

# Exceptionally high ion-induced electron emission yield from hydrogenated diamond and its decay

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Extremely high ion-induced electron emission (IIEE) yields- $\gamma$  (exceeding 400) are measured for boron-doped hydrogenated diamond, bombarded with sub-MeV Ar ions. These high values are found to rapidly diminish with an increasing number of ions impinging on the diamond surface, eventually reaching the low values of IIEE (of the order of 5) found for graphite and most materials. This reduction is shown to be caused by two processes: One, which affects a very large area around each ion-impingement point (and thus causes the rapid reduction in  $\gamma$ ), may be either due to electron transport limitations caused by point defects introduced by the ion during their slowing down in the diamond or to surface hydrogen loss induced by the outgoing electrons; the second, more gradual loss process, is attributed to local graphitization around each ion track. A material with such a high electron-emission yield as the presently studied B-doped hydrogenated diamond, may find an application in the detection and counting of single ions or molecules, as needed mainly for biological applications. © 2002 American Institute of Physics. [DOI: 10.1063/1.1521787]

## I. INTRODUCTION

Diamond is well known for its outstanding electron emission properties which have been attributed to the negative electron affinity (NEA) of a hydrogen terminated diamond surface. In previous publications,<sup>1,2</sup> we have reported on large ion-induced electron emission (IIEE) yields  $\gamma$ , defined as the number of electrons emitted per incident ion, caused by the impingement of sub-MeV ions on hydrogenated chemical-vapor deposition CVD diamond. These  $\gamma$  values (close to 200) were at least ten times larger than typical values reported for graphite or metal surfaces.<sup>3</sup> Interestingly these extremely large values were found to degrade very rapidly with increasing ion dose. The largest measured values of  $\gamma$  were found for the lowest dose measured ( $\sim 10^{12} \text{ cm}^{-2}$ ). Such huge electron emission yields measured for very low-dose ion impingement on B-doped hydrogenated diamond may find an application in the detection of single or molecular ions. However, the deterioration of the high yields for relatively small numbers of ion impacts may limit this application, unless ways are found for avoiding it or for recovering the diamond properties and restoring its unique high- $\gamma$  values. Nevertheless, even after the initial loss of  $\gamma$  has taken place, the remaining IIEE yields measured for slightly damaged diamond are still substantially higher than those known for other materials. Hence, applications free from the rapid deterioration, can rely on preirradiated diamond which exhibits more stable lower- $\gamma$  values, which are still substantially higher than other available surfaces.

In this article, we address the question, "How high can  $\gamma$  be at the very lowest doses experimentally accessible?" We examine the nature of the rapid decay of  $\gamma$  and offer some possibilities for its cause.

Results of IIEE measurements from diamond surfaces subjected to the impingement of ions commencing at doses as low as  $3 \times 10^9/\text{cm}^2$  are reported. Our results show that  $\gamma$  from hydrogenated CVD diamond may be as high as 450, i.e. about 100 times higher than  $\gamma$  values reported for most materials (see, for example, Refs. 3 and 4]. The ion-induced electron emission yield are found to decay by exhibiting two distinct regimes, one of very rapid decay at low doses, followed by a more gradual decay. These are suggested to be associated with two completely different processes, both involving ion-beam induced materials modifications.

## II. EXPERIMENT

Boron-doped ( $10^{20} \text{ cm}^{-3}$ ) freshly hydrogenated (in a micro-wave H plasma for 20 min at 700 °C) CVD diamond layers (5- $\mu\text{m}$  thick) grown on  $n^+$  Si were used. Details of the experimental procedure are given in Refs. 1 and 2. Essentially, the measurement is comprised of periodically alternating the bias on a repeller electrode placed in front of the target from +300 to -300 V, while monitoring the current on the target. When negatively biased, the impinging beam current is measured, while when positively biased, both impinging (positive) ions and the positive charge left in the target by the escaping electrons are measured. The ratio of these two measurements thus yields ( $\gamma - 1$ ).

As the present measurements focused on measuring IIEE for doses lower than measurable by our electrometer, the beam hitting the target had to be reduced, and known, even without being directly measurable. To achieve this goal, the beam was x-y raster scanned over a  $2.5 \times 2.5 \text{ cm}^2$  collimator in front of the chamber with a 3-mm diameter opening and its charge was integrated. Hence, only a well-known fraction of the beam hit the target. This setup was calibrated by mea-

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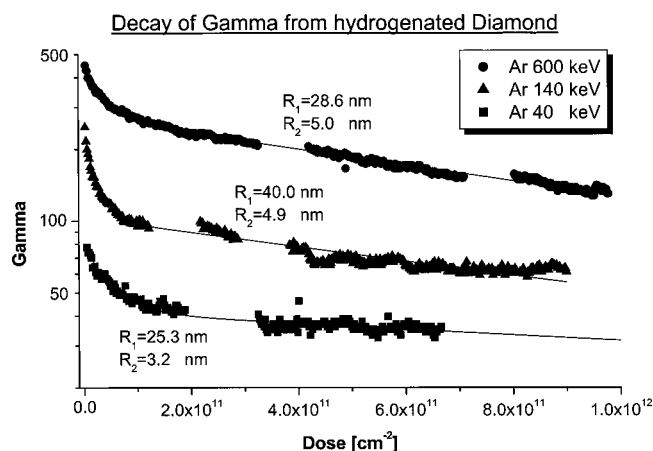


FIG. 1. Ion-induced electron emission yields,  $\gamma$  for 40, 140, and 600 keV Ar ions impinging on a hydrogenated B-doped CVD diamond for low doses. The lines through the data points are fits to Eq. (1).

asuring  $\gamma$  for the well-known nondeteriorating case of graphite.

