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**Ion beam induced surface graphitization of CVD diamond for x-ray beam position monitor applications**

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ABSTRACT *W*

**MASTER**

The Advanced Photon Source (APS) at Argonne National Laboratory is a third-generation synchrotron facility that generates powerful x-ray beams on its undulator beamlines for a variety of scientific and industrial user research programs. It is very important to know the position and the angle of the x-ray beam during experiments. Due to very high heat flux levels, several patented x-ray beam position monitors (XBPM) exploiting beneficial characteristics of chemical vapor deposition (CVD) diamond have been developed. These XBPMs have a thin layer of low-atomic-mass metallic coating so that photoemission from the x-rays generates a minute but measurable current for position determination. Another concept has been the graphitization of the CVD diamond surface to create a very thin, intrinsic and conducting layer that can stand much higher temperatures and have minimal x-ray transmission losses compared to the coated metallic layers. In the present study, a laboratory sputter ion source has been used to transform selected surfaces of a CVD diamond substrate into graphite. The effect of 1 - 5 keV argon ion bombardment on CVD diamond surfaces at various target temperatures from 200 to 500°C has been studied using Auger electron spectroscopy and *in-situ*

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electrical resistivity measurements. Graphitization after the ion bombardment has been confirmed, and optimum conditions for graphitization have been studied. Raman spectroscopy has been applied to identify the over-all diamond structure in the bulk of CVD diamond substrate after the ion bombardments. It was found that the target temperature plays an important role in the stability and electrical conductivity of the irradiated CVD diamonds.

## 1. INTRODUCTION

Diamond exhibits excellent physical properties for high-power x-ray applications. It is a good electrical insulator and excellent thermal conductor. Water-cooled diamond can stand very high heat load. Diamond is also a low-Z material that has acceptable transparency to x-rays. And it has excellent radiation resistance. Development in synthetic techniques of chemical vapor deposition (CVD) diamond has dramatically lowered the cost and eased the physical size limitation for diamond applications. At the Advanced Photon Source, for example, CVD diamond has been used in x-ray beam position monitors and beamline vacuum windows. In these applications, commercially available high quality CVD diamonds are used to handle the extreme high heat load due to the powerful third-generation synchrotron radiation x-ray beams. For the beam position monitor application, electrically conducting segments on the diamond substrate are needed for signal generation through the photoemission process under the x-ray. The signals are used to calculate the beam position and angle and to adjust the x-ray orbital during the operation. These metallic segments should be able to stand high temperatures and to give as little as possible interference to the x-ray spectrum. Instead of metallic layers, graphitization of the diamond surface can provide an intrinsic conducting layer that can stand the high temperature and introduce no extra transmission interference to the x-ray spectrum. In this paper, we present a systematic study of surface graphitization

of CVD diamonds by low energy  $\text{Ar}^+$  bombardments as a function of  $\text{Ar}^+$  energy and of the target temperature during irradiation.

The effect of high energy ion implantation on both natural and CVD diamonds has been extensively studied [1-7]. It is found that the behavior of natural diamond and CVD diamond under ion irradiation is remarkably similar [7]. The most noticeable effect of ion irradiation on diamonds is a significant reduction of resistivity. Resistivity measurements are used to monitor the ion irradiation effect on diamonds as a function of the ion dose, the target temperature, and the post-annealing temperature. Resistivity measured as a function of sample temperature has been used to identify the conducting mechanism of the irradiated surface [8]. Raman spectroscopy has been used to investigate the disorder and structure change in diamonds upon irradiation [3, 9, 10].

The influence of low energy  $\text{Ar}^+$  bombardment on diamond surface has been studied by using high energy electron diffraction (RHEED) [11] and electron spectroscopies [12-16]. It was found that the RHEED pattern diffuses and the C(KLL) Auger line shape becomes into more graphite-like, suggesting graphitization of the diamond surface after  $\text{Ar}^+$  irradiation. Most of these experiments were performed at room temperature, and no resistivity measurements were carried out because of the extreme thinness of the graphitized layer.

It is known that the target temperature during ion irradiation plays a crucial role in the graphitization process for high energy ion irradiation on diamond [2, 3]. The target temperature may be also a very important factor in obtaining a stable graphite-like layer on the diamond surface using low-energy ion irradiation.

