

## XAFS study on germanium nanoclusters embedded in silica glass

Tomoko Yoshida<sup>1</sup>, Shunsuke Muto<sup>1</sup>, Leny Yuliaty<sup>2</sup>, Hisao Yoshida<sup>2</sup> and Yasuhiro Inada<sup>3</sup>

<sup>1</sup>Division of Quantum Science and Energy Engineering, Department of Materials, Physics and Energy Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

<sup>2</sup>Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

<sup>3</sup>Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba 305-0801, Japan

It has been reported that the photosensitivity of silica windows and fibers are closely connected with an absorption band around 5 eV and the corresponding emission band centered around 3.1 eV, likely related to Ge impurities.[1,2] In the present study, we successfully obtained the Ge K-edge XAFS of Ge<sup>+</sup>-implanted silica glass samples containing Ge as low as ~0.002 at% within the X-ray probing depth region. The results were compared with the optical properties of the samples to gain insight into what is really responsible for the 3.1 eV emission band.

Fig. 1 shows PL spectra excited by 5 eV light before and after implantation. A weak and broad band is observed before implantation, while the new emission band around 2.7 eV appears after the implantation of  $2 \times 10^{15} \text{ cm}^{-2}$ . It is likely that the 2.7 eV PL band likely originates from the displacement damages, such as B<sub>2α</sub> oxygen deficient centers and/or small Si clusters. When the fluence is more than  $2 \times 10^{16} \text{ cm}^{-2}$ , a sharp and intense 3.1 eV PL band replaces the 2.7 eV band. Cannizzo et al. observed 3.1 eV PL for Ge-doped silica fabricated by a sol-gel method and assigned the PL to a two-fold oxygen-coordinated Ge atom (O=Ge:). On the other hand, Oku et al. claimed that the 3.1 eV PL band from a silica glass containing Ge and GeO<sub>2</sub> nanocrystals was due to the quantum size effect of Ge clusters [3].

Fig. 2(a) shows  $k^3$ -weighted and normalized Ge K-edge EXAFS spectra obtained from the  $2 \times 10^{16} \text{ cm}^{-2}$  implanted sample and the Ge powder. The main EXAFS oscillation of  $k = 6-12 \text{ \AA}^{-1}$  of the Ge<sup>+</sup> implanted sample is similar to, but its amplitude is much smaller than that of the Ge powder. The smaller amplitude of the EXAFS oscillation suggests that a large fraction of Ge atoms are undercoordinated, and/or lower symmetry around Ge atoms causes a fast decay of the amplitude. The Fourier transform (FT) of the Ge K-edge EXAFS spectrum in the 3-15.0  $\text{\AA}^{-1}$  region is shown in Fig. 2(b), as the radial structure function (RSF). At first sight the first peak appearing around 1.5  $\text{\AA}$  should correspond to the Ge-O bonds and the largest peak observed at 1.8-2.8  $\text{\AA}$  to the second-neighbor Ge atoms, judging from the peak positions.

To examine the local structure around Ge atoms in further length, we performed nonlinear least-square curve-fitting to the Fourier-filtered EXAFS including the first and the second coordination shells. In the Ge<sup>+</sup> implanted sample, the Ge-O distance was estimated to be 1.76  $\text{\AA}$ , which is much longer than the stable Si-O covalent distance, 1.60  $\text{\AA}$ . The coordination number (CN) of the adjacent oxygen atoms was estimated to be ca. 2 rather than 4. These results suggest that the implanted Ge atoms are not substituted for the Si site in the SiO<sub>4</sub> unit. On the other hand, the average Ge-Ge distance was estimated to be 2.47  $\text{\AA}$ , which is in good agreement with that of Ge powder. The coordination number (CN) for the second shell was estimated to be 1.5, which was much smaller than that of Ge powder. This implies the formation of small Ge clusters, which is quite consistent with the UV absorption results that the size of the particles should be no larger than 1-2 nm.

