Cluster size analysis in Ge-doped silica showing 3.1 eV luminescence by RMC-XAFS and HAADF-STEM

Tomoko Yoshida[1], Shunsuke Muto[2] and Hisao Yoshida[2]
[1] EcoTopia Science Institute, Nagoya University, Nagoya 464-8603, Japan.
[2] Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

The discovery of blue and violet photoluminescence (PL) from Ge-doped silica glass [1, 2] has drawn interest as a candidate light emitting material compatible with current Si processing. We found in Ge-implanted silica that the stability of the 3.1 eV emission strongly depended on the implantation dose (fluence): as-implanted samples exhibited the stable and intense emission when the fluence > 2 x 10^{16} cm^{-2}, while the 3.1 eV PL evolved only after X-ray irradiation for the fluence of 2 x 10^{15} cm^{-2}, which was significantly decayed after the exposure to air for months. UV-vis and XAFS analyses suggested that the as-implanted $Ge^{(4-x)+}$ ions (derived from Ge-O_y, $y = 1 - 4$) were reduced and aggregated by X-ray irradiation to form larger (~5 nm) and smaller (~1 nm) Ge clusters [3]. Those results imply that the 3.1 eV PL is attributable to small Ge clusters < ~1 nm.

The purpose of this paper is to discuss the relation between the optical properties and the local structure of implanted Ge atoms (Implanted energy: 30 keV) in the series of samples with the Ge fluence varied, applying X-ray absorption fine structures (XAFS) and scanning transmission electron microscopy (STEM) analyses.

Conventional EXAFS analysis provided the average structural parameters around Ge, whereas reverse Monte Carlo (RMC) fit to the EXAFS enabled us to deduce 3D atomic configurations based on the statistical pair distributions [4]. Results are shown in Table 1 and Fig. 1(a) for the as-implanted sample at the fluence of 2 x 10^{16} cm^{-2} showing the stable PL. As expected in the UV-vis spectroscopy results, most of Ge atoms are distributed as isolated atoms or in the form of small clusters such as dimers and trimers (< ~1 nm), as shown in Fig. 1(a). The Ge K-edge XANES was simulated using the FEFF code [5], based on the atomic configurations obtained by RMC-EXAFS analysis (Fig. 1(a)), which well reproduced the experimental XANES, whose profile exhibits the features between pure Ge and GeO_2, as shown in Fig. 1(b).

On the other hand, a HAADF-STEM image confirmed formation of larger Ge clusters of ~5 nm in the sample exposed to air after 2 x 10^{15} cm^{-2} implantation and X-ray irradiation (Fig. 2), which also confirmed the stable nature of the larger Ge clusters. The unstable smaller clusters in the low fluence sample are supposed to have unsaturated bonds, and they are oxidized and resolved in the matrix by exposure to air. On the other hand, the Ge clusters in the higher fluence sample may be formed due to the higher Ge density and stabilized by radiation-induced defects/diffusion.

References
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Table 1 Structural parameters deduced by conventional EXAFS analysis, where *R* is the interatomic distance and σ is Debye-Waller factor.

Sample	Atom pair	Coordination #	*R* (nm)	σ (nm)
As-implanted (2×10^{16} Ge^{+} cm^{-2})	Ge-O	1.9	0.177	0.009
	Ge-Ge	1.3	0.248	0.006
	Ge-Si	0.7	0.308	0.008
Ge powder	Ge-Ge	4.0	0.245	0.007
GeO_2 powder	Ge-O	4.0	0.176	0.006
	Ge-Ge	4.0	0.315	0.006