The experiments were carried out with 40, 140, and 600 keV Ar ions at a vacuum of  $2\text{--}5 \times 10^{-8}$  mbar with the target heated to 200 °C and the chamber separated from the implanter by a liquid nitrogen trapped passage.

### III. RESULTS

Figure 1 shows the  $\gamma$  values measured for very low doses ( $10^{10} < D < 10^{12}$  Ar/cm<sup>2</sup>) for 40, 140, and 600 keV Ar ions. Two distinct regimes in the  $\gamma(D)$  curves are apparent: A rapidly decaying region for very low doses (up to  $10^{11}$  cm<sup>−2</sup>) followed by a slower decay at higher doses.

The extremely large initial values of  $\gamma$  and their rapid decay with the ion dose obtained for only a very few Ar ions impinging on a H-terminated boron-doped diamond surface, also found for other ions impinging on similar diamond targets (to be reported elsewhere) are surprising.

These must be caused by an ion-beam-induced modification of the diamond resulting in the loss of one of the important factors for electron emission, i.e., either transport of the liberated electrons to the surface, or an increase in their escape barrier, i.e., loss of negative electron affinity, thus preventing electron emission into the vacuum.

We are inclined to believe that the first of these options is the dominant one contributing to the rapid reduction of  $\gamma$  measured here. This is based on previous results showing that when boron-doped diamond is subjected to light ion (H and He) irradiation,<sup>5</sup> it causes a dramatic reduction in electrical conductivity of many orders of magnitude, even when relatively low levels of defects are inflicted onto the conducting layer. This loss of conductivity by ions hitting the target may be the reason for the observed reduction in  $\gamma$  at low-ion doses.

An alternate possibility to be considered is related to the presence of hydrogen on the surface which, when lost, will result in an increase of the surface electron affinity. In order to investigate this possibility, we have measured the  $\gamma(D)$  dependence at low doses for two identical samples, one hydrogenated and one oxygenated (by acid treatment after

high-temperature hydrogen effusion). Although the results of this experiment are not conclusive, it seems as if the H-terminated sample did show a more rapid decay in  $\gamma$  than the oxygenated one.

The  $\gamma$  values measured for the oxygen-terminated sample were always lower than those measured for the H-terminated samples. Furthermore, part of a hydrogenated (deuterated) sample was irradiated with  $3 \times 10^{11}$  Ar/cm<sup>−2</sup>, a dose at which the rapid decay of  $\gamma$  is just about over, and the electron affinity of both irradiated and non irradiated parts of the sample were examined by ultraviolet photoemission spectroscopy (UPS). The virgin H-treated sample did show the distinct features, typical for a negative electron affinity (NEA) surface, whereas the ion irradiated one did not. Attempts to observe the presence of hydrogen (deuterium) on the surface and its loss caused by ion-bombardment by secondary-ion-mass spectroscopy (SIMS) did not yield any meaningful results, possibly because of the limited sensitivity of our SIMS to deuterium.

### IV. DISCUSSION

The results of the above measurements show that the ion-induced electron emission from B-doped hydrogenated diamond can be extremely high, higher than any previously reported value. However, these high- $\gamma$  values are found to diminish very rapidly with an increasing ion dose. These findings are intriguing. The extremely large ion-induced electron emission yields found here are unique to B-doped hydrogenated diamond. They must be related to the relatively undisturbed motion of electrons in the bulk of the diamond layer and to the ease of the escape of these electrons into the vacuum, i.e., to the negative electron affinity of the hydrogenated diamond surface. The rapid decay of  $\gamma$  has to be related to an ion-impact-induced modification of either the bulk or the surface of the material, from a highly emitting state to a less emitting one.

Below, we offer a model for such an ion-impact induced modification of the hydrogenated diamond layer: We assume that once a point has been hit by an ion, the emission properties in a certain area  $\alpha$  around the impingement point transforms from the highly to the low emitting state. This leads to an exponentially decaying dependence of the “unmodified” fraction ( $f$ ) of the area (i.e., the remaining area which still emits well) on the number ( $n$ ) of randomly selected points of “impingement.” Hence, a plot of  $\log f$  versus  $n$  gives a straight line with a slope which is proportional to the affected area  $\alpha$  around each point which was hit. Large values of  $\alpha$  are reflected in a large slope. The data for  $\gamma(D)$  plotted as  $\log \gamma$  versus  $D$ , (Fig. 1) exhibit two slopes, indicating that two processes are involved in the loss of  $\gamma$  with increasing number of ion hits. The data of Fig. 1 were thus fitted to the function

$$\gamma(D) = \gamma_0 + A_1 \exp(-D\alpha_1) + A_2 \exp(-D\alpha_2) \quad (1)$$

The solid lines in the figure represent the fit using  $A_1$ ,  $A_2$ ,  $\alpha_1$ , and  $\alpha_2$  as free parameters, imposing a value of  $\gamma_0 = 7$  (the  $\gamma$  value of graphite) for  $D \rightarrow \infty$ . The excellent fit is obvious. The values found for the areas  $\alpha_1$  and  $\alpha_2$  for the 40,