### References

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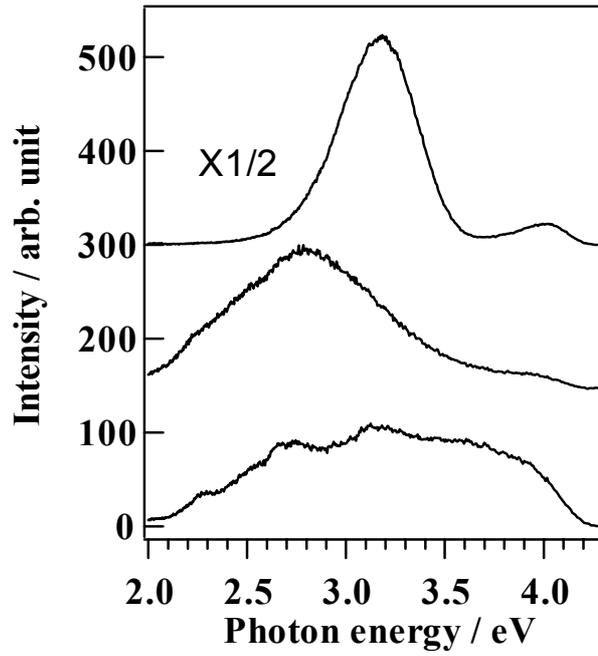


FIG. 1. PL spectra excited by 5 eV light for silica glass before and after  $\text{Ge}^+$  implantation.

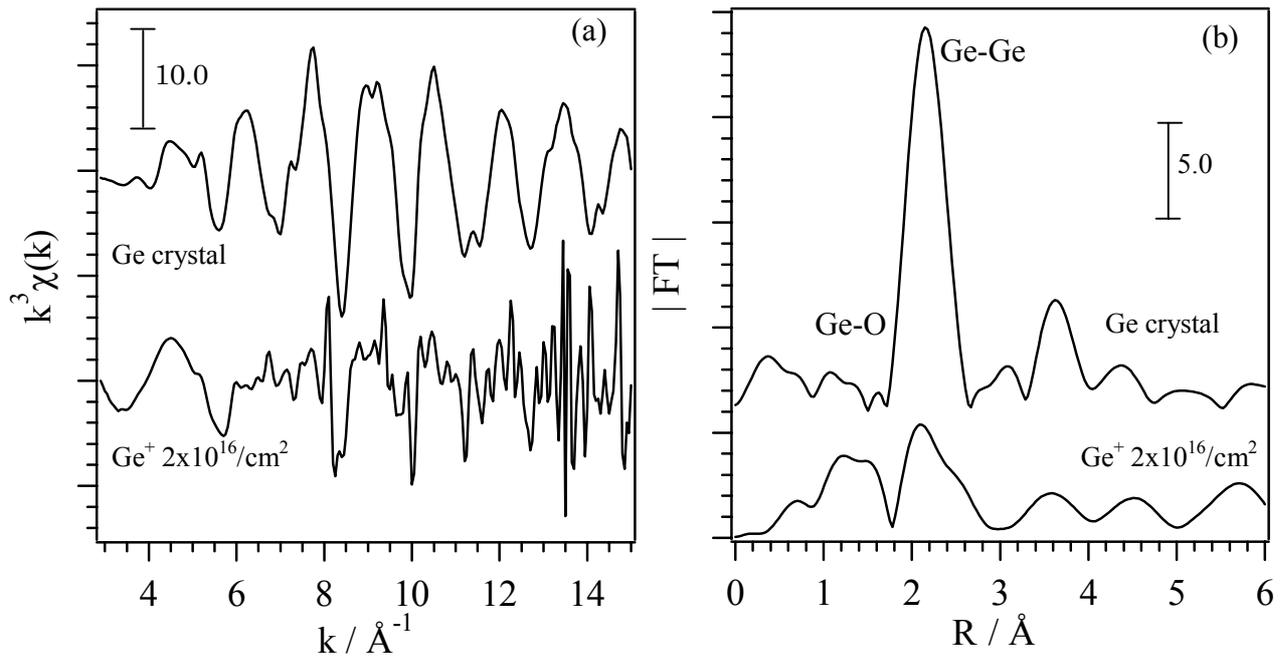


FIG. 2.  $k^3$ -weighted Ge K-edge EXAFS spectra of the silica glass sample implanted with  $2 \times 10^{16} \text{ Ge}^+ / \text{cm}^2$  and a Ge crystal (a), and their radial structural functions (b).