In this study, we used an *in-situ* resistivity measurement technique to study the influence of low energy  $\text{Ar}^+$  bombardment on CVD diamonds as a function of ion dose and target temperature. This technique was developed by one of us for ultrathin film *in-situ* studies [17]. The *in-situ* technique in ultrahigh vacuum (UHV) has the advantage of obtaining sample information without the complication of sample contamination. It also provides instant information on the sample during the experiment.

Auger electron spectroscopy (AES) and Raman spectroscopy measurements have also been performed in this study.

## 2. EXPERIMENT

All experiments, except the Raman spectroscopy measurements, were performed in a UHV surface analysis chamber, which has a base pressure of  $\sim 8 \times 10^{-11}$  Torr. High quality CVD diamond substrates (4 x 20 x 0.2 mm) were provided by the General Electric Company. They are transparent and slightly grayish in color. Both sides were lap finished by the manufacturer. To make a sample, the two ends of the substrate were coated with  $\sim 200$  nm of gold. They were bombarded by 5 keV  $\text{Ar}^+$  before the Au coating to ensure a good ohmic contact with the diamond [18]. The uncoated gap between the two Au coatings was 8 mm long and 4 mm wide.

The Au-coated sample was mounted on a sample holder with four Au wires mechanically clamped onto the two Au coatings for four-probe resistivity measurements. The Au wires and a large part of the Au films were covered by alumina ceramic pieces. A small portion ( $\sim 0.5$  mm) of the Au film on each end (neighboring the uncoated area of the sample) was exposed and subjected to ion irradiation during  $\text{Ar}^+$  bombardment. Underneath the sample, another alumina piece was added to prevent metal atoms in the sample holder from reaching the sample during  $\text{Ar}^+$  sputtering. A UHV bottom heater was used to heat the sample. The sample temperature was measured with an alumel-chromel thermal couple, which was clamped onto the Au coating on one end of the sample. The four Au wires were inserted into four insulated "push-on" connectors on the sample holder, which were connected to the outside through an electrical feedthrough on the vacuum chamber. The whole sample holder assembly was mounted on a XYZ manipulator.

The ion beam bombardment was performed *in-situ* using a Vacuum Generators Model AG5000 ion gun. The sample was bombarded at normal incidence with the whole

sample area irradiated uniformly. The Ar partial pressure during irradiation was  $\sim 3 \times 10^{-5}$  Torr in the chamber, which was partly pumped by a turbomolecular pump with the ion pump valve closed. The ion current was measured with a Faraday plate for each ion energy level.

Sheet resistance measurements were carried out using a Keithley Model 2000 digital multimeter with a four-probe configuration. The test current was set at 10  $\mu$ A. The initial resistance of the sample was out of the measuring range of  $10^{10}$   $\Omega$  of the multimeter. The resistance was recorded by a computer when the ion beam was put on pause (to eliminate the influence of the ion beam on the resistance reading). Stabilization time was allowed before taking the data after each ion dose.

AES was performed before and after the ion irradiation of the CVD diamond. An Auger spectrum was also measured for a highly oriented pyrolytic graphite (HOPG) sample, which was freshly cleaved using a Scotch tape.

Raman spectra were measured for both irradiated and unirradiated CVD diamonds using an argon ion laser (514.5 nm). The measurements were performed in air at room temperature.

### 3. RESULTS AND DISCUSSION

#### 3.1 Sheet resistance as a function of ion dose and ion energy

Figure 1 shows the sheet resistance measured at 200°C after periodic  $\text{Ar}^+$  irradiation at a target temperature of 200°C with ion energies of 1, 2, 4, and 5 keV. When the dose increased to  $\sim 9 \times 10^{15}$  ions/cm<sup>2</sup>, the sheet resistance decreased dramatically and saturated at a dose of  $\sim 1.8 \times 10^{16}$  ions/cm<sup>2</sup>. Subsequent higher energy  $\text{Ar}^+$  doses resulted in lower saturated sheet resistance as the ion energy was increased.

