Electronic and chemical state analyses of oxidizing graphene

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Abstract

In order to investigate the process of oxidizing graphene, the electronic and chemical states have been measured by photoelectron spectroscopy (PES) and X-ray absorption fine structure (XAFS). It was the same oxidation state for 30 seconds after oxidation. However, 45 seconds oxidation leaded to the different state and further 60 seconds oxidation became other states. It is thought that the oxidation firstly introduces the oxygen functional groups and then destroys the aromatic rings in the graphene.

1. Introduction

Graphene has attracted much attention as semiconductors in recent years. An oxidation of graphene leads to a different property from graphene, e.g. graphene is conductive while graphene oxide (GO) is insulating. In addition, GO is used as a support material, a precursor of graphene production, and so on. So far, the chemical states have been much studied and revealed that the existence of the functional groups such as epoxy, carboxyl, hydroxyl, and carbonyl groups. [1] Furthermore, our previous results also indicates the presence of other functional groups such as NO_2 group [2] than C-O direct bonding depending on the chemical treatments. The electronic structures have been also studied and found that the band gap opening and the appearance of the O 2*p* states. [3] However, oxidizing process and the formation of the functional groups are not understood. In order to investigate the process of oxidizing graphene, the electronic and chemical states have been measured by photoelectron spectroscopy (PES) and X-ray absorption fine structure (XAFS).

2. Experimental

Preparation of single-layer GO (SLGO)

SLGO was formed on α-Al_2O_3(0001) (sapphire(0001)). Before synthesizing SLGO, single-layer graphene (SLG) was grown on a sapphire(0001) substrate. The substrate was annealed at 900 °C in open air in order to obtain atomically flat surface. Then, the substrate was introduced into a vacuum furnace. The base pressure of the furnace was 6×10^{-6} Pa. After evacuating, the substrate was annealed up to 1000 °C for 1 hour. For the graphene growth, a methanol vapour was used as a precursor. SLG was grown by introducing 200 Pa methanol vapour for 30 min [4]. After the SLG growth, the SLG was oxidized based on the modified Hummers method. The procedure was as follows: The mixture of H_2SO_4 and $KMnO_4$ was prepared by slowly adding $KMnO_4$ (1.8 g) into concentrated H_2SO_4 (20 ml) and stirring in the beaker. SLG/sapphire(0001) was dipped in the mixture for 5-60 sec. The oxidized specimens were washed with purified water and dried under nitrogen gas blow.

Electronic state analysis

The PES was performed at the linearly polarized soft x-ray beamline BL-7 of SR center, Ritsumeikan University, using a hemispherical electron energy analyzer, SCIENTA SES2002. Utilizing the analyzer, we can obtain the position-resolved electronic structures. The measurements were performed at room temperature under ultrahigh vacuum of $\sim 1\times10^{-7}$ Pa. Photon energy was set to 60 eV. No surface treatment was performed.

Chemical state analysis

XAFS measurements were performed at the BL-8 of SR Center at Ritsumeikan University, equipped with a grazing incidence monochromator with a varied-line-spacing plane grating. Carbon and oxygen *K*-edge XAFS spectra of the samples were measured in partial electron yield by a micro-channel plate detector with retarding grids. The retarding voltage was set to -150 V, -350 V, respectively. The incident angle of SR with respect to the surface normal was varied. The measurements were performed at room temperature under ultrahigh vacuum of $\sim 1\times10^{-7}$ Pa. No surface treatment was performed.

3. **Results and Discussion**

Figure 1 shows the position-dependent valence band of each sample. The SLG (0 sec) has the characteristic features of graphene, that is, the structure around the binding energy of ~ 3 eV comes from C 2*p* π states, while the structure around ~ 6 eV comes from C 2*p* σ states. There is no difference between regions A and B, indicating that the uniform SLG is grown in the entire regions of the sample. For 5 sec oxidization of SLG, the characteristic features of graphene become smeared out in some regions (region A). For 10 sec oxidization of SLG, the characteristic features of graphene near the Fermi level still exist in some regions (region A). For 20 and 30 sec oxidization of SLG, the characteristic features of GO appears in the entire regions of the sample. The band gap is opened. The broad structure of O 2*p* appears around ~ 8 eV. For 45 sec oxidization of SLG, the characteristic features of GO changes in some regions (region A). For 60 sec oxidization of SLG, a new electronic state other than GO appears in some regions (region A). Figure 2 summarizes the characteristic electronic structure changes with oxidization of SLG. The oxidizing graphene firstly leads to the decrease of C 2*p* π states, then to the increase of O 2*p* states, and finally to the formation of the other electronic states, maybe due to the destruction of the aromatic rings.

