Absolute quantum photoyield of ion damaged diamond surfaces

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We report on the absolute quantum photoyield (QPY) measurements from defective diamond surfaces in the 140–200 nm spectral range. The effect of defects on the photoemission properties of polycrystalline diamond films is studied by intentionally introducing damage using room temperature 30 keV Xe+ ion bombardment at doses ranging from $2 \times 10^{13}$ to $2 \times 10^{15}$ ions/cm$^2$. Ion bombardment results in a drastic degradation of the QPY, to less than 1% at 140 nm, even at the lowest implantation dose, compared to $\sim 11.5\%$ measured for the unimplanted diamond film. The decrease in QPY is associated with a change of the electron affinity from negative to positive as determined by secondary electron emission measurements. Microwave hydrogen plasma treatment of the damaged diamond films results in complete regeneration of the photoemission properties for diamond films implanted to Xe+ doses up to $2 \times 10^{14}$ ions/cm$^2$; however, only partial recovery is obtained for films irradiated with higher ion dose. © 2000 American Institute of Physics.

INTRODUCTION

It is very difficult to prepare synthetic diamond films free of defects and impurities in their crystal structure. The defects in microcrystalline diamond films mainly originate from grain boundaries, where the electronic properties of diamond may differ from those of the bulk crystal. Another source of defects in diamond, as well as in other semiconducting materials, is doping. The introduction of foreign atoms, such as boron, nitrogen, or phosphorus for preparation of either p- or n-type semiconducting diamond, always produces damage in the crystalline structure. The introduction of defects in diamond may affect its photoemission properties by changing some of the main parameters which determine the absolute quantum photoyield (QPY): the optical absorption coefficient, the electron diffusion length, and the surface escape probability. Low dose ion implantation produces point defects in the diamond crystal structure. The chemical nature of point defects, especially of those located in the near-surface region, is yet unclear. From conductivity measurements they have some effect on the electrical properties of diamond, however, they cannot be detected by Auger, Raman, and x-ray photoelectron spectroscopies due to their low concentration and lack of long range order. To the best of our knowledge, the influence of point defects on the QPY of diamond has not yet been investigated.

One of the common methods of introducing defects of predetermined concentration and depth is by bombardment with noble gas ions. It was found that there are two critical doses which depend on the nature of the ion but are almost independent of ion energy. These critical doses are $D_1$, which results in transformation of diamond to highly insulating $sp^3$-bonded amorphous carbon, and $D_2$, where a drop of resistivity occurs due to subsequent formation of conductive $sp^2$-bonded amorphous carbon and graphite. The spatial distribution of implanted ions in diamond (as well as other materials) may be calculated by Monte-Carlo molecular dynamics simulations (TRIM computer program), and can be verified by secondary ion mass spectrometry depth profiling. Low energy (<50 keV) ions (e.g., Ar+, Xe+) mainly affect the near-surface region of $\sim 100–150$ Å and may influence the photoemission properties through modification of the diamond surface structure and formation of electronic states in the band gap.

It was found in previous works that freshly hydrogenated diamond films have negative electron affinity (NEA) and exhibit QPY of $\sim 12\%$ at 140 nm (8.9 eV). Here we extend our studies to the effect of ion induced defects on the QPY. In the present work we carried out QPY measurements in the 140–210 nm (8.9–6.2 eV) ultraviolet (UV) range for hydrogenated diamond films implanted with 30 keV Xe+ ions and compared their photoemission properties with those of the unimplanted hydrogenated diamond film prepared under similar conditions. The results of our QPY measurements are complemented using secondary electron emission (SEE) spectroscopy, by which the existence of NEA may be identified. The samples subjected to ion irradiation were analyzed by Auger and Raman spectroscopies. Finally, the

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ion implanted diamond films were subject to microwave (MW) hydrogen plasma treatment to examine the possibility of recovering the damage induced by ion bombardment.

**EXPERIMENT**

The polycrystalline diamond films were deposited on silicon substrates by a standard hot filament chemical vapor deposition method using conditions described elsewhere. The thickness of the as-grown films was 3–5 μm. Following deposition the diamond film surfaces were hydrogenated by exposure to a MW hydrogen plasma at a substrate temperature of 800 °C. The ion irradiation was performed at room temperature using 30 keV Xe ions at three doses: $2 \times 10^{13}$ ions/cm$^2$ (assigned as “low dose”), $2 \times 10^{14}$ ions/cm$^2$ (“medium dose”), and $2 \times 10^{15}$ ions/cm$^2$ (“high dose”). The distribution of the defects in the near surface region, as calculated by TRIM-95, extends from the surface to a depth of ~130 Å. These doses result in the formation of isolated point defects in the crystalline diamond matrix, a large degree of disordered $sp^3$-bonded structure and in fully amorphous, mainly $sp^2$-bonded, carbon material, respectively.