The dose dependence shown in Fig. 1 agrees well with those obtained using high energy ion implantation for both natural and CVD diamonds [1-3, 7]. Apparently a

similar mechanism of ion-induced graphitization of diamond applies to both the high energy irradiation case and the low energy case. The ion impact causes structural changes on the diamond surface. The locally affected zones overlap when the ion dose reaches a certain critical value, and the diamond surface becomes conducting. It is of interest to note that, although the gap between the electrodes in our sample is substantially larger than that reported for high energy ion implantation of diamond [1, 6] (8 mm vs. 1 mm), the critical doses in these two cases have the same order of magnitude, and they are all greater than the density of C atoms on the diamond surface.

The saturated resistance after ion irradiation for low energy bombardments is much higher than that for high energy implantation. This is expected because low energy ions cannot penetrate as deeply as do the high energy ions, resulting in a shallow conducting layer. The saturated sheet resistance decreases as the ion energy increases, as shown in Fig. 1.

### 3.2 Sheet resistance as a function of target temperature and annealing temperature

A series of  $\text{Ar}^+$  irradiation experiments were carried out for the same sample at various target temperatures. The results of each sequence are shown in Fig. 2. Curve 1 in Fig. 2 shows the temperature dependence of the sheet resistance for the sample that has gone through the bombardment sequence as described in section 3.1. The sheet resistance decreased dramatically as the temperature was brought up from  $200^\circ\text{C}$  to  $300^\circ\text{C}$ . At  $300^\circ\text{C}$ , the sample was bombarded again with  $5\text{ keV Ar}^+$  and a  $\sim 2 \times 10^{16}$  ions/cm<sup>2</sup> dose. The sample temperature was then increased to  $400^\circ\text{C}$ . The correspondent sheet resistance is shown in Curve 2. At  $400^\circ\text{C}$ , the sample was again bombarded and the temperature was increased to  $500^\circ\text{C}$  afterwards. The sheet resistance is shown in Curve 3. Up to this point, as can be seen from Fig. 2, the sheet resistance becomes lower and lower when the target temperature rises. However, when the sample was bombarded



at 500°C, the sheet resistance increased, as shown in Curve 4. When the sample temperature was dropped back to 400°C, the sheet resistance was still higher compared to the correspondent one in Curve 3. Another Ar<sup>+</sup> bombardment at 400°C brought the resistance down, to the Curve 3's level, as shown in Curve 5. When the sample temperature was decreased to 200°C, the sheet resistance was significantly lower than the correspondent one in Curve 1. The interesting part is that when this sample was bombarded again at 200°C, the sheet resistance increased again, as shown in Curve 6. Curve 6 also shows the temperature dependence of sheet resistance from 200°C to 500°C. Not shown in Fig. 2 (for clarity) is that a final bombardment at 400°C brought back the resistance to the level shown in Curve 3 and Curve 5. This series of experiments demonstrates that a target temperature of ~400°C is the optimum condition to obtain the lowest resistance for a 5 keV Ar<sup>+</sup> bombardment on CVD diamonds. The same result has been obtained for another CVD diamond sample.

Sato and Iwaki [3] have studied the target temperature dependence of sheet resistivity for high energy Ar<sup>+</sup> implanted natural diamonds in the range from -60 to 300°C. They found that the electrical resistivity decreases as the target temperature rises, and the structure of implanted layers is mainly amorphous for low temperature implantation and disordered graphite for high temperature implantation. Similar behavior is expected for the low energy Ar<sup>+</sup> bombarded CVD diamonds, so only elevated temperatures were used in our experiments. One interesting part of our finding is that the trend of decreasing sheet resistance with rising target temperature is broken when the target temperature reaches ~500°C.

When sufficient Ar ions bombard the diamond surface, most of the diamond bonds (sp<sup>3</sup>) in the surface layer are broken. How the carbon atoms rearrange themselves will determine the structure and the electrical conductivity of the surface layer. When the target temperature is too low, the carbon atoms do not have sufficient kinetic energy to arrange themselves, leading to an amorphous structure. When the carbon atoms have

sufficient kinetic energy, they can then rearrange into  $sp^2$  bonds, which are thermodynamically more stable than  $sp^3$  bonds. The graphite-like,  $sp^2$  bonded structure has been confirmed by AES [12-16] and Raman [3] spectroscopies for  $Ar^+$  irradiated diamonds. At certain temperatures, starting at about  $500^\circ C$ , a metastable phase of diamond may grow [19-21]. In other words, some of the carbon atoms at  $500^\circ C$  may rearrange into diamond bonds, resulting in an increase in resistivity. These diamond bonds can be broken again and rearranged into graphite bonds at  $\sim 400^\circ C$ , as demonstrated in our experiments. The fact that these experiments are reversible is an indication that the dramatic change in electrical conductivity upon ion irradiation is solely due to the rearrangement of carbon atoms.