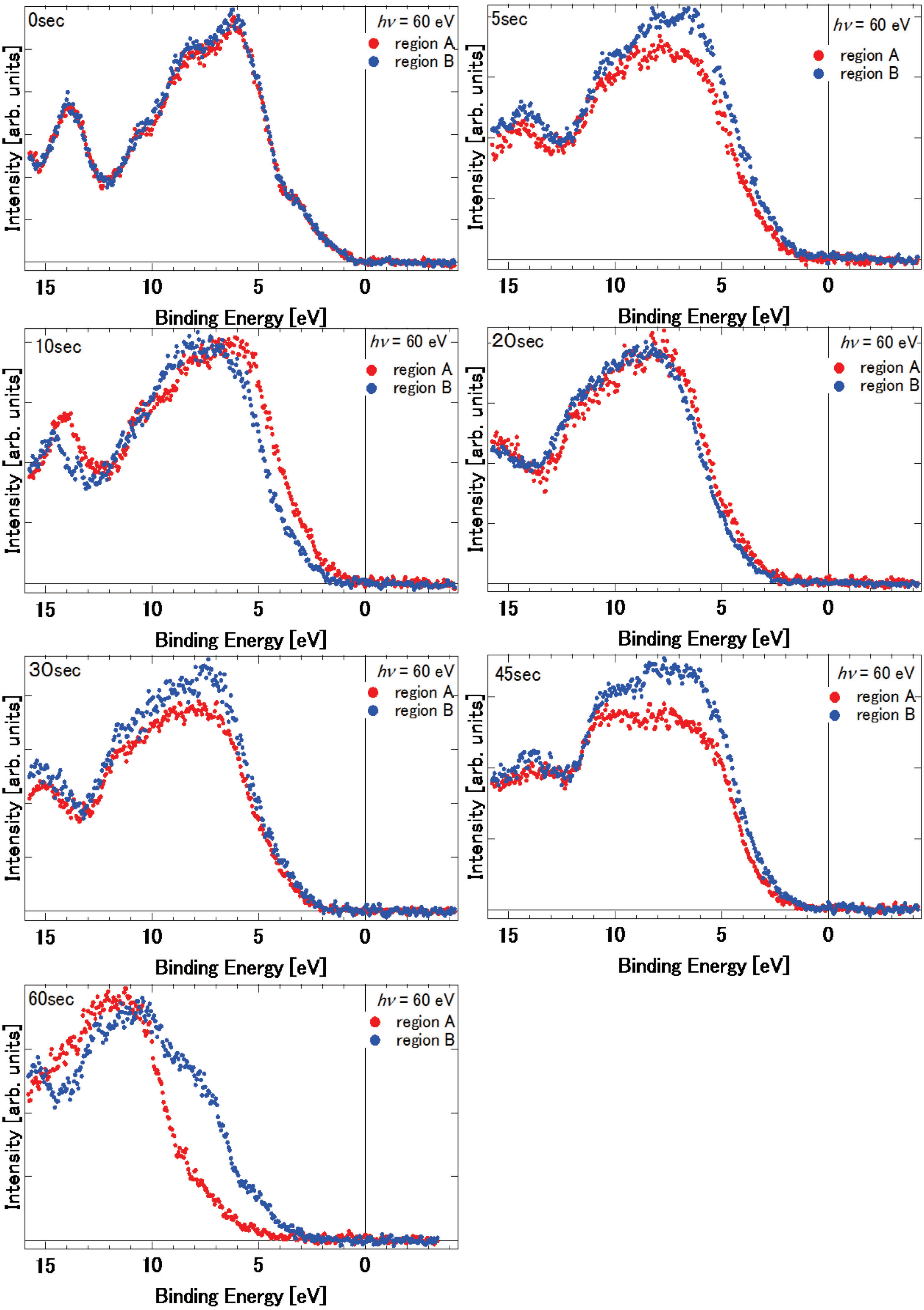

Fig. 1 Position-dependent valence band for each oxidization of single-layer graphene.

