Materials Science

27A/20070G058

Study on the behavior of oxygen atoms in swift heavy ion irradiated CeO_2 by means of synchrotron radiation X-ray photoelectron spectroscopy

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Introduction

Previously, we have reported that swift heavy ion irradiation induces a large amount of oxygen atom displacements from their regular sites. This irradiation effect was observed through the synchrotron radiation X-ray experiments as a decrease in Ce valence state not only at the specimen surface but also inside it[1]. In this report, we show the dependence of the amount of Ce^{3+} and Ce^{4+} states on the fluence of 200 MeV Xe ions, which has been obtained by the curve fitting of the XPS spectra. Then, we discuss the contribution of electronic excitation to oxygen atom displacements.

Experimental procedure

Specimens were CeO_2 bulk pellets which were prepared by sintering. powder at 1400C. They were irradiated with 200 MeV Xe ions up to the fluence of $6x10^{13}/cm^2$. X-ray photoelectron spectra (XPS) for irradiated CeO_2 pellets were acquired at 27A beam line of KEK-PF.

Results and discussion

The Ce-3d spectra for the irradiated specimens show that the intensity of XPS peaks for Ce^{4+} decreases and that for Ce^{3+} increases with increasing the ion fluence. This result implies that in the irradiated specimens, both Ce^{4+} and Ce^{3+} states coexist and the amount of Ce^{3+} state increases by the ion irradiation. To discuss the change in Ce valence state more quantitatively, the data reduction of measured XPS Ce-3d spectra has been performed by the symmetric Gaussian-Lorentzian function curve fitting using six peak components of Ce^{4+} reference spectrum and four peaks components of Ce^{3+} reference spectrum. The details of the analysis are described in ref. [2]. From the area under each component, the relative amount of Ce^{3+} state can be estimated. The result is shown in Fig. 1. The relative amount of Ce^{3+} state gradually increases with increasing the ion-fluence. As the XPS spectra for Xe ion irradiated CeO_2 were, however, measured after they were irradiated and were once kept in the atmosphere, the surface of the irradiated CeO_2 may possibly have been to some extent re-oxidized. To obtain XPS spectra which were not affected by the re-oxidization, we measured the XPS spectra again after sputtering the specimens slightly with 3 keV Ar ions without any more exposure to atmosphere. The Ar sputtering, however, caused the 7% increase in relative amount of Ce^{3+}. We therefore plot the data in Fig. 1 after removing the sputtering effect. The figure shows that the relative amount of Ce^{3+} state for the slightly sputtered CeO_2 is larger than that for unsputtered CeO_2. The difference is due to the effect of re-oxidation which has occurred during keeping the specimens in atmosphere. As the figure shows, the relative amount of Ce^{3+} state which is induced by the irradiation reaches 20%, meaning that 5% of the oxygen atoms are displaced from the regular lattice sites. The value of 5% oxygen displacements cannot be explained if we only consider the effect of the elastic interaction between CeO_2 and 200 MeV Xe ions, because the value of dpa (displacement per atom) near the specimen surface is below 0.01 even for the Xe ion-fluence of $10^{14}/cm^2$. To understand the change in Ce valence state and accompanying oxygen atom displacements by the irradiation, the effect of high density electronic excitation on atomic movements has to be considered.

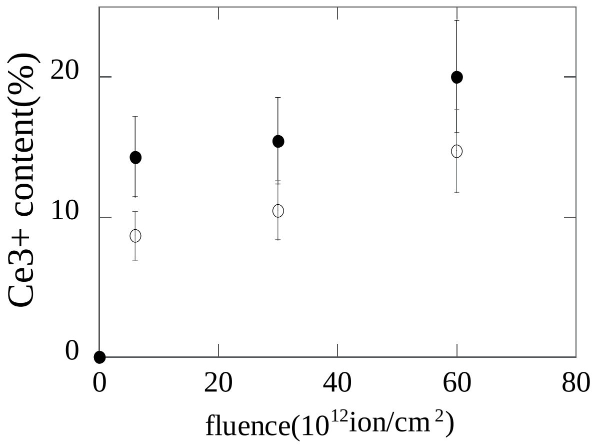

Fig. 1 Relative amount of $Ce3^+$ state as a function of ion fluence. Open circles; for CeO_2 irradiated with 200MeV Xe ions. Solid circles; for CeO_2 irradiated with 200MeV Xe ions and then slightly sputtered with 3keV Ar ions.

References

[1] H. Ohno et al., Nucl. Instr. Meth. B266(2008) 3013-3017.
[2] A. Iwase et al.., Nucl. Instr. Meth. B267(2009) 969-972.

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