Our results indicate that, even at a target temperature of  $200^\circ C$ , the carbon atoms may still do not have enough kinetic energy to arrange into the most stable position, resulting in a higher resistivity. Notice that the  $200^\circ C$   $Ar^+$  bombarded CVD diamond has a stronger temperature dependence of resistivity (cf. Fig. 2, compare Curves 1 and 6 with Curves 2, 3, 4, and 5). This is an indication that after a  $200^\circ C$   $Ar^+$  bombardment the damaged layer is not stable. This can be seen more clearly from the sheet resistance as a function of settling-time measurements as described below.

### 3.3 Sheet resistance as a function of settling time

Figure 3 shows sheet resistance as a function of settling time for a CVD diamond after a 5 keV  $Ar^+$  bombardment at two different target temperatures: (a) at  $200^\circ C$  and measured at  $200^\circ C$  and (b) at  $400^\circ C$  and measured at  $400^\circ C$ . When the sample was bombarded at  $400^\circ$ , the sheet resistance stabilized in about three minutes after the ion beam was stopped and stayed almost constant over time. However, when the sample was bombarded at  $200^\circ C$ , its sheet resistance kept dropping for over half an hour after the bombardment, as shown in Fig. 3 (a). This long settling time is an indication that some

of the carbon atoms in the damaged layer had difficulty finding stable positions after the ion bombardment at 200°C. The damaged layer is much more stable after a 400°C ion bombardment, indicating a more stable graphite-like structure.

Notice that the sheet resistance of the sample irradiated at 200°C and subsequently annealed to 500°C is higher than that of the 400°C-irradiated samples (cf. Fig. 2), which indicates that the dynamic energy provided by the Ar<sup>+</sup> ions together with the target temperature play an important role in the graphitization process of diamond under ion irradiation.

The resistivity for the graphite-like layer on the CVD diamond after a 400°C ion bombardment is approaching that of graphite, but the exact value is difficult to obtain because of the uncertainty in determining the layer thickness. The color of the sample surface became black after the ion irradiation.

### 3.4 Auger spectra

AES was performed to compare the structural change of CVD diamond before and after the ion bombardment. An electron beam energy of 3 kV with a beam current of ~1 μA was used to minimize the electron charging effect on the diamond surface. Fig. 4 shows the Auger spectra for (a) HOPG, (b) Ar<sup>+</sup> irradiated CVD diamond, and (c) CVD diamond before ion irradiation. All Auger spectra were measured at room temperature. Slight charging still occurred on the unirradiated CVD diamond, which caused a shifting in the Auger peak positions (Fig. 4c). The charging effect disappeared after a critical Ar<sup>+</sup> dose, and the Auger line shape became similar to that of graphite (Fig. 4b and 4a), in agreement with earlier reports[12-16].

The Auger spectrum in Figure 4b was obtained for a sample that had been irradiated at 400°C by 5 keV Ar<sup>+</sup> with a dose of ~3 x 10<sup>16</sup> ions/cm<sup>2</sup>. AES measurements carried out for different irradiation conditions, such as 200°C and 500°C target

temperatures, yielded spectra similar to that shown in Fig. 4b. Apparently AES line shape change is not as sensitive as the resistivity change that we observed for the irradiated CVD diamond under various conditions.

### 3.5 Raman spectra

To study the lattice structure change of the ion irradiated CVD diamond, a Raman spectrum was measured for the CVD diamond that has been subjected to the irradiation processes as described in the previous sections, and the spectrum was compared with the spectrum of another CVD diamond that had not been irradiated. Fig. 5 shows the results of these two Raman spectra.