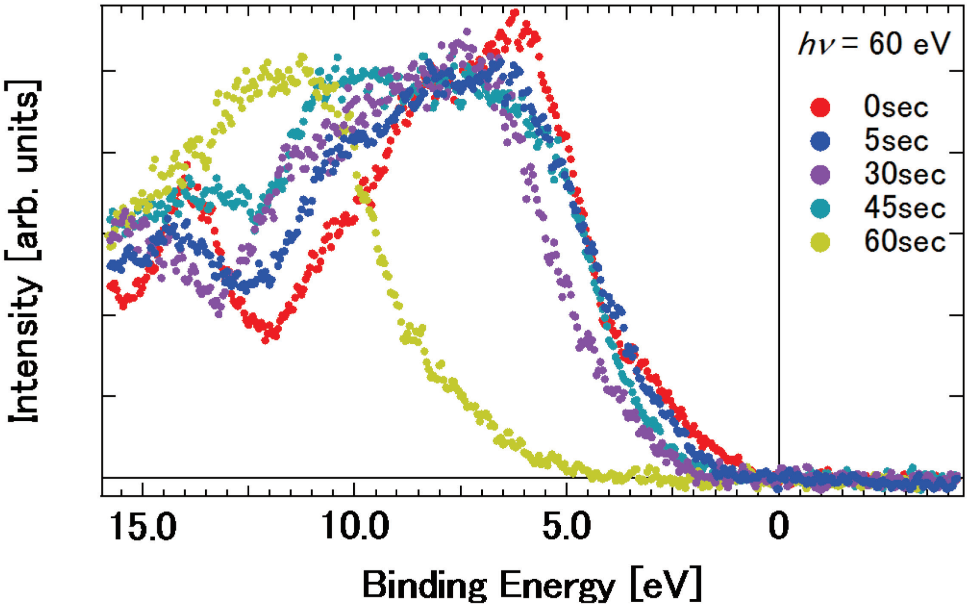

Fig. 2 Valence band spectral changes under oxidization process of single-layer graphene.

Figure 3 shows the O *K*-edge XAFS spectra of the samples. The prominent structures around the photon energy ~ 535 eV is σ* states of the sapphire substrates. After the oxidization of SLG, a shoulder structures appear around ~530 eV. For 60 sec oxidization of SLG, however, the intensity of this structure decreases. Spectral analysis of this structure shown in Fig. 4 indicates that the shoulder consists of three components. These are assigned to π* (O=C) and σ* (O-C, O-H). The polarization-dependent XAFS spectra (Fig. 5) indicate that the C=O bond, such as carboxyl groups in SLGO, is oriented roughly in the substrate plane, i.e., in the graphene.

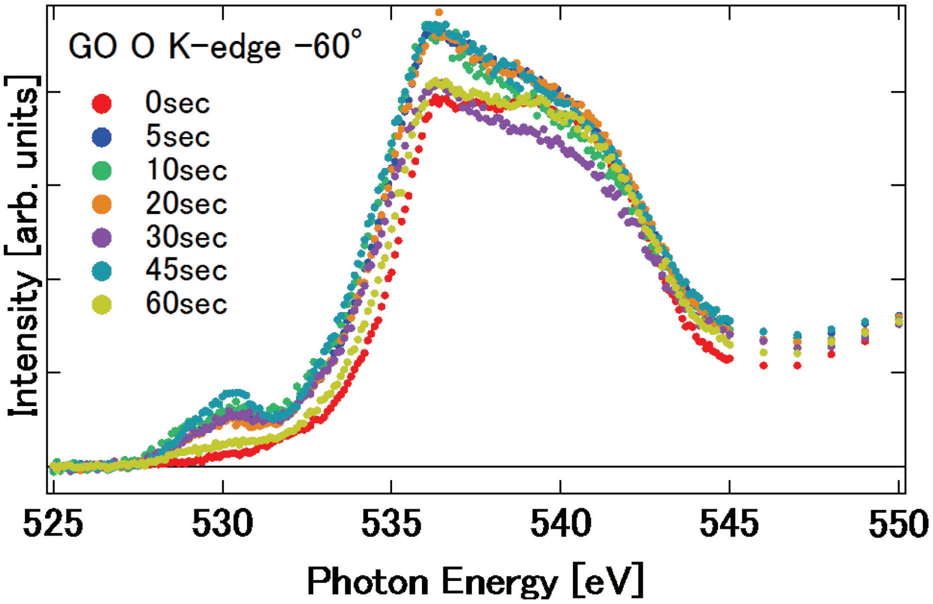

Fig. 3 O K-edge XAFS spectral changes under oxidization process of single-layer graphene.

