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STM OF GLOW-DISCHARGE TREATED SURFACES

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KEY WORDS: Glow-discharge treatment; surface imaging; STM

ABSTRACT

As a model surface, graphite slides were treated by pure nitrogen gas plasma for different periods (15 sec - 5 min). These samples were kept in air or under argon atmosphere in sealed holders. STM images were obtained at constant current mode. Results showed that both the number and the size of clusters formed by plasma deposition increased with exposure time.

INTRODUCTION

The surfaces of biomaterials may be readly modified physically or chemically in order to increase their biocompatibilities, and also to add functionality to the respective surfaces. Glow-discharge treatment (i.e., the so-called plasma treatment) is one of the recent surface modification methods which have also been applied to biomaterials (1-3). In order to understand, reproduce or optimize the treatment conditions, it is necessary to analyze both composition and structure of the plasma treated surfaces and to relate these parameters to the specific properties of interest.

Scanning Tunnelling Microscopy (STM) is a new and fast growing surface analysis and imaging technique. In the ten years since its invention by Binnig and Rohrer, STM has been gradually increasing in popularity in the imaging of conducting and semi-conducting surfaces (4,5). In this study, we have used STM to analyse plasma exposed surfaces. "Highly Oriented Pyrolithic Graphite" (HOPG) was selected as a model surface. Because STM requires conductive (or semi-conductive) samples, we have applied this technique for the early stage (before total coverage of the surface) analysis of the plasma processing. This short communication reports the results of our preliminary experiments.

MATERIALS AND METHODS

The glow-discharge reactor consisted of a glass tube with length of 30 cm and inside diameter of 9 cm (6). Two external cupper electrodes (4x14 cm) were placed in a paralel manner around the glass tube. The upper electrode was connected to the radio frequency (RF) generator (Tasarim Ltd., T-RF-1100, Turkey) through an impedance matching network (Tasarim Ltd., T-RF-1200, Turkey), whereas the lower electrode was grounded.

Pyrolithic graphite samples (900x900 Angstrom) (Union Carbide) were cleaved by an adhesive tape, and placed in the plasma reactor. The reactor was evacuated down to 0.4 mbar, the nitrogen gas flow rate of 30 ml/min was allowed. The radio frequency discharge (13.56 MHz, 10 Watts) was fed to the reactor.The exposure time was varied between 15 sec to 5 min. The HOPG samples were kept under air or argon atmosphere in desiccators for about 6 days before STM imaging.

An home-made STM with a magnetically driven sample positioner and a single tube scanner, which was explained elsewhere in detail (7), was used during the experiments. Tips were made of platinium. STM images were obtained in constant current mode. Parameters for a typical constant current mode were 10 mV bias voltage, tips being positive with respect to samples. 0.5 nA tunneling current and 4 Hz scan rate in x direction. The tube scanner was calibrated by the lattice parameter of HOPG substrate. Images were processed by a low filter to eliminate high frequency noise.

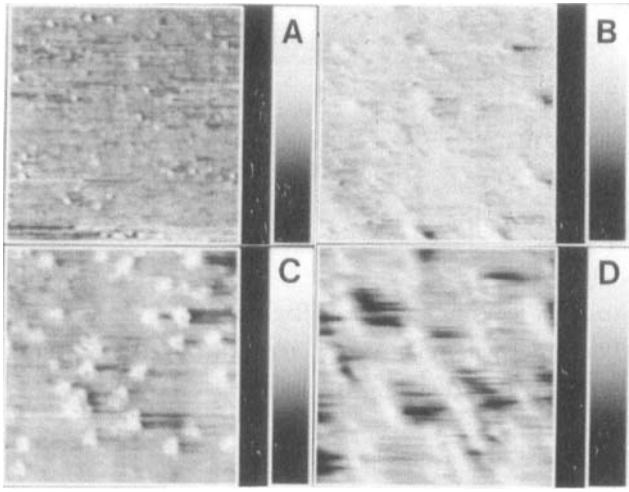

Fig 1. Images of the Nitrogen Plasma Exposed HOPG Surfaces (Stored in Air Atmospere for 6 days): The Plasma Exposure Times: (A) 15 sec; (B) 30 sec; (C) 60 sec; and (D) 5 min.

