Nuclear Inst. and Methods in Physics Research B 420 (2018) 23–26

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research B

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

Surface structure modification of single crystal graphite after slow, highly charged ion irradiation

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ARTICLE INFO

Keywords:
Ions
Surface modification
Single crystal graphite

ABSTRACT

Single crystal graphite was irradiated by slow, highly charged ions. The modification of the surface structure was studied by means of Low-Energy Electron Diffraction. The observed damage cross section increases with the potential energy, *i.e.* the charge state of the incident ion, at a constant kinetic energy. The potential energy is more efficient for the damage production than the kinetic energy by more than a factor of twenty. Comparison with earlier results hints to a strong link between early electron creation and later target atom rearrangement. With increasing ion fluence, the initially large-scale single crystal is first transformed into μm-sized crystals, before complete amorphisation takes place.

1. Introduction

Due to the layered structure of graphite, electrical and thermal conductivity are very different in the direction normal to the layers (the *c*-direction) and in the plane of the layers [1]. For instance, the electrical conductivity along the *c*-axis is about a thousand times lower than in the perpendicular direction [2,3]. The easily accessible version of crystalline graphite is the so-called highly oriented pyrolytic graphite (HOPG). It is of interest to be discussed here, since the evolution of the LEED pattern of HOPG can be used to explain the respective LEED pattern evolution of single crystal graphite (SCG) used in this work. HOPG consists of μm-sized crystalline grains, whose layers are well aligned, *i. e*. the spread of the *c*-directions of the grains at the surface, the so-called mosaicity parameter, amounts only to a few degrees. HOPG samples are used quite frequently in ion-surface interaction studies [4,5]. However, SCG samples are used less often, due to their poor availability. They present important model systems for plasma-wall interactions in fusion research. In addition, they are inert in air and easy to cleave.

Surface modifications due to ion impact at low energies are mainly governed by two effects. On the one hand, the ion interacts with the target atoms by means of direct collisions, leading to the so-called nuclear stopping [6]. On the other hand, the charge state of the ion induces electron capture in front of the surface, leaving the impact area of the projectile on the target charged and thus strongly instable [7]. This perturbation of the electronic system is similar to the perturbation induced by swift heavy ions [8]. Irradiation of single charged ions can induce a nano-modification on the surface of HOPG, like small hillocks (Protrusions), nanodots and $\sqrt{3} \times \sqrt{3}$ – R30° superstructures [9,10]. This reconstruction is typically localized next to hillocks, which are attributed to point defects in the electronic structure of graphite [9,11]. The size of these features created by Ar^{8+} ions impinging on HOPG are of about 1 nm in diameter at a kinetic energy E_{kin} = 400 eV [12]. In the case of Highly Charged Ions (HCI), many kinetic electrons are produced by means of capture and Auger processes, due to the high charge state of the ion. These electrons then heat the impact area, due to electron–phonon coupling, and therefore produce the observed surface modifications [12]. Moreover, HCIs generate electron emission from clean HOPG, the ejection patterns depend on the orientation of the target *i. e*. the electronic conductivity and consequently the mean free path of the electrons inside the target [3]. At high ion doses, sp^2 bonds are converted to sp^3, resulting in disordering of surface atoms and high-density defects formation [13,14]. With respect to the sputtering of target atoms by ion impact, no charge state effect of the sputtering yield has been found for conducting surfaces [15,16]. For insulating surfaces, the sputtering yield increases dramatically with the potential energy carried into the collision by the impinging ion [17–19].

So far all studies have employed local probes [20–22]. In this report we use LEED to study the irradiation damage. The size of the electron beam spot is about 1 mm^2 and in contrast to scanning probe methods,

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https://doi.org/10.1016/j.nimb.2018.01.024
Received 11 October 2017; Received in revised form 23 January 2018; Accepted 25 January 2018
Available online 08 February 2018
0168-583X/

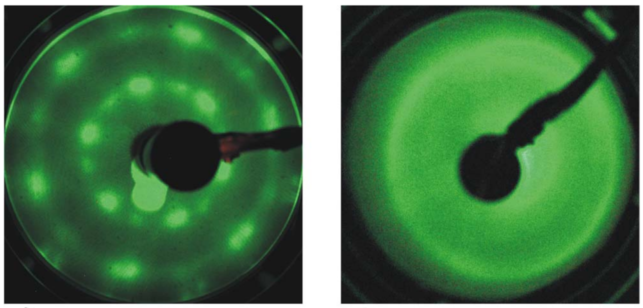

Fig. 1. LEED pattern on freshly cleaved SCG (a) and HOPG (b) at an electron beam energy of 185 eV. (b) was taken with another LEED setup and is only shown for clarification purposes.

large areas of the surface are easily investigated. The coherence length of the electron beam (or transfer width of the instrument) is typically about 150–200 Å which allows the investigation of extended periodic structures with a periodicity smaller than this length scale [23]. In addition, electrons in this energy range penetrate only a few Å into the solid [24]. LEED thus offers a surface sensitive tool that is well suited to study modifications of the lattice structure due to irradiation.

