Local structures in graphite-like carbon oxide

Iwao SHIMOYAMA, Tetsuhiro SEKIGUCHI, Yuji BABA
Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195, Japan

Introduction

Carbon oxide is one of the basic materials in chemistry. Besides CO and CO_2, 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 (CO_x), we attempted to synthesize CO_x 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. CO_x films were prepared by low energy (1-3keV) O_2^+ ion implantation in highly oriented pyrolitic 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-pyrone, furan, CO_2, 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 CO_x film were measured at low fluence (1.7×10^{15} atoms/cm^2). O *K*-edge NEXAFS spectra of condensed furan and diethylether were measured. A few monolayer of γ-pyrone 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 CO_x film reached up to 13% at the fluence of 1×10^{17} atoms/cm^2. 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 P_1, P_2, and P_3 are observed in the O1s XPS spectrum. CO_2 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 P_1 and P_2 and close to that of P_3. The O 1s BEs of the most reference materials in which ether are included are rather closer to the energy of P_2 than that of P_1. γ-pyrone showed two O 1s BEs corresponding to different oxygen sites, *i.e.*, carbonyl group and ether, which are close to those of P_1 and P_2 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 CO_x show two discrete peaks P_a and P_b 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-pyrone (curve d). Among the peaks, the high-energy peak correspond to the π* resonance of furan (curve e). On the other hand, diethylether did not show discrete π* resonance in the spectrum (curve f). This means that P_a and P_b 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 CO_x 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.

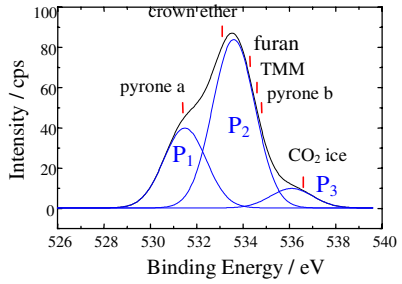

Figure 1 (up). O1s XPS spectrum of the CO_x film synthesized at the ion fluence of 3.4×10^{17} atoms/cm^2. Bars show the binding energies of reference materials.

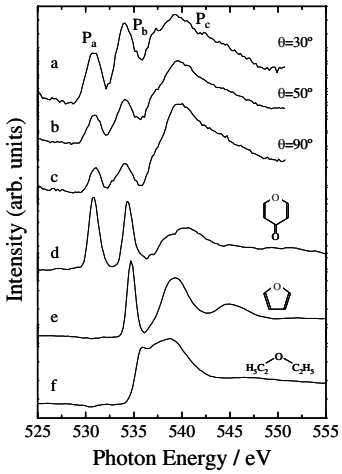

Figure 2 (center). O *K*-edge NEXAFS spectra of the CO_x film and reference materials. θ shows x-ray incident angle.

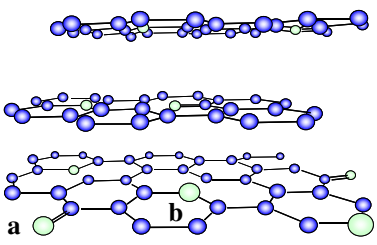

Figure 3. Schematic figure of local structures in the CO_x film synthesized at low fluence. White and dark balls show oxygen and carbon atoms, respectively. **a**: quinone-like structure, **b**: in-plane ether structure