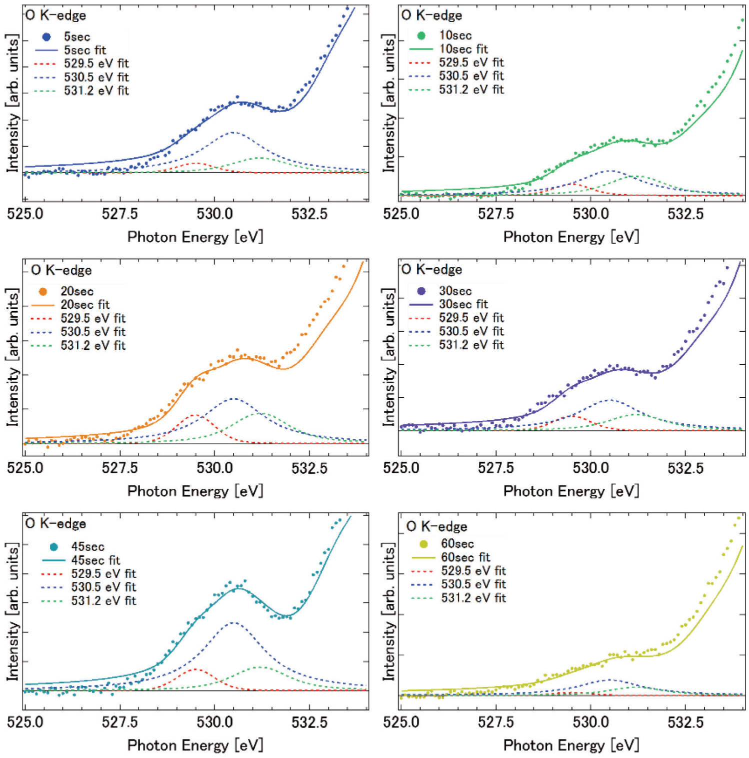

Fig. 4 Spectral analysis of O K-edge XAFS spectra of oxidized single-layer graphene.

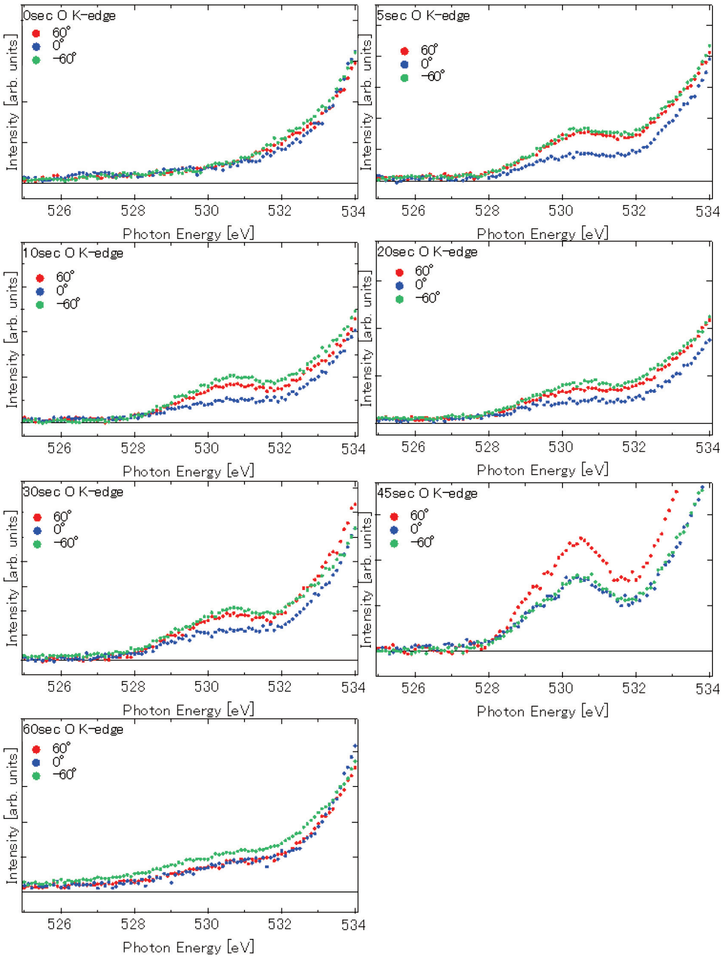

Fig. 5 Polarization-dependent O K-edge XAFS spectra for each oxidization of single-layer graphene.