2. Experimental setup

An SCG target with (1000) orientation was used to perform this experiment. The dimension of the sample was approximately $10 \times 10 \times 0.5\,mm^3$. The SCG sample was cleaved in air with adhesive tape and immediately put into the ultra-high vacuum chamber (base pressure below 10^{-9} mbar) by means of a load lock. The experimental chamber consists of two main levels; in the lower level the target is irradiated, and the load lock is mounted. In the upper level the LEED setup (OMICRON 4-grid) is mounted. The LEED images were taken by a digital camera, only the green channel was used to suppress noise. The contrast of the LEED images in Figs. 1 and 2 was enhanced to clarify the patterns. The raw data has been taken for the quantitative discussion below.

This experiment has been performed at the ARIBE beam line (Accelerateur de Recherche sur les Ions de Basses Energies) [25] of the GANIL facility (Grand Accelerateur National d'Ions Lourds) in Caen, France. We used Xe ions with charge states Xe^{14+} and Xe^{26+} to measure the charge state effects on the surface. The corresponding potential energy (E_{pot}) of the impinging ions is 1.9 keV and 8.9 keV, respectively [26]. Both ions were accelerated to the same kinetic energy of 200 keV. The ion beam had a flux of about 10^{11} ions $cm^{-2}\,s^{-1}$. The irradiation of the SCG has been performed under normal incidence.

The surface crystallinity was studied by LEED before and after each irradiation step. Each irradiation consisted of an incremental fluence of 10^{12} ions/cm^2. After each irradiation, the target was re-positioned in front of the LEED setup. Special care was taken to ensure the same position of the target relative to the LEED, especially the distance between LEED electron gun and target. However, it was difficult to reproduce the same electron beam current as the LEED instrument was shut off during irradiations. Therefore, it was necessary to normalise the LEED patterns with respect to each other by means of the intensity of the spot below and to the right of the electron gun. This spot originates from a reflection and is directly proportional to the electron beam intensity.

3. Results

Fig. 1 a) shows the LEED pattern of freshly cleaved SCG. It consists of two hexagons rotated by an angle of 30° with respect to each other, with two levels of brightness. The lower-intensity hexagon in the LEED pattern cannot originate from the intermediate layer of graphite, as the B layer of the ABA stacking is only shifted and not rotated with respect to the A layer. This second, lower intensity hexagon was not seen by other groups [27]. We therefore assume that we used a lower-quality SCG in which a second orientation is present, rotated by 30°. Additionally, we see an inner ring, also with the double-hexagon structure, rotated by 30°. This is similar to the pattern reported earlier [27], except for the second hexagon pattern with lower intensity, and can be attributed to a higher-order diffraction pattern. All of these four groups (two hexagon groups on each ring, inner and outer ring) do behave similarly, as far as we could determine with the statistics obtained. For the analysis presented here we only use the brighter group on the outer ring, due to the higher intensity and therefore better statistics.

In Fig. 2 the LEED patterns at different irradiation fluences are shown. In order to quantify the spot intensities and therefore the crystallization of the target during irradiation, we integrated the spot intensity of the intense outer hexagon, excluding two other distributions, whose physical explanation will be discussed later: a circle and a general background.

The spot intensity in Fig. 2 decreases with increasing fluence of the ion irradiation. We fitted an exponential decay curve $I_D = I_0 \exp(-\sigma_D F)$, where F is the fluence, to the normalised and corrected intensity of the diffraction spot, yielding a damage cross section σ_D.

Fig. 3 shows the exponential decay of the spot intensity, and the fitted decay curve, for the irradiation by Xe^{14+} and Xe^{26+} ions. The obtained damage cross sections are $(3.1 \pm 0.1)\times 10^{-13}\,cm^2$ and $(5.2 \pm 0.5)\times 10^{-13}\,cm^2$, respectively. As the product of these cross sections and the maximum fluence used for the fit is only of the order of 0.1, the overlap at these fluences is very small. We were not able to use data points at higher fluences, because the spots (and later the ring structure) became so faint, that a distinction from the background was not possible anymore.

The ratio of the damage cross sections is $\sigma_{26+}/\sigma_{14+} = 1.7 \pm 0.2$. We can compare this value to the ratio of the total energies

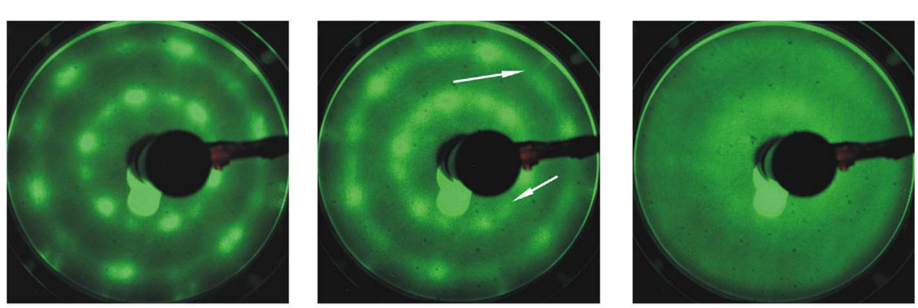

Fig. 2. LEED pattern of SCG irradiated with Xe^{14+} at a kinetic energy of 200 keV. (a) Virgin sample, (b) sample irradiated with 3×10^{12} ions/cm^2 (the arrows show the apparition of the inner and outer ring), (c) sample irradiated with 8×10^{12} ions/cm^2.