RESULTS AND DISCUSSION

In the first group experiments, we have planned to study with nitrogen containing compounds (pure nitrogen gas, ammonia, primary, secondary and tertiary amines, etc.), which are widely used to modify biomaterial surfaces for a variety of applications. In this paper, the first STM images of pure nitrogen gas treated surfaces are exemplified. Figure 1 shows the nitrogen plasma exposed HOPG surfaces, which were kept in air for about six days before STM imaging. Note that four pictures for each treatment time were selected and presented here as representatives of many observation events.

Roughly spherical dot-like features on these images can be easily seen. Notice that, they are distributed homogeneously on the surfaces. In some images orientation in one direction were observable, which may be attributed to orientation in plasma medium due to continuous gas flow during plasma deposition. Adsorption from the atmosphere was not given strong consideration because freshly cleaned HOPG

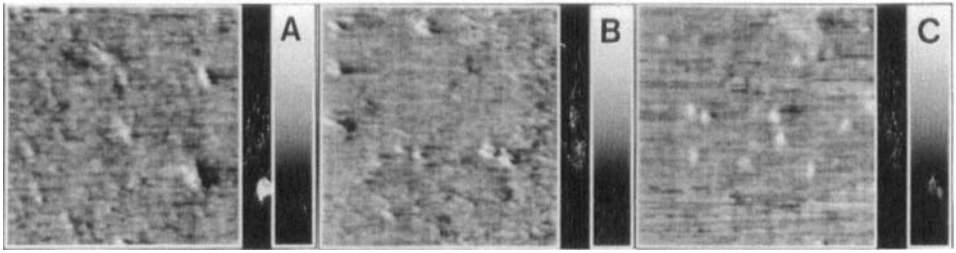

Fig 2. Images of the Nitrogen Plasma Exposed HOPG Surfaces (Stored in Argon Atmospere for 6 days): The Plasma Exposure Times: (A) 15 sec; (B) 30 sec; and (C) 60 sec.

samples were used in each treatment and were kept in sealed holders. To be sure, adsorption from atmosphere were also checked on the surfaces of the clean HOPG control samples which had undergone identical sample preparation procedures except plasma treatment, and similar images were not seen. Therefore we have concluded that these dots are atoms deposited due to plasma treatment.

As can be seen on the images, both the number and size of the spots on the substrate surface increase with the deposition time. By increasing the deposition time from 15 sec to 60 sec the diameter of the features increased, but their heights did not change significantly. The average hight of the spots was about 10-15 Å. This may be an indication of monolayer film formation at the very early stage of plasma treatment. We have also observed that about 5 minutes the substrates were totally covered by a thin nonconductive film. We were not able to get tunneling in most of these samples. However, as seen in Figure 1d, in some samples exposed to plasma even for about 5 min we could obtained tunneling current and observed large, poorly reproducible clusters. We concluded that the nonconductive monolayer plasma film on the surface had been punched by the STM tip, to obtain tunnel current.

During these early studies we have noticed that, the plasma treated surfaces were dynamic. We have repeated STM imaging on the same sample up to 6 days after plasma treatment. We did observe the increase of the number of features on the plasma exposed surface in time. Dynamic behavior (i.e., change of the chemical

structure of the coating) of the plasma treated surfaces is a rather general phenomenon, but for long period of times (1). However, in our case the time was rather short. Therefore, we have designed the second group experiments, which were identical to the previous ones, except the plasma exposed HOPG samples were placed into a desiccator and kept under argon atmosphere instead of air until they were imaged in STM. Figure 2 exemplifies the images of those samples. However, comparison of Figure 1 and 2 reveals that the storing conditions after plasma treatment affect the surface deposition substantially. It seems that the active points created during plasma treatment on the plasma exposed surfaces remain active even during storing, and more atoms present in air (i.e. nitrogen and oxygen) are adsorbed at these active points. Therefore, cluster formation on the surfaces is enhanced if the samples are kept in air, rather than in argon.

Work related to plasma processing of graphite surface with other nitrogen containing compounds are under investigation.

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