SCANNING TUNNELING MICROSCOPY OF HIGHLY ORIENTED PYROLYTIC GRAPHITE ABLATED WITH EXCIMER LASER

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1. Introduction

The ablative photodecomposition of polymers [1], metals [2] and ceramics [3] using excimer lasers has been investigated extensively over the past decade. Some morphological microstructures were observed on the ablated surface of these materials. We have already reported that periodic microstructures appear on the surface of poly(ethylene naphthalate) (PEN) and polyethersulfone (PES) films by the laser ablation [4,5]. The formation mechanism, however, was not still clear because of complicating higher-order structures and internal stress of the polymer films.

In the present letter, we describe a morphological investigation on the surface of highly oriented pyrolytic graphite (HOPG) which is ablated with a KrF excimer laser. Since HOPG consists of pure carbon atoms having $sp^2$ hybrid orbital and highly oriented cleavage plane without internal stress, it was well suited for the morphological studies of polymer surface ablated by laser irradiation. The surface microstructures of HOPG were analyzed by scanning tunneling microscopy (STM) [6,7]. The STM provides surface images having nanometer-level resolution without mechanical contact between sample surface and a tunneling tip. It has been already reported that surface roughness of silicon and graphite after an argon-ion etching was observed by STM [8,9]. In addition, reflective IR absorption spectroscopy of HOPG was carried out to elucidate the chemical composition of the surface after laser ablation.

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2. Experimental

A cleaved surface of HOPG (manufactured by le Carbone-Lorraine) was irradiated with a KrF excimer laser (Lambda Physik: EMG 201 MSC, wavelength: 248 nm, fluence of 2 J cm\(^{-2}\)) in the atmosphere of helium (1 atm), oxygen (1 atm), vacuum (10\(^{-4}\) Torr), or ambient air. A tunneling microscope (Digital Instruments Inc.: NanoScope II, D-Head or G-Head) was used in ambient air with a mechanical polished platinum wire or an electrolytic etched tungsten wire as a tunneling tip. Measurements of STM were performed with a constant tunneling current of 1 nA and bias voltage of 21 mV with the sample at positive polarity. Chemical compositions of HOPG after the ablation were analyzed with a Fourier transform IR spectrophotometer having a reflective IR microscope (Shimadzu: FTIR-8500).

3. Results and discussion

Figure 1 shows a STM image of a cleaved HOPG surface in ambient air before laser irradiation. It is obvious that no microstructure was observed in an area of 2 \(\mu\)m x 2 \(\mu\)m on the surface. After the irradiation with KrF excimer laser in helium atmosphere (1 atm), the microstructure consisting of topographical dots, whose dimensions were ca. 30 nm on vertical scale and 300 to 500 nm on lateral scale, appeared on the ablated surface of HOPG (Fig.2). The vertical scale in Fig. 2 was ca. 100 times magnified in comparison with the lateral scale. Although HOPG has a layer structure, it is revealed in Fig. 2 that surface layers ablated with the KrF laser were not removed as a layer unit. The shape and size of the microstructures were smaller than those of laser-ablated PEN and PES films [4,5].
The morphology of ablated HOPG surface depended upon surrounding gases in the ablation. When HOPG was ablated in vacuum, oxygen, and ambient air, the size of the microstructures was ca. two times larger than that in helium. It is widely known that surrounding gases affects the ejection velocity of fragments from the surface in the ablation [10]. The influence of surrounding gases upon the morphology would be accounted for by the redeposition of fragments onto the ablated HOPG surface.

Figure 3 shows the time-course of morphological change of ablated HOPG. Domain boundaries and crater-like microstructures were formed for a period of 10 hours after the ablation. It is found, as shown in Fig. 3, that the morphology of microstructures on laser-ablated HOPG was gradually changed in air, although the microstructures on the ablated polymer films are stable in air. The size of these domains on HOPG surface was estimated to be 10 µm (Fig. 4). It seemed that the boundaries in Fig. 4 were formed on the surface at random.

![STM image of HOPG surface immediately after laser ablation. The surface was irradiated with KrF excimer laser (2 J cm⁻², 10 shots, 10 Hz) in helium atmosphere (1 atm). The image extends over an area of 8 µm x 8 µm.](image)
Chemical composition of HOPG surface was changed by the laser irradiation. After the ablation in air, a broad absorption band between 1650 cm\(^{-1}\) and 1850 cm\(^{-1}\) was observed with a reflective IR measurement, whereas fresh HOPG surface is inactive for an IR absorption spectroscopy. The broad band arose from the formation of amorphous carbons [11] and carbonyl groups on the ablated surface. The formation of the amorphous carbons and carbonyl groups seems to be ascribable to the redeposition of fragments and to the photo-oxidation of HOPG surface in the laser ablation. The change of chemical compositions induced by the laser ablation is observed frequently in the ablation of polymer films [4, 5, 12].

Fig. 3 The top-view STM images of HOPG surface after the KrF excimer laser ablation in oxygen (1 atm); (a) after 0 hour, (b) after 10 hours, (c) after 33 hours (d) after 46 hours. The each image was observed on different locations of the sample, and extended over an area of 8 µm x 8 µm.
The surface morphology of HOPG was modified by the ablation with the KrF excimer laser. The shape and size of microstructures differ from those of polymers [1, 4, 5, 12] and composite ceramics [13]. These phenomena would be ascribed to the different mechanism of photochemical decomposition in the ablation. It is assumed that the change of chemical composition, transient fluidization on laser-irradiated surface, and the redeposition of fragments in laser ablation play a key role in the formation of microstructures on HOPG surface. Further investigation concerning the mechanism of the microstructure formation is in progress.

References