Figure 6 shows C *K*-edge XAFS spectra of the samples. The two prominent structures around ~285 eV and ~305 eV are C π* states and C σ* states, respectively. After the oxidization of SLG, the intensity around ~285 eV significantly decreases while the intensity around ~288 eV does not change (Fig. 7). These two peaks are assigned to π* (C=C) and σ* (C-H, C=O), π* (C-OH), respectively. The polarization-dependent XAFS spectra (Fig. 8) indicate that the C=C bond in SLGO is oriented in the substrate plane, i.e., the graphene sheet is parallel to the substrate surface.

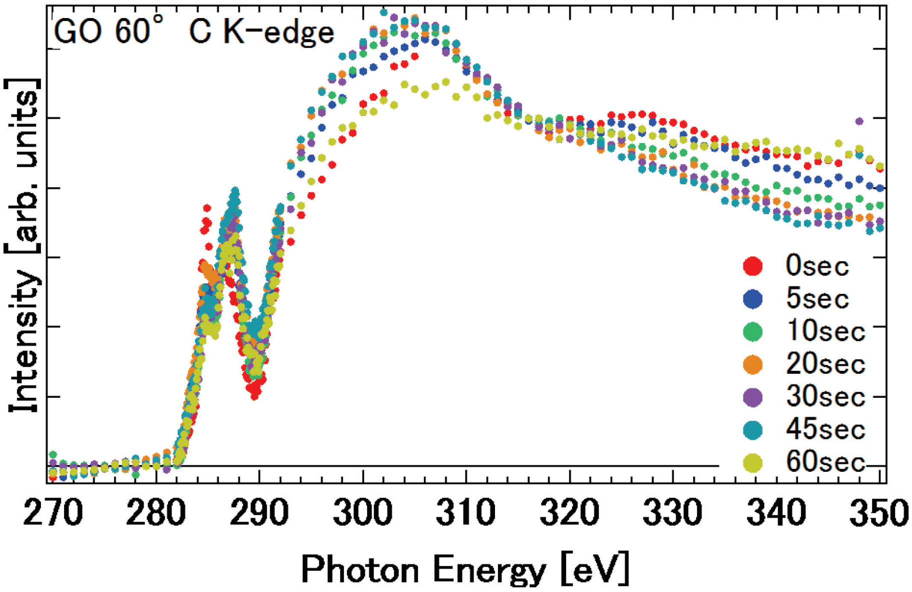

Fig. 6 C K-edge XAFS spectral changes under oxidization process of single-layer graphene.

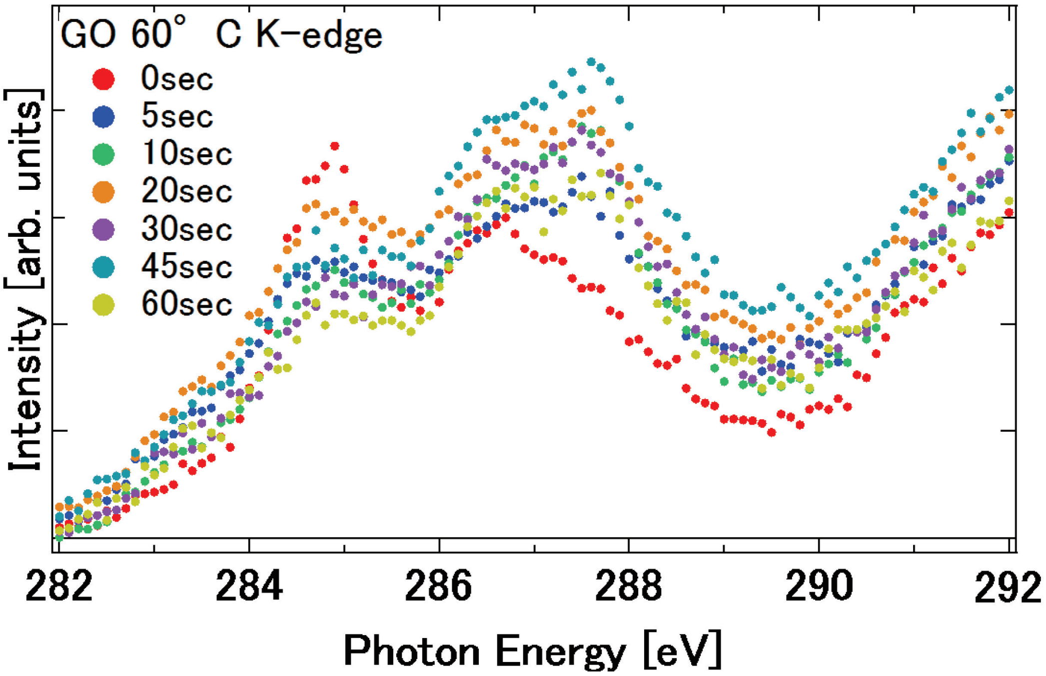

Fig. 7 Spectral analysis of C K-edge XAFS spectra of oxidized single-layer graphene

