed on the etched surfaces of CZ-Si wafers increased as the Ge concentration increased. From an energy dispersive X-ray (EDX) analysis, O was observed to be one of the major components of the precipitates. Moreover, Ge was found as one of the components in the precipitate observed on the heavily Ge ($>1 \times 10^{18}\text{ cm}^{-3}$) codoped CZ-Si wafers. These results suggest that the grown-in O precipitates increase as the O_i concentration decreases when the Ge concentration increases in the Si crystal. The Ge-vacancy (V) complex in the Si lattice probably acted as a heterogeneous nucleation center and may enhanced the grown-in O precipitates thereby reducing the dissolved O_i concentration in the Si lattice.

Keywords: A2. Czochralski method; B2. Semiconductor Silicon; A1. Codoping; A1. Point Defects

PACS: 81.10.Fq, 61.72.sh, 71.55.Ak

*Corresponding Author: Mukannan Arivanandhan

Email: rmarivu@ipc.shizuoka.ac.jp

Phone: +81 53 478 1338

Fax: +81 53 478 1338

1. Introduction:

Currently, the world's industrial production of solar cells is mainly based on boron (B)-doped crystalline silicon (c-Si) which includes single crystalline and multicrystalline (mc) silicon. Generally, solar cell elements using a single-crystal Si substrate have higher conversion efficiencies than that of mc-Si due to their structural perfections. The single crystal Si substrate material is produced by the Czochralski method using high-purity poly Si. However, the light-induced lifetime degradation (LID) in B-doped Czochralski-grown silicon (CZ-Si) – due to the formation of B-oxygen complexes with high recombination activity – limits the minority carrier lifetime (MCL) thereby the efficiency of solar cells [1-3]. In contrast, gallium (Ga)-doped CZ-Si was recently identified as a promising substrate material for solar cells since it shows high MCL with no LID effect [3]. Although the Ga-doped CZ-Si shows a high MCL, different types of grown-in micro-defects (GMDs), such as A, B, D, and I type defects may exist in dislocation-free crystals [4], and limit the MCL by acting as recombination centers [5]. Therefore, to further improve the MCL of Ga-doped CZ-Si, thereby the conversion efficiency of the solar cell, it is essential to understand the GMD formation mechanism in CZ-Si and its effects on MCL as well.

In our previous work, we observed a high MCL in Ga-doped CZ-Si by Ge codoping with no LID effect [6,7]. Moreover, we observed that the flow pattern defect (FPD) density was reduced as the Ge concentration increased in the Ga and Ge codoped CZ-Si. The experimental

results were consistently explained by a defect suppressing model based on a Ge-vacancy (V) defect complex, which enhanced the O precipitates by acting as a heterogeneous nucleation center [7]. Watkins [8, 9] observed a similar substitutionally placed Ge and vacancy ($\text{Ge}_s\text{-V}$) defect complex in Ge containing Si by electron paramagnetic resonance (EPR) studies. Moreover, similar proposals were reported in the literature [10-13] based on infrared absorption and defect studies. In addition, recent computation work by Chen et al [14] highly supports this proposal. In contrast, Chroneos et al [15] reported that the contribution of Ge to the stability of the GeV_n (V_n is the vacancy clusters with more than two vacancies) clusters is relatively small due to small difference (0.35 eV) between the binding energies of GeV_n and V_n clusters and hence Ge does not act as a site that traps a significant proportion of V, contradicting the proposal by Chen et al [14]. Nevertheless, further investigation is needed on experimental as well as theoretical aspects to clarify the effect of Ge on the formation of Ge-V defect complex and O precipitates in CZ-Si. In the present report, the interstitial oxygen (O_i) concentrations in the Ga and Ge codoped CZ-Si wafers were measured by means of Fourier transform infrared (FTIR) spectroscopy. The chemical composition of the grown-in O precipitates on the etched surfaces of the Ga and Ge codoped CZ-Si wafers were analyzed by energy dispersive X-ray (EDX) spectroscopy. The results support our proposed model for the defect suppressing mechanism in Ga and Ge codoped CZ-Si crystals [7].

2. Experimental procedure:

2.1 Crystal growth:

A series of Ga and Ge codoped $\langle 100 \rangle$ Si single crystals were grown by the Czochralski method with varying Ge concentration at fixed Ga ($1.5 \times 10^{16} \text{ cm}^{-3}$) concentration. The concentration of Ge in the crystals varied from 1×10^{17} to $1 \times 10^{20} \text{ cm}^{-3}$. The growth parameters,

such as the crystal rotation rate (~ 20 rpm), crucible rotation rate (~ -10 rpm), growth rate (0.70 mm/min during the growth of the crystal body), and crystal diameter (about 70 mm) were controlled for all the experiments. Sliced Si wafers (corresponding to 30% of the solidified fraction) from the grown ingots with different concentrations of Ge (1×10^{17} cm $^{-3}$ to 1×10^{20} cm $^{-3}$) were chosen (see Table 1) for the present investigation. The wafers were chemically mirror finished using a mixed acid solution of HNO $_3$ and HF.

