Diamond & Related Materials 18 (2009) 399–402

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Fabrication of fullerene nanoring on an oxidized HOPG surface

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ARTICLE INFO

Available online 5 November 2008

Keywords:
Fullerenes
Scanning probe techniques
Molecular beam epitaxy (MBE)

ABSTRACT

Fabrication of fullerene C_{60} nanorings on a highly oriented pyrolytic graphite (HOPG) was carried out by molecular beam epitaxy (MBE). Morphological characteristics of C_{60} were investigated using an atomic force microscope (AFM). An oxidized HOPG, on which circular etch-pits were formed, was used as the template for the fabrication of fullerene nanorings. Evaporated C_{60} molecules were selectively adsorbed on the etch-pits edges where the pre-deposited Au islands existed. The diameter of the etch-pits for nanoring template was controlled simply by the oxidation temperature of HOPG.

1. Introduction

For realizing nanometer-sized devises, it is important to control the arrangement of atoms or molecules on substrates. To fabricate useful structure on a nanometer-scale, self-assemblies of C_{60} are important as they are expected to bring about high throughput in the fabrication process. Moreover, conventional lithography techniques for the fabrication of a nanometer-scale circuit of organic materials cannot be applied, not only because most organic solids are apt to be destroyed but also because fullerene's chemical properties are similar to those of resist materials. Therefore, attempts to control the self-assembly formation of C_{60} were performed by many researchers on varied substrates of Si(111) [1,2], GaAs [3] Sapphire (0001) [4], MoS_2 [5], and Ni(110) [6]. In most cases, selective growth of C_{60} was accomplished using surface defects as the adsorption sites.

Formations of C_{60} film on layered materials have been reported in many research papers [7–14] due to the characteristic growth style by the weak van der Waals interaction between C_{60} and substrate. On layered materials as HOPG, Hunt et al. reported that the C_{60} grows via layered growth [8]. To fabricate a nanostructure by self-assembly, it is necessary to limit nucleation only on the adsorption site. However, in the case of HOPG, C_{60} islands grow laterally on the substrate terraces at room temperature except an initial growth stage of C_{60} [11]. This is caused by the difference in interactions, i.e., the interaction between C_{60} and graphite is slightly stronger than that between C_{60} and C_{60} [13]. Therefore, the three-dimensional fabrication of C_{60} nanostructure has been difficult on layered materials.

In this study, we present the fabrication of C_{60} nanorings on HOPG substrate by using Au particles as a buffer. The template for selective adsorption of C_{60} molecules consist of etch-pits prepared by thermal oxidation of HOPG. By decorating the etch-pits edges with Au, C_{60} nanorings with nanometer-scale diameter were fabricated on HOPG. Au islands, deposited in advance, work as the capture site for C_{60} molecules due to the relatively strong interaction caused by the charge transfer between C_{60} and Au [6]. Firstly, we show the C_{60} formation around the etch-pits without buffer of Au, and then the fabrication of C_{60} nanorings on HOPG by the deposition of C_{60} where Au exists.

2. Experiments

The fabrication process of C_{60} nanorings consists mainly of three steps as illustrated in Fig. 1. HOPG (ZYA Grade, Advanced Ceramics Corporation) was used as the substrate. HOPG was cleaved in air just before the oxidation. Oxidations of HOPG were conducted in a quartz tube cleaned by the pre-heating with the oxygen flow at a pressure of 1.3×10^4 Pa and a temperature of 650 °C. Etch-pits formation was observed by AFM in ambient air (Nanoscope IIIa, Digital Instruments).

C_{60} film was deposited on an oxidized HOPG by evaporating powdered C_{60} (99.9% pure, MER Corporation, Tucson, Arizona) from a well degassed PBN crucible. The oxidized HOPG was mounted on a molybdenum plate with indium solder, and cleaned by heating at 400 °C for 10 h under ultrahigh vacuum (1.0×10^{-7} Pa). Then the substrate temperature was lowered to the growth temperature, and one monolayer of C_{60} molecules was deposited. After the deposition of C_{60}, the samples were taken out of the MBE chamber, and observed by AFM in ambient air. Images were taken in a non-contact mode with a Si cantilever, to avoid destruction of the grown C_{60} film. Selective growth of C_{60} was achieved using Au pre-deposition on oxidized HOPG. Three monolayer of Au was deposited at room temperature and annealed at 400 °C for 2 h. Then, one monolayer of C_{60} was deposited on the Au layer mounted on the oxidized HOPG at 250 °C.

3. Results and discussion

3.1. Oxidation of graphite

Fig. 2 shows typical AFM images of oxidized HOPG. In Fig. 2(a), etch-pits with about 500 nm in diameters and one layer of graphene sheet in

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doi:10.1016/j.diamond.2008.10.044

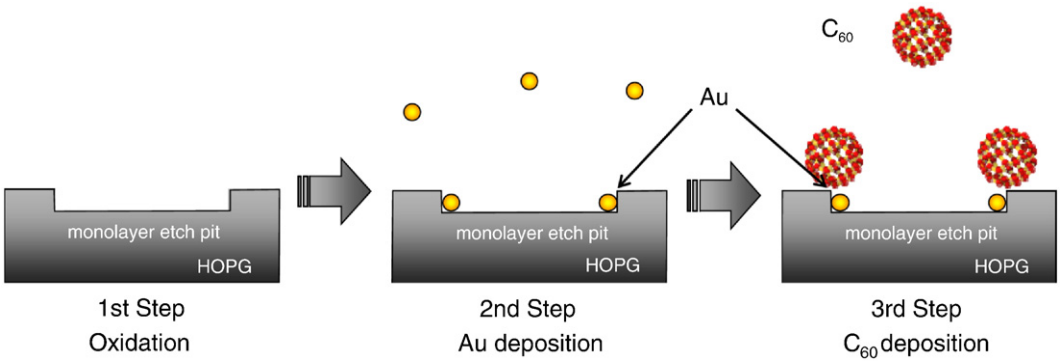

Fig. 1. Schematic illustration of the three step procedures for fabricating C_{60} nanoring.