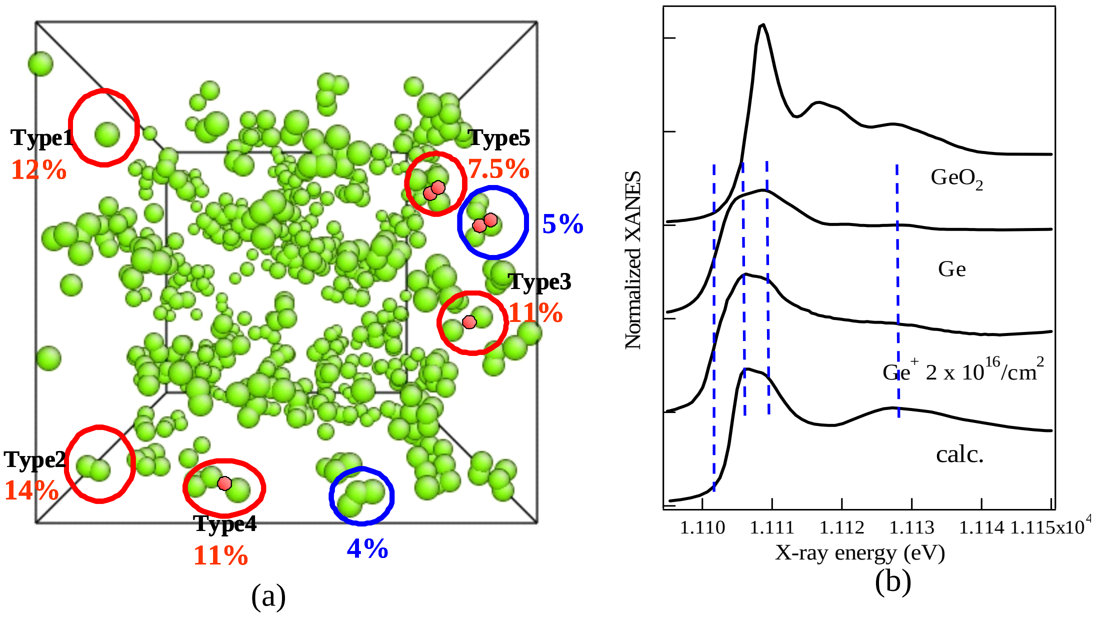

FIG. 1 (a) Perspective view of spatial distribution of Ge atoms in silica glass, derived by RMC fit to EXAFS of the sample implanted at the fluence of 2×10^{16} cm^{-2}. (b) Experimental Ge K-edge XANES of pure Ge, GeO_2, the implanted sample and theoretically calculated XANES by FEFF code, based on the model obtained by RMC-EXAFS fit (a).

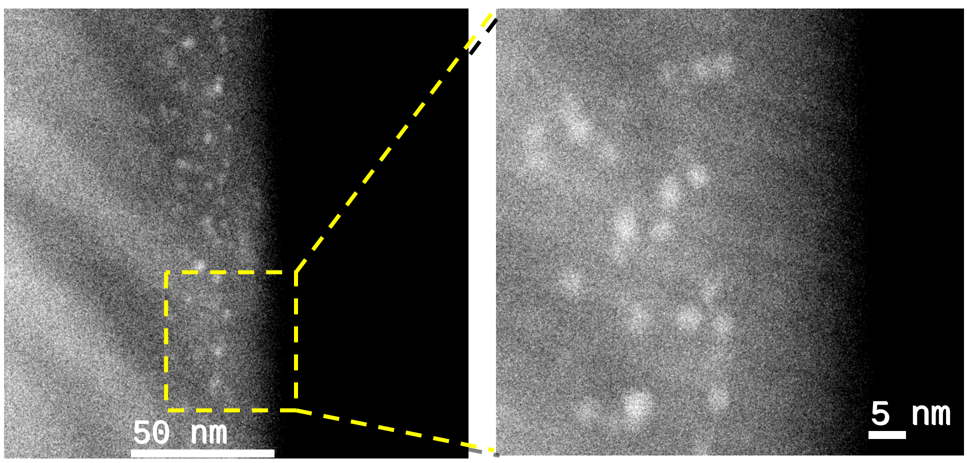

FIG. 2 HAADF-STEM images of the sample implanted at the fluence of 2×10^{15} cm^{-2}, irradiated with X-ray and exposed to the air, taken by Jeol ARM200F operated at 80 kV.