The remarkably strong and sharp diamond peak (D peak) near  $1330\text{ cm}^{-1}$  shown in Fig. 5 is an indication of the high quality of the CVD diamond that we used. For the ion-irradiated sample (a), a broad peak around  $1600\text{ cm}^{-1}$  can be observed. It is known that the first-order Raman spectrum of single crystal graphite has a single peak, the G peak, at  $\sim 1580\text{ cm}^{-1}$ . The broad peak we see in Fig. 5 thus indicates a disordered graphite structure in the ion-irradiated sample. For the unirradiated sample (b), there is also a broad peak near  $1600\text{ cm}^{-1}$ , but the intensity is lower.

The dominant feature in Fig. 5 is the D peak, which demonstrates that the over-all diamond structure in the bulk of the sample remains intact even after the  $\text{Ar}^+$  bombardment at  $500^\circ\text{C}$ . This is in sharp contrast with an earlier report that found that substantial structural and property changes occurred for a diamond-like carbon film after vacuum annealing at temperatures higher than  $400^\circ\text{C}$  [10]. Our experiments demonstrate that high quality CVD diamonds can maintain the diamond structure in UHV at temperatures of  $500^\circ\text{C}$  or even higher. This is quite encouraging for the high-power x-ray applications of CVD diamonds.

#### 4. SUMMARY

The effect of low energy Ar<sup>+</sup> bombardment on CVD diamond has been studied in detail using *in-situ* resistivity measurements. It was found that the sheet resistance of the irradiated CVD diamond decreases dramatically after a critical dose of  $\sim 9 \times 10^{15}$  ions/cm<sup>2</sup> for 1 keV Ar ions. The saturated sheet resistance decreases as the ion energy increases. The optimum target temperature for obtaining a stable, low-resistance graphite-like layer on CVD diamond by low energy Ar<sup>+</sup> bombardment is around 400°C. From 200°C to 400°C, the sheet resistance decreases as the target temperature rises. However, the sheet resistance increases at a target temperature of 500°C. The fact that the target temperature dependence of sheet resistance is reversible indicates that the graphitization of diamond surface is solely due to the rearrangement of carbon atoms during ion irradiation.

Auger and Raman spectroscopy measurements confirm the presence of disordered graphite structure on the diamond surface after Ar<sup>+</sup> bombardment at elevated temperatures. The over-all diamond structure in the bulk of the CVD diamond, however, remains intact even after repeated ion bombardments at 500°C. This stability of high quality CVD diamond at high temperatures in UHV is very important for high power x-ray applications.

Surface graphitization of CVD diamond by energetic ion beams can create a very thin, intrinsic, and conducting layer on diamond, which can stand the most powerful x-rays and introduce very little interference to the x-ray spectrum. The electrical resistance of the modified surface layer can be lowered by using high energy ions. A graphite mask can be used to create patterns of the conducting electrodes to avoid contamination of other elements caused by sputtering. Thus it is feasible to make single-element CVD diamond transmitting x-ray beam position monitors.

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#### FIGURE CAPTIONS

Fig. 1 Sheet resistance of a CVD diamond at 200°C as a function of Ar<sup>+</sup> dose at 1, 2, 4, and 5 keV energies.

Fig. 2 Sheet resistance of a 5 keV Ar<sup>+</sup> irradiated CVD diamond as a function of temperature for the following sequences: (1) the sample was bombarded at 200°C and then the sample temperature was increased to 300°C, (2) bombarded again at 300°C and then increased to 400°C, (3) bombarded at 400°C and then increased to 500°C, (4) bombarded at 500°C and then decreased to 400°C, (5) bombarded at 400°C and then decreased to 200°C, (6) bombarded at 200°C and then increased to 500°C. The ion dose in each sequence from (2) to (6) was  $\sim 2 \times 10^{16}$  ions/cm<sup>2</sup>. The bombardment history for sequence (1) is as described in the text. The lines through data points serve as a guide to the eye.

Fig. 3 Sheet resistance for a CVD diamond (a) at 200°C as a function of settling time after a 5 keV Ar<sup>+</sup> bombardment at 200°C, and (b) at 400°C as a function of settling time after a 5 keV Ar<sup>+</sup> bombardment at 400°C.

Fig. 4 Auger spectra of (a) HOPG, (b) 5 keV Ar<sup>+</sup> irradiated CVD diamond, and (c) unirradiated CVD diamond. The shift in peak positions in (c) is due to charging.

Fig. 5 Raman spectra for (a) Ar<sup>+</sup> irradiated and (b) unirradiated CVD diamonds.