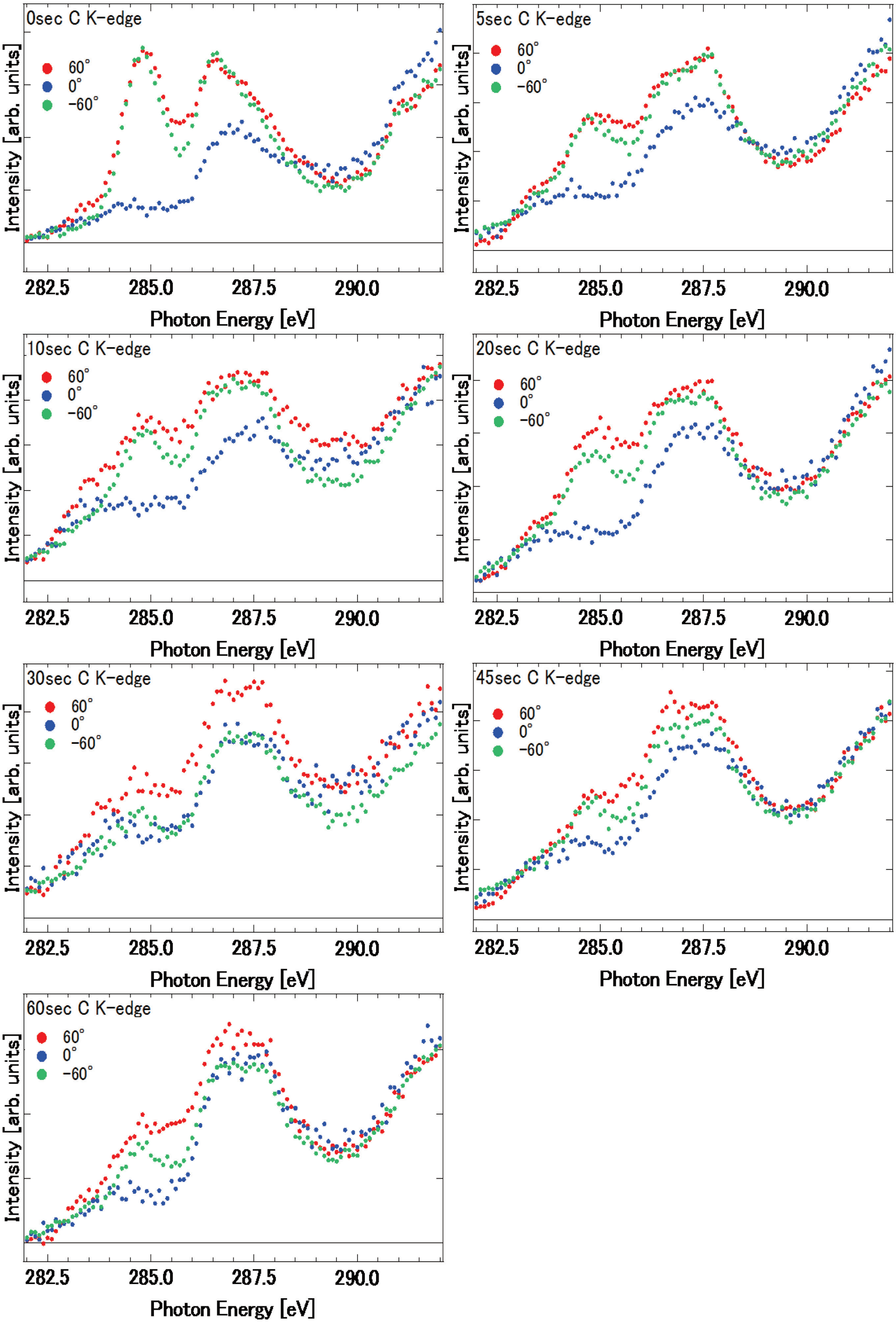

Fig. 5 Polarization-dependent C *K*-edge XAFS spectra for each oxidization of single-layer graphene.

4. Conclusions

We have performed photoelectron spectroscopy and X-ray absorption fine structure measurements on oxidized single-layer graphene. It is thought that the oxidation firstly introduces the oxygen functional groups and then destroys the aromatic rings in the graphene.

References

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