2.2 FTIR Investigations:

The concentrations of dissolved O $_i$ in the grown Ga and Ge codoped CZ-Si wafers (Table 1) were measured by FTIR using a JEOL WIN SPEC-50 at room temperature in atmospheric air. The resolution and number of accumulation of the spectrum were set to 4 cm $^{-1}$ and 32 times, respectively. The background of the spectrum was calibrated using a sample-free spectrum. Interstitially dissolved O in Si exhibits an absorption peak at 1107 cm $^{-1}$ at room temperature [16]. The concentration of dissolved O was determined from the absorption coefficient of the peak at 1107 cm $^{-1}$ using the standard calibration factor 3.14×10^{17} cm $^{-2}$ [17]. Moreover, a broad peak at 1224 cm $^{-1}$ can be observed in the spectrum which is related to SiO $_2$ precipitates. This peak can be explained by the excitation of the longitudinal optical (LO) phonon mode of SiO $_2$. The LO mode is normally infrared inactive for bulk SiO $_2$ but can become active for particles that are small enough to become electrically polarized. Hu's theoretical calculations show that the 1224 cm $^{-1}$ band arises from particles that are smaller than $\lambda/2\pi n_m$, where λ is the wavelength of the incident radiation and n_m the refractive index of the embedding matrix and have a plate-like shape [16].

2.3 SEM and EDX analysis on the etched CZ-Si wafers:

The wafers were etched using Secco etchant for 10 min to observe the grown in O precipitates by scanning electron microscopy (SEM) (JOEL JSM-5510). The composition of the grown-in O precipitates in the etched surfaces of the Ga and Ge codoped CZ-Si wafers were analyzed by EDX spectroscopy.

3. Experimental results:

In Fig. 1(a-e) the FTIR absorption spectra of samples 1-5 (spectra a-e, respectively) are shown in the spectral range from 900 to 1300 cm^{-1} . The spectrum of sample 1 is recorded for CZ-Si wafer doped only with Ga, while those of samples 2-5 (Table 1) show the behavior of the IR spectrum as a function of Ge concentration. All the recorded spectra showed a sharp peak at about 1107 cm^{-1} related to O_i concentration. Moreover, no peaks were observed at 1224 cm^{-1} in all spectra, probably the grown-in O precipitates are IR-inactive due to their large size [16] (which was later confirmed by SEM). Spectrum b of Fig. 1 does not show any remarkable change, being almost the same as spectrum a; it also reveals that a Ge concentration of $1 \times 10^{17} \text{ cm}^{-3}$ induces a relatively small number of O precipitates as evidenced in etching studies (Fig. 4). By increasing the Ge concentration to $1 \times 10^{18} \text{ cm}^{-3}$, the O_i -related peak at 1107 cm^{-1} showed a relatively low intensity (spectrum c in Fig. 1) and the intensity of the peak further decreased as the Ge concentration increased to $1 \times 10^{19} \text{ cm}^{-3}$ (spectrum d in Fig. 1) and $1 \times 10^{20} \text{ cm}^{-3}$ (spectrum e in Fig 1).

The O_i concentration converted from the absorption coefficient of the IR absorption peak by a standard conversion factor is plotted in Fig. 2 as a function of Ge concentration. As shown

in Fig. 2, the O_i concentration decreased as the Ge concentration increased in the Si crystal from $1 \times 10^{17} \text{ cm}^{-3}$ to $1 \times 10^{20} \text{ cm}^{-3}$. The relatively high O_i concentration obtained even for a low intensity peak (spectrum d in Fig. 1) at a Ge concentration of $1 \times 10^{19} \text{ cm}^{-3}$ was probably due to the thinness of the particular wafer (refer Table 1). The uncertainty in the converted value of O_i concentrations (Fig. 2) are possible to occur due to possible errors in the data treatment and the effect of wafer's surface on the peak height is high especially for the thin wafers ($< 500 \mu\text{m}$ thick) [18]. However, the effect is same for all the wafers and thus the reduction of O_i concentration in Ga and Ge codoped CZ-Si wafers is obvious. These experimental results suggest that the formation of Ge-V complexes (as confirmed by FPD density reduction in our previous report, ref. 7) due to Ge codoping may have forced O_i to precipitate. As a result, a reasonable decrease in O_i was observed in CZ-Si as a function of Ge concentration. This behavior was also reported in Ge-doped Si [12].