140, and 600 keV Ar data, respectively, which represent the rapid and the slower decaying parts of the  $\gamma(D)$  curves, are:  $2.4 \times 10^{-11}$ ,  $6.8 \times 10^{-11}$ , and  $3.4 \times 10^{-11}$  cm<sup>2</sup>/ion for the rapid parts, and  $1.0 \times 10^{-12}$ ,  $4.3 \times 10^{-12}$ , and  $2.1 \times 10^{-12}$  cm<sup>2</sup>/ion for the slow parts of the higher dose data. The average radii which correspond to these areas are about 30 nm for the fast decaying part and 5 nm for the slower one.

The similarity of the values found for the different energies and the excellent fits obtained give confidence in the present analysis and its underlying model that assumes two different mechanism to be responsible for the loss of electron emission properties of the hydrogen terminated B-doped diamond. The value of  $\alpha_2$  for the slowly decaying part of the curves is in accord with the size of graphitized region around each ion-impingement point, as deduced from electrical conduction measurements.<sup>6</sup> In that work, the loss of resistivity of a high-resistivity diamond as a function of ion dose, presumably due to local graphite around each ion track, was measured. The radii deduced from the data of Ref. 6 are about 2 nm for heavy ion (Xe) impingement on diamond, close to the values deduced here for the slow decaying regime in  $\gamma$ . Hence, we can associate the slow reduction in the  $\gamma(D)$  curve with the gradual ion-beam-induced graphitization of the diamond. Indeed, for very high-bombardment doses,  $\gamma$  approaches the very low, well known, value of graphite<sup>3</sup>  $\gamma_{\text{(graph)}} = 7$ .

The extremely large values obtained for  $\alpha_1$ , extending to distances from the point of impingement ten times larger than those directly affected by the damage due to the ion-impact ( $\alpha_2$ ), are difficult to account for by just considering the spacial extend of the area affected by the impingement of a single ion, which are of the order of  $\alpha_2$  [as is also well predicted by computer simulations (*TRIM*)<sup>7</sup>]. This part of the  $\gamma(D)$  curve must be associated with either a loss of the negative electron affinity related to the removal of hydrogen from the diamond surface or to the trapping of the outgoing electrons by defects accompanying the slowing down of the moving ion.

A possible way by which H can be lost from a very large area around the impact point of an ion may be an electron-impact hydrogen loss due to electrons liberated by the ion during its slowing down inside the diamond. The number of such electrons which manage to escape from a fresh NEA diamond surface can exceed 500. Substantially more electrons are most likely liberated inside the diamond, but fail to escape into the vacuum. If some of these electrons, which are likely to form a cone upon their motion towards the surface, are trapped by native defects or cause the dissociation of hydrogen atoms from the surface, the large affected area found experimentally can be accounted for. The loss of H from the surface due to the "thermal spike" which accompanies the penetration of an energetic ion through the surface may also be considered as a possible mechanism for the reduction of NEA.

It is unlikely that all hydrogen atoms which terminate the area  $\alpha_1$  are lost already at low doses, due to the outgoing

electrons initiated by the ion impact. However, even partial loss of H may result in a large reduction in the NEA as was also reported in Ref. 8 in photoemission measurements on hydrogenated diamond surfaces, which was greatly reduced by the adsorption of only a few percent of water molecules. The loss of NEA over quite a large area due to the desorption of Cs from a well emitting cesiated diamond surface by low-energy ion impact was recently observed.<sup>9</sup> This reduction was suggested in Ref. 9 to be due to electron-induced Cs desorption, presumably caused by the outgoing electrons, a process very similar to that proposed here.

The possible trapping of outgoing electrons by damage-related native defects is, at present, the more likely cause for the rapid reduction of  $\gamma(D)$ . Preliminary results of experiments meant to clarify the mechanism for the rapid reduction of  $\gamma$  in which several ion species were used, indicate that the large radii related to the rapid drop in  $\gamma$  seem to scale with the energy lost by the moving ion by nuclear (damaging) collisions in the diamond layer from which electrons can escape (of the order of 50 nm); hence, lending support to the latter explanation.

A material with very high-electron emission yield, as the diamond layers studied here, may find a practical application in single-ion or single-molecule counting. Such are in need mainly in various biological studies. It will be interesting to investigate whether the phenomena described here hold also for lower-energy ions, and for other wide band-gap materials. If other, high-electron-emitting noncarbon materials will be found, this may open up further applications utilizing materials which may not be so amenable to damage-related reduction in ion-induced electron emission as is B-doped hydrogenated diamond.

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