Local structures in graphite-like carbon oxide

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Introduction

Carbon dioxide is one of the basic materials in chemistry. Besides CO and CO₂, some kinds of carbon oxide are also known. All of them are gas or liquid at ambient temperature and pressure, and it is believed that stable solid carbon oxide does not exist. In this work, for the quest of solid carbon oxide (CO₂), we attempted to synthesize CO₂ by ion implantation. Though this method is superior in synthesis of novel materials via non-equilibrium process, variety of possible local structures could be formed and long-range order is expected to be lacking due to the damage induced by the incident particles. Then we studied local structures of the products around oxygen sites by XPS and NEXAFS spectroscopy.

Experimental

XPS and NEXAFS experiments were performed at BL-27A and BL-11A, respectively. All experiments were carried out in situ to avoid the contaminant effect. CO₂ films were prepared by low energy (1-3keV) O₂+ ion implantation in highly oriented pyrolic graphite at room temperature. XPS spectra were measured by monochromatic 1.8 keV x-ray with the resolution of 0.9 eV. The composition ratio of the products was obtained from XPS. As references, the O 1s binding energies (BE) of 18-crown 6-ether powder and condensed γ-pyrene, furan, CO₂, and tetramethoxymethane (TMM) were also measured. NEXAFS spectra were measured by total electron yield mode for various x-ray incident angles. To minimize the damage effect, NEXAFS spectra of the CO₂ film were measured at low fluence (1.7×10¹⁵ atoms/cm²). O K-edge NEXAFS spectra of condensed furan and diethyl ether were measured. A few monolayer of γ-pyrene was adsorbed on Cu(100) at 250 K and NEXAFS spectrum of this system was also measured.

Results and discussion

The [O]/[C] ratio of the CO₂ film reached up to 13% at the fluence of 1×10¹⁷ atoms/cm². As compared with the [Ar]/[C] ratio (=4%) in the case of Ar⁺ ion irradiation, the value is quite large. As shown in figure 1, two dominant and one minor components P₁, P₂, and P₃ are observed in the O 1s XPS spectrum. CO₂ ice (dry ice) is well known as molecular solid of carbon oxide, and the O 1s BE is by far different from the energies of P₁ and P₂ and close to that of P₃. The O 1s BEs of the most reference materials in which ether are included are rather close to the energy of P₃ than that of P₁. γ-pyrene showed two O 1s BEs corresponding to different oxygen sites, i.e., carbonyl group and ether, which are close to those of P₁ and P₂ respectively. These results imply that the dominant products are not interstitial carbon oxide compound but carbonyl or ether structures in graphite matrix. As shown in figure 2 (curves a-c), the O K-edge NEXAFS spectra of the CO₂ show two discrete peaks P₁ and P₂ which have graphite-like clear polarization dependence. This implies that the local structures corresponding to the peaks have orientation which is parallel to graphite plane. The energies of the peaks coincide with the two π⁺ resonances in O K-edge NEXAFS spectrum of condensed γ-pyrene (curve d). Among the peaks, the high-energy peak correspond to the π⁺ resonance of furan (curve e). On the other hand, diethyl ether did not show discrete π⁺ resonance in the spectrum (curve f). This means that P₂ and P₃ are assigned to the π⁺ resonances which originates from carbonyl groups and ether structures in graphite plane. Consequently, we propose a structural model of the CO₂ film as shown in figure 3. When ion fluence is small, graphite crystal structure would be preserved. In this situation, the orientation of carbonyl groups is parallel to graphite basal plane and form quinone-like structure. Ether lies in graphite basal plane and has graphite-like orientation.

![Figure 1](image1.png)

**Figure 1** (up). O 1s XPS spectrum of the CO₂ film synthesized at the ion fluence of 3.4×10¹⁵ atoms/cm². Bars show the binding energies of reference materials.

![Figure 2](image2.png)

**Figure 2** (center). O K-edge NEXAFS spectra of the CO₂ film and reference materials. θ shows x-ray incident angle.

![Figure 3](image3.png)

**Figure 3.** Schematic figure of local structures in the CO₂ film synthesized at low fluence. White and dark balls show oxygen and carbon atoms, respectively. a: quinone-like structure, b: in-plane ether structure.