The SEM micrographs of the etched surfaces of samples 1, 3 and 5 (refer to Table 1) are shown in Fig. 3 (a-c). On the etched surface of sample 1 (Fig. 3a), only few grown-in precipitates were observed while on the etched surface of sample 3, grown-in precipitates increased relatively and the average precipitate size was about $\leq 1 \mu\text{m}$. In contrast, the density of grown-in precipitates increased in sample 5 (Fig.3c) with an average size of about $\leq 2 \mu\text{m}$. The variation in density of grown-in precipitates as a function of Ge concentration is shown in Fig. 4. As can be seen from Fig. 4, the density of grown-in precipitates increased as the Ge concentration increased in Ga and Ge codoped CZ-Si.

Figure 5a and 5b show the EDX spectra recorded for positions A and B marked in Fig 3b. The spectra indicate that the precipitates contain O and Si, while no O-related peak was

observed in the EDX spectrum recorded on the precipitate-free surface (Fig. 5b). Figure 6a and 6b show the EDX spectra obtained from two locations marked A and B in Fig. 3c. As can be seen from the spectra, two peaks related to O K_{α} , and Ge L_{α} were observed in the spectrum recorded on the precipitate in addition to the prominent Si peak. However, the spectrum for precipitate-free Si surface shows only a Ge L_{α} peak with a prominent Si peak. The Ge-related peak in the EDX spectra recorded for the Ga ($1.5 \times 10^{16} \text{ cm}^{-3}$) and Ge ($1 \times 10^{18} \text{ cm}^{-3}$) codoped CZ-Si wafer (sample 3; Fig.5a and 5b) was absent, probably due to a low concentration of Ge. According to Hu's [16] theoretical calculations, O precipitates which are larger than about $0.36 \mu\text{m}$ ($\lambda/2\pi n_m$) become infrared inactive; as a result, the 1224 cm^{-1} peak cannot be observed in infrared absorption spectra. As shown in the SEM images (Fig. 3), the grown-in O precipitates in the present experiments are relatively larger ($\geq 1 \mu\text{m}$) than $0.36 \mu\text{m}$ and hence, the corresponding peak was not observed in the IR spectrum. The experimental results revealed that the O_i concentrations decrease and the grown-in O precipitates increase as the Ge concentration increases in the Ga and Ge codoped CZ-Si single crystals.

4. The role of Ge-V defects on O precipitates

It is known that the free vacancies in Si diffuse over the lattice with a migration energy of 0.35 eV at high temperature ($T > T_{vn}$, where T_{vn} is the void nucleation temperature) [19]. Moreover, the free vacancies can diffuse over the Si lattice and form vacancy clusters (V_n , where n is 1,2 3....) on subsequent cooling, which can diffuse over a large distance in the Si lattice without dissociation [20]. The activation energy for diffusion of the smallest vacancy cluster, i.e., divacancy, is about 1.25 eV , while that for dissociation of a divacancy is higher than 1.6 eV [11].

In addition, the growth of faceted voids proceeds by nucleation of a two-dimensional (2D) nucleus and subsequent expansion of the nucleus over the whole facet. The growth of larger voids is rapid since 2D nucleation becomes easy in a larger facet area [21]. The larger voids (which contain up to 4×10^7 vacancies) can differ from the vacancy clusters in their number of vacancies [21]. It is expected that the as grown crystals contain both vacancy clusters and voids. Moreover, in CZ-Si crystals, the cluster density is in the order of 10^8 cm^{-3} , which is four to five orders smaller than FZ-Si crystals, since vacancies are consumed mostly by voids. In this sense, when $T < T_{vn}$, the vacancy clusters in Ge-free CZ- Si crystals are likely to interact with the dissolved O_i and form V-O and/or V_2 -O related complexes. These defects act as O precipitation nuclei and are grown as O precipitates on subsequent cooling ($T \ll T_{vn}$). This is a possible reason for the small number of grown-in precipitates and large number of FPD defects related to void defects (evidences for FPDs are presented in ref. 7 and 22) observed on sample 1 (Fig. 3a).

In the presence of substitutionally codoped Ge, the fast diffusing divacancies and/or other vacancy clusters can interact with Ge atoms ($T > T_{vn}$) in the course of post-growth cooling and form a Ge- V_n defect complex. The formation of such a complex is more feasible when the ingot temperature T is higher than T_{vn} , since the binding energy of the Ge- V_n defect complex is higher – up to 0.35 eV – compared to V_n clusters [15] and the activation energy for vacancy diffusion is then low – about 0.36 eV²⁰. Furthermore, there is infrared absorption evidence for the interaction of divacancies (V_2) with impurities [11, 23]. As a result of the Ge- V_n complex formation, the free vacancy concentration reasonably reduced and thus the void nucleation were possibly suppressed. On subsequent cooling of the ingots ($T \ll T_{vn}$), the supersaturation of O_i in Si becomes larger and the O_i precipitates may be grown using Ge- V_n as a nucleation site. Furthermore, when the Ge concentration increases, the possibility of a Ge- V_n complex formation

is relatively increased which results in large number of precipitates on the heavily Ge codoped CZ-Si wafers (Fig. 3c). Subsequently, the experimental results suggest that the reduction of O_i in Ga and Ge codoped CZ-Si is probably due to O precipitation growth using Ge-V defect complex as nucleation sites. Moreover, it is worthwhile to mention that the grown-in precipitates would have less ability to limit carrier lifetime in the presence of D-type void defects as they are smaller than void defects [4].