depth were formed at the oxidation conditions of 600 °C, 1.3×10^4 Pa, and 15 min. At the higher temperature of 650 °C and 700 °C, it was observed that the length of the diameter of the ecth-pits was increased as the rising temperature in Fig. 2(b) and (c). Lee et al. reported that vertical etching did not occur at the 560 °C [15]. Therefore, the oxidation at 600 °C resulted in monolayer etching of graphite, whereas multilayer at 700 °C. Most of the monolayer etch-pits used as the template have nearly circular shape as shown in Fig. 2(a) and (b). Fig. 3 shows XPS spectra of HOPG before (a) and after oxidation (b). From these spectra, it was thought that adsorption of oxygen molecular occurred at the created surface defects when HOPG was oxidized. For the fabrication of C_{60} nanorings, these monolayer etch-pits with about 500 nm in diameter were used. The fact that the diameter of etch-pits strongly depend on the oxidation temperature may indicate that a fabrication of C_{60} nanorings with arbitrary length in diameter are possible.

3.2. Fullerene deposition

Fig. 4 shows AFM images of 1ML C_{60} coverage on oxidized HOPG at the substrate temperature of 150 °C (a), and 230 °C (b). It can be seen that dendritic islands were formed at both temperatures. However, the islands increased in size at higher temperature of 230 °C. At substrate temperature of 150 °C, no dependency for the film growth on the step edge was observed as shown in Fig. 4(a), while at 230 °C, it is clearly seen that the C_{60} formation depends on the two step edges as shown in Fig. 4(b). Kenny et al. reported that, on cleaved HOPG at room temperature, C_{60} nucleation predominantly occurred at the steps on the surface with negligible island formation on the terraces [11]. In the present case at 230 °C, C_{60} islands do not form on the step but on the terraces. This must be caused by the oxygen adsorption at the step edges. As the result, the preferential adsorption of C_{60} molecules at the edges of the step and the etch-pit, pointed by the arrow in Fig. 4(b), were not observed. Therefore, it can be mentioned that C_{60} film growth on HOPG is very sensitive to the surface conditions due to the weak interaction of C_{60} with HOPG.

Fig. 5 shows AFM images of Au at coverage of 3ML on the oxidized HOPG. At room temperature, isolated Au islands were observed in Fig. 5(a). Because of the limited mobility of the Au clusters on the HOPG surface at this temperature, Au clusters did not adsorb on the etch-pit edges (indicated by an arrow A). This suggests strong interaction of Au with HOPG, because the effective diffusion length of Au clusters is short by the strong interaction. With an annealing at 400 °C for 2 h, Au islands were formed selectively on the step edge (indicated by an arrow B) as well as on the etch-pits edges (indicated by arrows C) in Fig. 5(b). It is likely

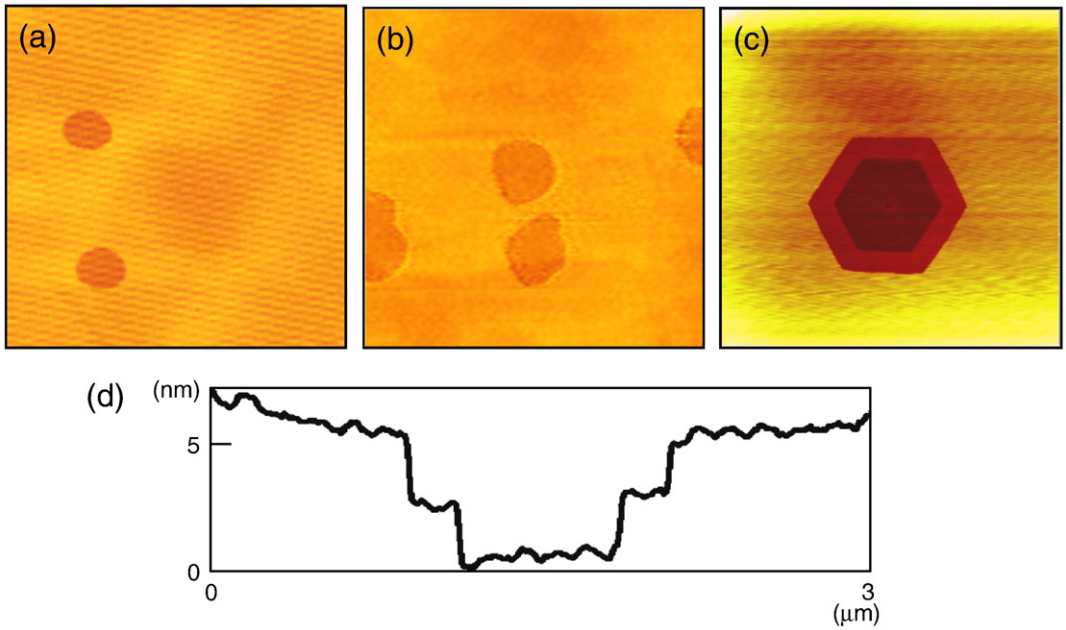

Fig. 2. AFM images (3.0×3.0 μm^2) of etch-pits on HOPG oxidized at 600 °C, 1.3×10^4 Pa, 15 min (a), at 650 °C, 1.3×10^4 Pa, 15 min (b), and at 700 °C, 1.3×10^4 Pa, 15 min (c). The cross section of (c) was shown in (d).