Surface nanostructure formation by the interaction of slow xenon ions on HOPG surfaces

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Abstract. Experiments on nanostructure formation on highly oriented pyrolytic graphite (HOPG) surfaces irradiated by slow highly charged Xe⁺⁺⁺ (q=23-29) ions have been carried out at a new experimental terminal for surface physics on the 320 kV ECR platform at the Institute of Modern Physics (IMP). In the tapping mode atomic force microscope (AFM) image, the nano-sized hillocks protruding from the surfaces are probed. The height and diameter of the nanostructures increase with the projectile charge state. The present results reveal a similarity between the nanostructure formation produced by slow highly charged ions and the track formation induced by swift heavy ions.

1. Introduction

Ion-surface collisions have been studied intensively during recent years. Ions deposit energy either as kinetic energy dominated relevant to the interaction of swift heavy ions (SHI) in matter or as potential energy carried by slow (eV to keV) highly charged ions irradiated on surfaces. In comparison with SHI, highly charged ions (HCI) carry several tens of keV of potential energy which is delivered into only a few atomic layers of the surface, resulting in many different phenomena that are significantly dependent on the potential energy deposition, e.g., potential electron emission [1, 2], potential sputtering [3], X-ray emission [4] and surface defects [5]. Slow HCI can be used as a unique tool for surface etching, ultra-thin film growth and nanostructure fabrication [6].

Surface defects observed by a scanning probe microscope (SPM) in both scanning tunneling microscope (STM) and atomic force microscope (AFM) modes have been studied in some famous laboratories recently[5-10]. As is known, STM observation gives information on the electronic density of states, while AFM observation directly gives topographic surface structure. AFM has three modes: tapping, contact and non-contact. It is noted that a contact-AFM observation is often not very reliable in discussing topological structures while the tapping mode AFM was successfully applied to observe protrusions induced by 1 keV Ar⁺ ions [11]. For Xe²⁶⁺ ions, the protrusion-like dots were visible not only in the STM image but also in the non-contact mode AFM image taken at the same impact site [12]. Up to now, a number of observations have been performed for ion-induced defects on surfaces like HOPG, mica, CaF₂, Al₂O₃, Si, SiO₂ and other materials [6-12]. HOPG is a common and useful material for surface etching and the nuclear fusion industry. Its lamellar structure gives rise to high thermal conductivity and semimetallic electrical conductivity parallel to the layers and poor conductivity normal to the planes.
2. Experimental Method
The experiments were carried out with the 14.5 GHz ECR ion source at the 320 kV experimental platform in the national laboratory of the Heavy Ion Research Facility in Lanzhou (HIRFL), China. The ion source used was the high charge state all-permanent magnet ECR ion source no. 2, where the extraction voltage of ions is 5-320 kV [13]. The ion beam was extracted from the ion source, selected by two 90° analyzing magnets and focused by two quadrupole lenses, then deflected by a 60° magnet and finally transported into the experimental chamber. By such procedure we can obtain a well-aligned ion beam with high purification. The beam was collimated to a divergence of about 0.7° by a pair of four-jaw slits and then impact onto the target holder where were mounted on a goniometer in the center of an ultra-high vacuum (UHV) chamber (base pressure is about 5×10⁻¹⁰ mbar, 8×10⁻⁹ mbar during sample irradiation). The projectile current was measured by a Faraday Cup with a pico-ampere meter (Model 6458, Keithley, USA). A cage which has an aperture of 5 mm with a pico-ampere meter was isolated in front of the target holder. The current at the target holder was also measured with a pico-ampere meter. By adjusting a pair of four-jaw slits, the incident ion beam was able to reach the target holder when the current of the cage was zero and the current of the target holder reached the maximum value. After focusing the ion beam, the HOPG samples which were freshly cleaved in the air with adhesive tape were transported to the target holder. During the experiment, we adjust the acceleration voltage for each charge state of xenon ions in order to remain the same projectile energy of 383 keV. The ion current density was kept below 5nA/cm². Total ion fluxes of about 1×10¹⁰ ions/cm² were applied under normal incidence.

After irradiation, the HOPG samples were exposed to air, transported and set on a sample holder of a SPM (Nano III, USA). In the present study, all the measurements have been done in the tapping AFM mode in order to observe the real topographic surface structures.

3. Results and Discussion
Figure 1 shows a typical AFM image of the HOPG surfaces after xenon ion irradiation. The 1000×1000 nm² images show distinct hillock-like nanostructures on the initially flat surface for xenon ion with charge state 29 and 27. For Xe²³⁺ and Xe²⁵⁺, small dots are observed in the 300×300 nm² images. In contrast, we have also tested a freshly cleaved HOPG surface with AFM. It is almost flat and smooth before the irradiations.