5. Conclusion:

We have experimentally shown that the dissolved O_i concentration decreased and the number of grown-in O precipitates increased as the Ge concentration increased in Ga and Ge codoped CZ-Si crystals. From the EDX analysis, it was observed that O was one of the major components of the grown-in precipitates. Moreover, Ge was found to be one of the components in the precipitate observed on heavily Ge ($>1 \times 10^{18} \text{ cm}^{-3}$) codoped CZ-Si wafers. The results suggested that the grown-in O precipitates increased with a decrease in O_i concentration as the Ge concentration increased in the Si crystal. From the results one can infer that the Ge- V_n defect complex may acted as a favorable heterogeneous nucleation center for the O precipitates especially in the heavily Ge codoped CZ-Si wafers thereby enhanced the density of grown-in precipitate during post growth cooling of the ingot.

Acknowledgement:

This work was financially supported by a Grant-in-Aid for Young scientist B (no. 22760005) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References:

- [1] S.W. Glunz, S. Rein, W. Warta, J. Knobloch, and W. Wettling, Proceedings of the 2nd world conference on Photovoltaic Energy Conversion, Vienna, Austria (European Commission, Ispra, Italy, 1998), P. 1343.
- [2] J. Schmidt and A. Cuevas, J. Appl. Phys. 86, (1999) 3175.
- [3] S.W. Glunz, S. Rein, J.Y. Lee, and W. Warta, J. Appl. Phys. 90, (2001) 2397.
- [4] A.J.R. De Kock, Appl. Phys. Lett., 16, (1970) 100.
- [5] T. H. Wang, T. F. Ciszek and T. Schulier, Solar cells, 24, (1988) 135.
- [6] M. Arivanandhan, R. Gotoh, K. Fujiwara, S. Uda, Appl. Phys. Lett. 94, (2009) 072102.
- [7] M. Arivanandhan, R. Gotoh, K. Fujiwara, S. Uda, J. Appl. Phys. 106, (2009) 013721.
- [8] G. D Watkins, IEEE Trans. Nuclear Science 16, (1969) 13.
- [9] G. D. Watkins, Chin. J. Phys., 15, (1977) 92.
- [10] A. BreLOT and J. Charlemagne, Radiat. Eff. and Def. Sol., 9, (1971) 65.
- [11] Yu. V. Pomozov, M. G. Sosnin, L. I. Khirunencko, N. V. Abrosimov, and W. Schroder, Semiconductors, 35, (2001) 890.
- [12] D. Yang, X. Yu, X. Ma, J. Xu, L. Li and D. Que, J. Cryst. Growth 243, (2002) 371.
- [13] J. Chen, D. Yang, X. Ma, W. Wang, Y. Zeng, and D. Que, J. Appl. Phys., 101, (2007) 113512.
- [14] J. Chen, T. Wu, X. Ma, L. Wang, and D. Yang, J. Appl. Phys., 103, (2009) 123519.
- [15] A. Choneos, R. W. Grimes, and H. Bracht, J. Appl. Phys., 105, (2009) 016102,.
- [16] S. M. Hu, J. Appl. Phys., 51, (1980) 5945.
- [17] H. J. Moller, L. Long, M. Werner, D. Yang, Phys. Status Solidi a, 171, (1999) 175.

- [18] Y. Itoh, T. Nozaki, *Jpn. J. Appl. Phys.* 24 (1985) 279.
- [19] G. D. Watkins, *J. Phys. Soc. Japan* 18, (1963) 22.
- [20] G. D. Watkins and J. W. Corbett, *Phys. Rev.* 138, (1965) A543.
- [21] V. V. Voronkov, and R. Falster, *J. Cryst. Growth* 204, (1999) 462.
- [22] R. Gotoh, M. Arivanandhan, K. Fujiwara, S. Uda, *J. Cryst. Growth* (in press) 2010.
- [23] V P Markevich, A. R. Peaker, J. Coutinho, R. Jones, V. J. B. Torres, S. Oberg, P. R. Briddon, L. I. Murin, L. Dobaczewski and N. V. Abrosimov, *Phys. Rev. B* 69, (2004) 125218.

Table 1: Characteristics of the six CZ-Si wafers studied

Sample number	Ga concentration (cm^{-3})	Ge concentration (cm^{-3})	Thickness of the wafers (μm)
1	1.5×10^{16}	0	450
2	1.5×10^{16}	1×10^{17}	450
3	1.5×10^{16}	1×10^{18}	450
4	1.5×10^{16}	1×10^{19}	350
5	1.5×10^{16}	1×10^{20}	450

Figure captions:

Figure 1: Infrared absorption spectra of samples 1-5 (curves a-e). The spectra have been shifted for clarity.

