Local Atomic Structure Analysis of Silicon in White and Black Si–O–C(–H) Ceramics

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1. Introduction

Si–O–C ceramics derived from silicone resins or condensates of silicon alkoxides by pyrolysis in an inert atmosphere have been investigated as low-cost and heat-resistant materials in forms of coatings, fibers and binders. In most cases, however, color of the obtained materials is black due to existence of free carbon. This free carbon in Si–O–C amorphous structure is known to play an important role in electric conductivity and high temperature creep resistance of the Si–O–C ceramics. In recent years, however, white Si-O-C ceramics with reduced carbon contents were synthesized by CVD method or precursor method. They show apparent white PL under excitation of ultraviolet (UV) light in general. Our group in Osaka Prefecture University succeeded in synthesizing it through a simple route: pyrolyzing a polymer precursor (silicone resin particle) under a H_2 flow [1,2]. The pyrolysis under a H_2 flow reduced the absolute carbon content by 70-75%, whereas the pyrolysis increased the hydrogen content. Strong white PL under the UV excitation was also observed. On the other hand, structural information of the obtained white Si–O–C(–H) ceramics is not sufficient even at present. XRD analysis did not give meaningful information because of the quite amorphous nature of the ceramics. Signal intensity of ^{29}Si NMR was very weak in general, perhaps due to very long spin relaxation times of Si atoms in the system. XANES spectra of Si K-edge is expected to give precious information, which is highly important in thinking of environments and coordination of individual Si atoms in the system. In this study, we analyze XANES spectra of the white Si–O–C(–H) ceramics in comparison with the black Si–O–C ceramics obtained by pyrolysis of the same precursor under an Ar gas flow.

2. Experiments

The white and black ceramics for the XANES analysis were derived from silicone resin microspheres (chemical composition: $SiO_{1.66}C_{1.00}H_{3.36}$, diameter: 2 μm) at temperatures at 800 and 1100 ^{O}C. The white ceramics synthesized in a H_2 gas flow were named H800 and H1100, whereas the black ceramics synthesized in an Ar gas flow were named Ar800 and Ar1100.

Synthesis method and basic characterization of the materials have been described in previous studies [1, 2]. The Si K-edge XANES analyses were carried out on the BL-10 at Ritsumeikan University, SR Center (Shiga, Japan). XANES spectra were mainly recorded in a total electron yield (TEY) method by using InSb (111) as a dispersive crystal.

3. Results and Discussion

Figure 1 shows the Si K-edge XANES spectra of H800, H1100, Ar800 and Ar1100 with spectra of references (β-SiC, silicone microsphere and silica). All the spectra of the pyrolysis products show main peaks at 1847 eV, whereas that of the original resin shows the peak at 1845 eV.

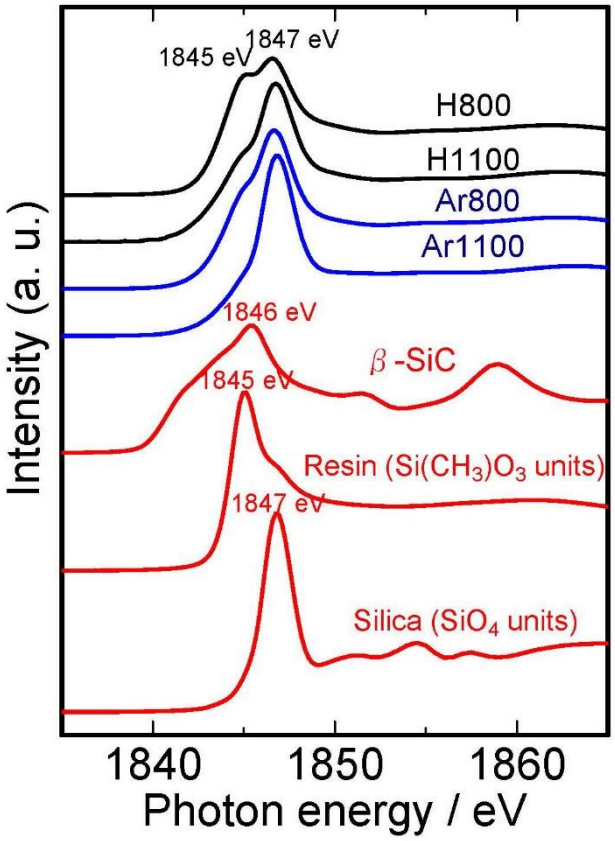

Fig.1: Si K-edge XANES spectra of Si–O–C(–H) ceramics with references.

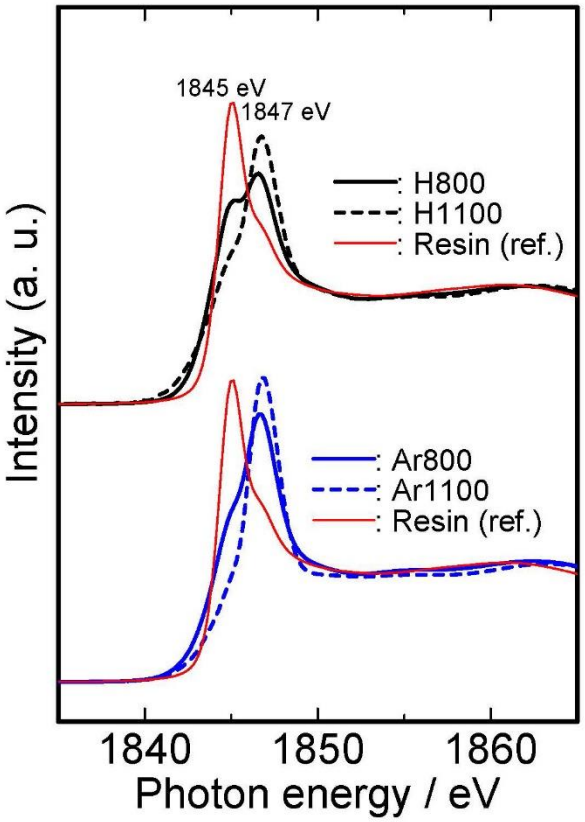

Fig.2: Overwritten XANES spectra of the white and the black ceramics

These results suggest that SiO_4 units are formed with consumption of original SiO_3C units during the pyrolysis. On the other hand, edge positions of the spectra shift to a lower energy range.

Figure 2 shows overwritten XANES spectra of the white ceramics and the black ceramics with the original silicone resin spectrum. In the white ceramics, relatively large shift in the edge position should be assigned to formation of SiO_2C_2 and $SiOC_3$ units. In the black

ceramics, however, the shift of the edge position is not substantial, whereas the peak of SiO_4 units at 1847 eV is strengthened. Perhaps, the pyrolysis in H_2 accelerates Si–CH_2–Si and Si–CH(–Si)–Si bridging reactions effectively, and relatively homogeneous Si–O–C network develops as compared with the pyrolysis in Ar.

References

[1] M. Narisawa et. al, *Bull. Chem. Soc. Japan*, **85**, 724-726 (2012).
[2] M. Narisawa et. al, *Scripta Materialia*, **69**, 602-605 (2013).