Figure 2 shows the height and diameter of the dots as a function of charge state. More than 30 dots were probed with the AFM for ion beams in each charge state. The error bars in the figure represent the standard deviations. The height and diameter of the dots shows a strong charge state dependence.
When the charge state is equal to or higher than 27 there is a significant increase in the height and size of dots on the surfaces.

According to previous results obtained from the STM images, it was shown that there is no significant kinetic or potential energy dependence of the nanodot height and width irradiated by Ar\(^{q^+}\) (q=1, 8, 9, 11) ions on HOPG at the hundreds of eV kinetic energies range [14], in contrast with the conclusions of a strong charge state dependence and no kinetic energy dependence of the defect size from HOPG by xenon and argon ions at the large incident kinetic energy [15]. However, in our observation for Xe\(^{27^+}, 29^+\) ions with kinetic energy of 383 keV impact on HOPG surfaces, nanodots were observed in the AFM tapping mode, and shown size increases as increasing charge state. For Xe\(^{23^+}\), a height of about 0.5 nm and a diameter of several nm have been observed in this measurement and in Nakamura’s group with a STM [12, 15]. Our results clearly gave the evidence that the nanostructures correspond to the topographical change on the surface depend on the potential energy of incident ions. The dot size discrepancy between our and the previous results could be due to the differences in the kinetic energy of the incident ions or the SPM modes.

Since the kinetic energy of the incident ions was rather large, we could not specify which is more effective for the surface deformation between the kinetic and potential energies. Thus, in this study, we have studied the incident ion charge dependences of the nanodot size and height at the same kinetic energy range (383 keV, \(v=7.5\times10^5\) m/s). In the interaction of xenon ions on graphite surface, the nuclear stopping power \(S_n\) is 2.3 keV/nm and the electronic stopping energy \(S_e\) is 0.95 keV/nm (calculation using SRIM-2003) [16]. It was reported that for incident ions with \(S_e\leq 7.3\) keV/nm, the damage process on HOPG surface is dominated by nuclear stopping [17]. The energy transferred to the lattice will eventually lead to heating and melting of the crystal. Until the relatively slow processes of melting and recrystallization occur, cooling process sets in, leading to the formation of nanostructures.

The average height of nanodots we have found for Xe\(^{29^+}\) ions irradiated is 3.6±1.5 nm. They are of hillock shape with a diameter of 25.3±4.9 nm and are similar to the nanodots and chains on SrTiO\(_3\), TiO\(_2\) and Al\(_2\)O\(_3\) surfaces created by xenon ions with energies of several tens of MeV with under grazing angles [18]. The thermal spike model [17, 18] has been developed to describe the formation of cylindrical tracks or recrystallized materials in the solid irradiated by SHI, where electronic stopping dominates over nuclear stopping. As the model has described, swift ions deposit their kinetic energy mainly by inelastic collisions with lattice atoms. When this energy is enough to increase the lattice temperature locally above the melting temperature, a rapid quenching is followed, thereby causing excitation and ionization processes. How this electronic excitation finally leads to the modification of the material (craters, hillocks) is still not exactly known. Accordingly, a modified inelastic thermal
spike model has been developed to consider the process of electronic excitation by the potential energy of HCI and the subsequent phase transitions (heating, melting and restructuring) induced by HCI impacting on the surface[10, 19]. Although the mechanism of energy deposition between HCI and SHI is fundamentally different in the beginning, strong electronic excitation on the surface within a nanometer scale region by HCI is very similar to the ion trajectory in the solid by SHI during the restructurization process. This may explain why nanostructures on the surface produced by slow HCI have a similarity of the tracks induced by SHI in the solid.

For further understanding, systematic studies are still ongoing for the energy and material dependences of nanostructures’ height and size not only using STM and AFM, but also applying other complementary techniques e.g. Raman spectroscopy, low energy electron microscopy and small angle X-ray scattering, etc. In addition, simulations and calculations must be set up to clarify the surface modification mechanism.

Acknowledgments
This work was supported by the National Natural Science Foundation of China through Grant No. 10405025 and Found of president’s excellent scholarship of Chinese Academy of Sciences. We would like to thank J. Liu, C. Trautmann and Y. Yamazaki for many fruitful discussions, and J. Y. Li and P. Z. Wang of the 320 kV ECR platform for help during the experiments.

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