Figure 2: O_i concentration as a function of Ge concentration in the Ga and Ge codoped CZ-Si crystals.

Figure 3: SEM images of the etched surfaces of Ga and Ge codoped CZ-Si crystals. (a). Ge-free CZ-Si, (b). Ge ($1 \times 10^{18} \text{ cm}^{-3}$) codoped CZ-Si, (c). Ge ($1 \times 10^{20} \text{ cm}^{-3}$) codoped CZ-Si.

Figure 4: Density of grown-in O precipitates as a function of Ge concentration.

Figure 5: (a) EDX spectrum of the grown-in precipitate (position A marked in Fig. 3b).; (b) EDX spectrum of the precipitate-free surface (position B marked in Fig. 3b).

Figure 6: (a) EDX spectrum of the grown-in precipitate (position A marked in Fig. 3c); (b) EDX spectrum of the precipitate-free surface (position B marked in Fig. 3c).

Fig. 1

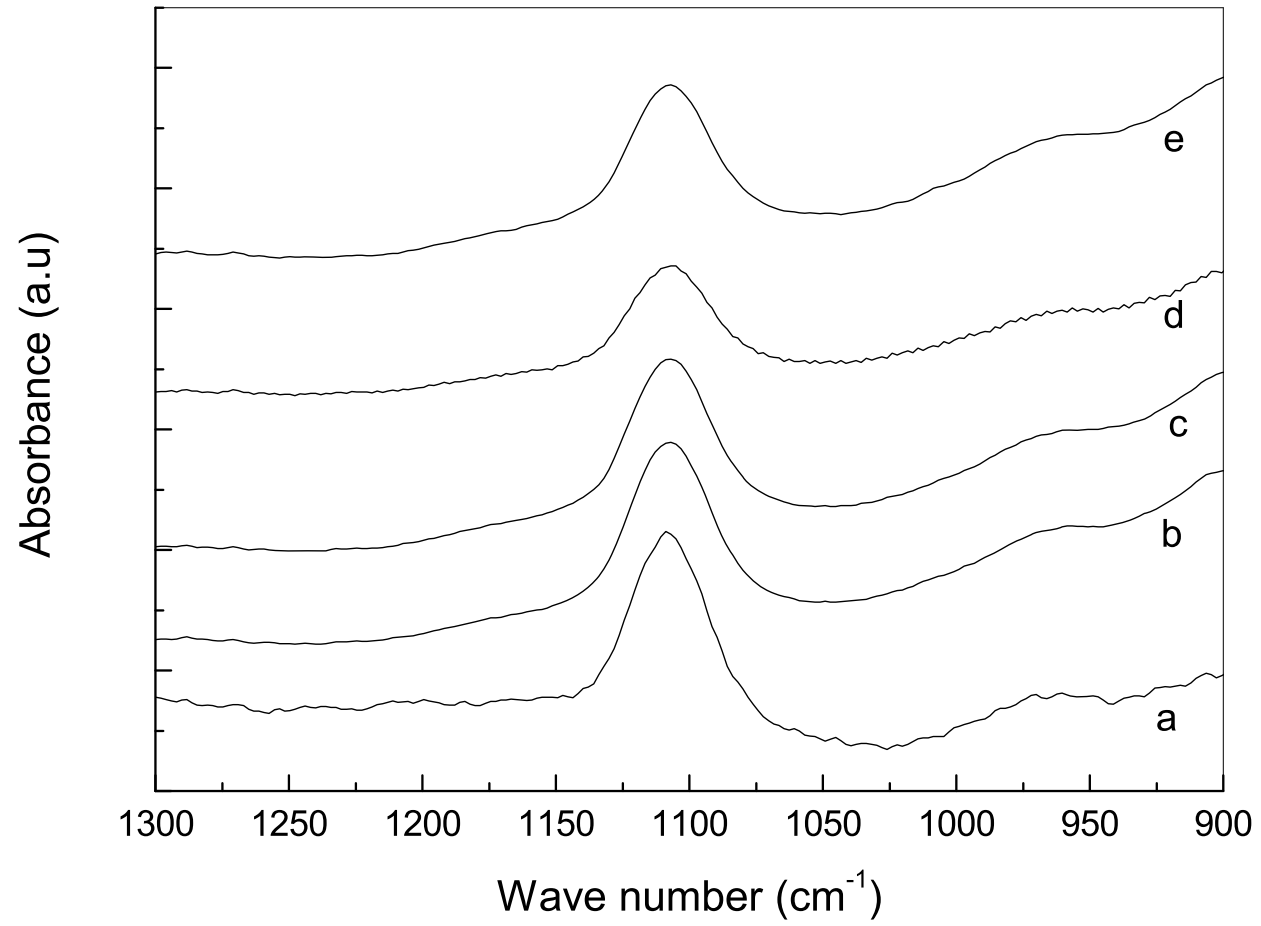


Fig. 2

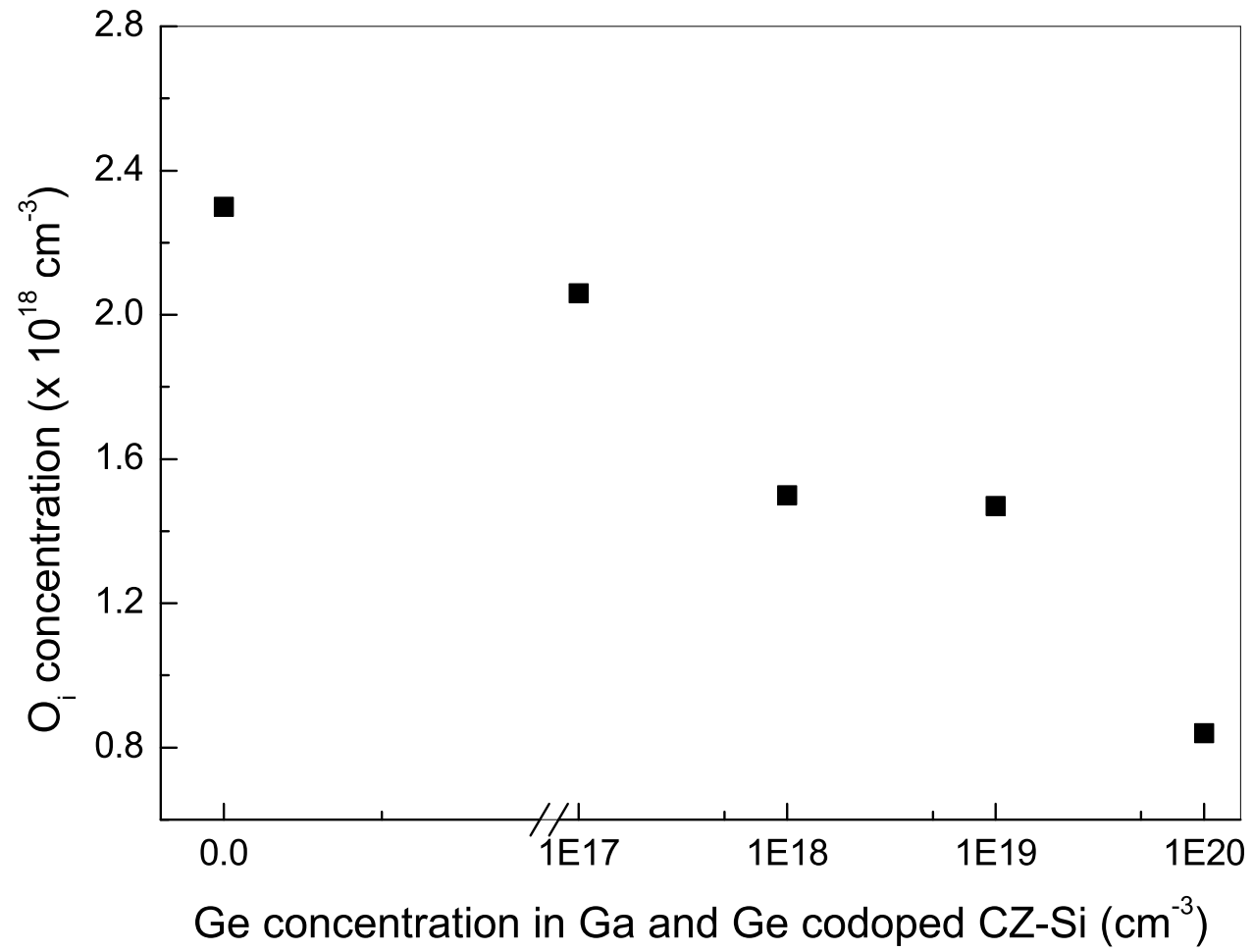


Fig. 3

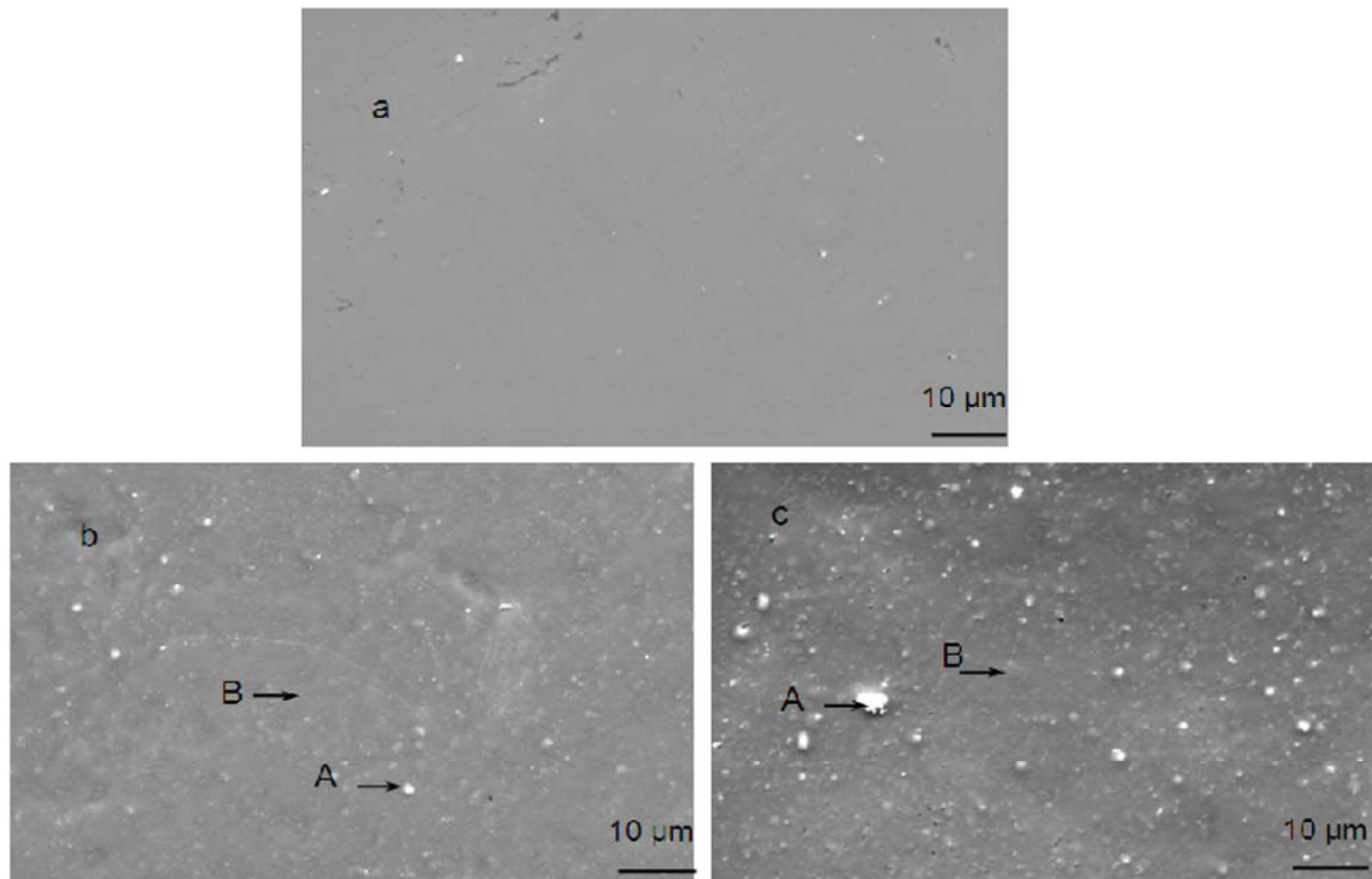


Fig. 4

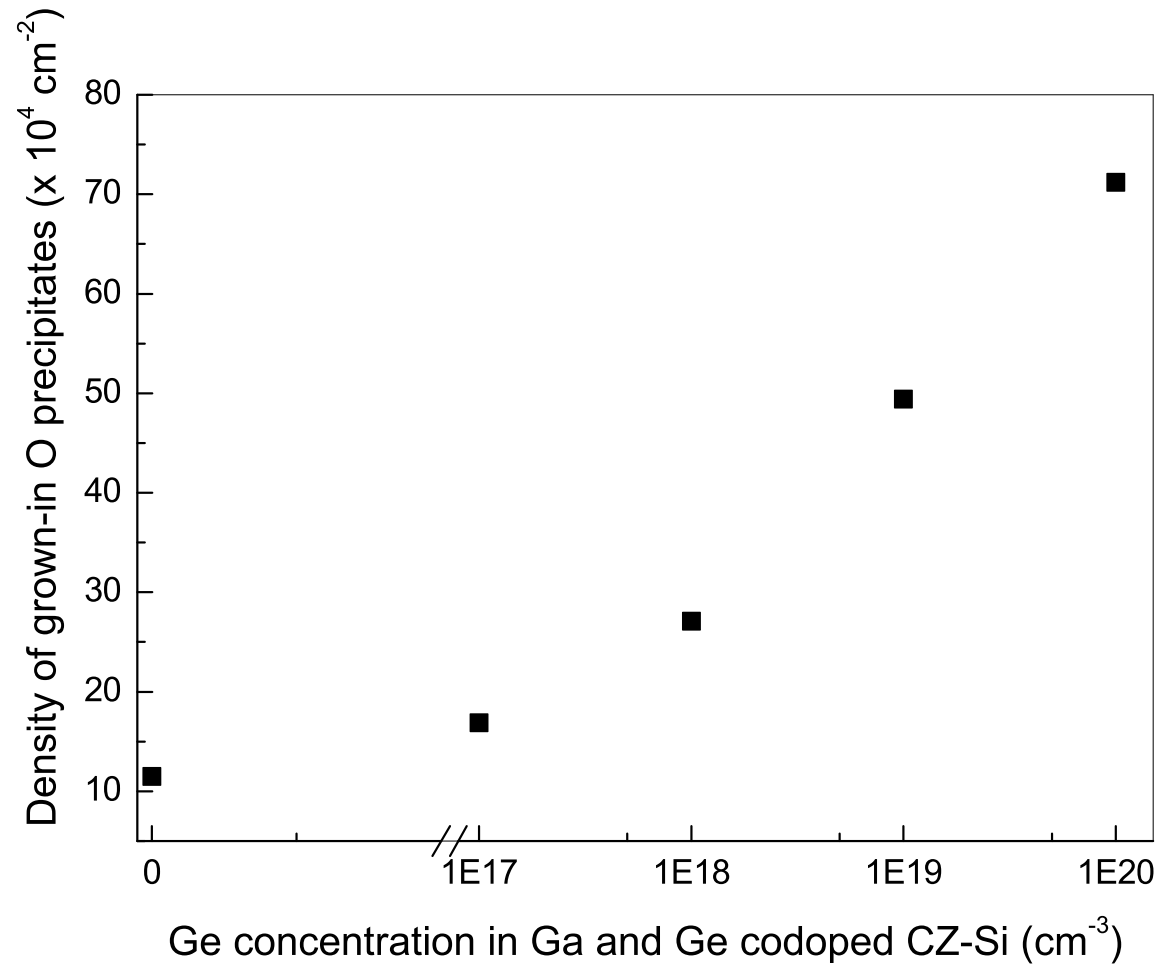


Fig. 5

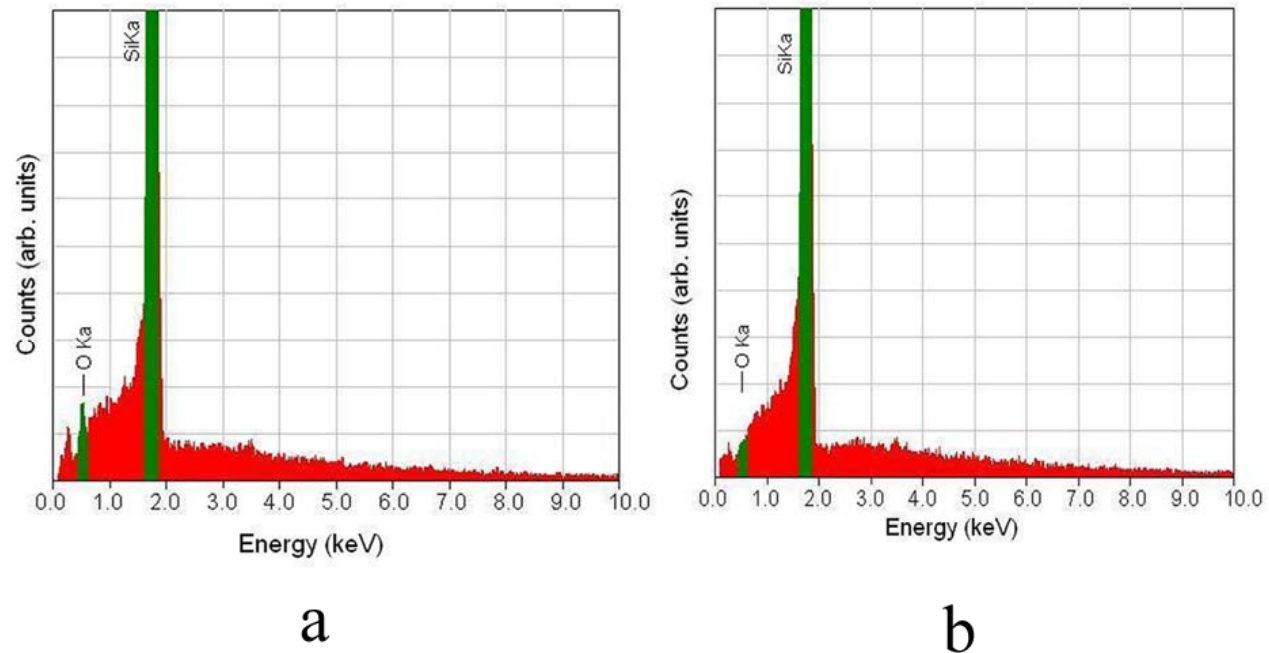


Fig. 6

