Photon Factory Activity Report 2016 #34 (2017)

BL-6A/2015G711

Control of Carbon Layer Orientation in Phenolic Resin- and Polyimide-Based Carbon Films by Dispersing Graphene Oxides

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1 Introduction

The present study intends to produce highly oriented carbon films with enhanced carbon layer orientation in parallel to the film surface by high temperature carbonization of polymers containing graphene oxides (GOs). It has been reported that the electrical conductivity of the carbon film derived from a resol type phenolic resin containing GOs is twice as high as that of the carbon film derived from "kapton" which yields a well-oriented graphite film. [1] In this experiment, the comparison was made on the carbon layer orientation between the carbon films derived from a resol type phenolic resin and a polyimide both containing GOs. The development of the orientation of GOs in the matrix polymers during drying stage of the wet film forming process was investigated by using the synchrotron radiation small-angle X-ray scattering (SAXS).

2 Experimental

A resol type phenolic resin and a polyimide were dissolved in N,N-dimethyl formamide (DMF) separately and GOs with the layer size of 4 μm were added to these solutions. These mixtures were cast into a vessel and the precursor polymer films were obtained by leaving the vessel in a draft chamber for evaporating DMF. The carbon films were derived by high temperature carbonization of the precursor polymer films in nitrogen atmosphere at 1000 °C for 10 min.

The SAXS measurements were performed at intervals during the drying stage of the film forming process at BL-6A in PF. The X-ray wavelength was 0.15 nm, the sample-to-detector distance was 2 m and the scattering intensity was measured using Pilatus 3. The wide-angle X-ray diffraction (WAXD) measurements of the precursor polymer films and the carbon films were also performed. From the full width at half maximum (FEHM) of the azimuthal distributions of SAXS and WAXD intensity, the degree of orientation was calculated as $(\pi\text{-FWHM})/\pi$. The degree of orientation was determined for the GOs in the precursor polymer films using SAXS and for the benzene rings in the precursor polymer films and the carbon layers in the carbon films using WAXD.

3 Results and Discussion

The SAXS and the WAXD of the precursor polymer films are caused by the GOs and the stacks of benzene rings, respectively. The WAXD of the carbon films is caused by the carbon layer stacks in the matrix carbon yielded from polymers. All these planar structure components were preferentially oriented in parallel to the film surface. The degree of orientation of GOs and benzene rings in the precursor polymer films, that of the carbon layers in the carbon films and the electrical conductivity of the carbon films are shown in Table 1. It is found that the electrical conductivity and the orientation of the carbon layers are higher for the phenolic resin-based carbon films as compared with the polyimide-based carbon films. It is considered that during the film forming process, the GOs are oriented in parallel to the film surface and the benzene rings of the polymer chains are oriented in parallel to the GOs and during carbonization process, the carbon layers oriented in parallel to the GOs are developed. The higher orientation of GOs in the precursor polymer films and the stronger interaction between GOs and the methylol groups in resol are considered to lead to the higher degree of carbon layer orientation in the phenolic resin-based carbon films.

Table 1: Degree of orientation of GOs and benzene rings in precursor polymer films, that of carbon layers in carbon films and electrical conductivity of carbon films. Precursor polymer contained GOs with the size of 4 μm by 10 wt %.

Precursor polymer	Precursor film	
	Orientation of GOs	Orientation of benzene rings
Phenolic resin	0.49	0.092
Polyimide	0.18	0.070

Precursor polymer	Carbon film	
	Orientation of carbon layers	Electrical conductivity (S cm^{-1})
Phenolic resin	0.54	418
Polyimide	0.38	168

Acknowledgement

The authors are indebted to Profs. N. Igarashi, N. Shimizu and T. Mori at PF for their experimental support.

Reference

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