Absolute QPY measurements of diamond films were performed in a vacuum UV monochromator system, similar to that described previously, using 140–200 nm radiation from a 30 W deuterium lamp. The emitted electrons were collected by an 81% transparent stainless steel anode mesh, mounted 2 mm above the sample and held at 200 V. The photocurrent was measured by a Keithley 610B electrometer; the dark current (~0.03–0.05 pA) limited the sensitivity of the measurements to QPY values of about $5 \times 10^{-5}$. The absolute QPY values were obtained by normalization to a National Institute of Standards and Technology-calibrated vacuum photodiode.

Characterization of the implanted and reference unimplanted diamond films was performed by micro-Raman and Auger electron spectroscopy (AES). The micro-Raman measurements were performed using a Dilor XY system with Ar 514.5 nm, 10 mW unpolarized laser light focused to a spot of ~2 μm in diameter. The Auger spectra were measured in the first derivative mode, using a cylindrical mirror analyzer in a Perkin–Elmer, PHI model 590A scanning Auger microscope. The system was operated with a 3 keV, 1 V modulation and 1 μA primary electron beam under an incident angle of 60°.

SEE measurements were performed using synchrotron radiation as a primary excitation source. The measurements were performed in the SA72 beam line of SUPERACO at Laboratoire pour l’Utilisation du Rayonnement Electromagnétique (LURE). The energy resolution of the monochromator was better than 0.15 eV near the carbon K edge (~290 eV), and the photon beam was focused to a spot of ~0.2×5 mm in size. Prior to introduction into the ultrahigh vacuum chamber kept under a base pressure of less than 5 × 10$^{-11}$ Torr, the samples were baked out to ~150 °C for 48 h. The chamber was equipped with a hemispherical electrostatic electron energy analyzer (CLAM 2), applied for determination of the kinetic energy of secondary electrons escaping the substrate surface. An incident photon beam of 270 eV was used, and the energy distribution of the emitted secondary electrons was measured. By appropriate grounding of the substrate holder, the kinetic energy of the emitted electrons was referred to the Fermi level of the samples, which for unintentionally doped diamond films is near the valence band maximum. Therefore, to a good approximation, the kinetic energy scale may be related to the maximum of the valence band. The intensities of the SEE spectra were normalized by recording simultaneously the intensity of the photon beam with a gold mesh.

**RESULTS AND DISCUSSION**

Figure 1 shows the results of the QPY measurements as a function of photon energy in the 140–200 nm UV range, for the unimplanted hydrogenated diamond film and those implanted to three different ion doses. It can be clearly observed that ion bombardment results in a strong decrease of the QPY over the entire range examined. The film implanted to the lowest dose of $2 \times 10^{13}$ ions/cm$^2$ exhibits QPY of 0.9% at 140 nm, compared to 11.5% for the unimplanted diamond film. The samples implanted to higher doses show further degradation of photoemission properties, resulting in the decrease of the QPY to less than 0.5% at 140 nm after irradiation at $2 \times 10^{15}$ ions/cm$^2$.

To further explore the effect of ion bombardment on the electronic properties of diamond we first analyzed the implanted samples by micro-Raman and Auger spectroscopies. Micro-Raman measurements of the implanted samples and...
of the reference unimplanted diamond film (data not shown) were characteristic of that of a good quality diamond, with a sharp peak at 1332 cm\(^{-1}\). No graphitic or amorphous structures were detected on any of the analyzed samples. Such a result is expected, bearing in mind that the depth sensitivity of the Raman spectrum in diamond (~3000 Å) is more than an order of magnitude higher than the thickness of the region modified by the irradiation process (~130 Å).

High resolution Auger C(KLL) measurements of the hydrogenated unimplanted diamond film and the film implanted at a low dose show the main features characteristic of diamond. The film implanted to a high dose displays a C(KLL) line shape characteristic to amorphous carbon, whereas that measured for the medium dose implanted sample is intermediate between the two. A characteristic shoulder appears at the high energy side of the C(KLL) line in the spectrum of the samples irradiated to medium and high ion doses. These changes in the C(KLL) Auger line shape show that the modified region extends to the upper surface, consistent with our TRIM calculations. The Auger measurements of the sample implanted to a medium dose were complicated by a strong charging. The effect of charging was less significant when measuring the high dose implanted sample, and it was not detected at all for the low dose and unimplanted samples. This effect was previously observed and was attributed to the formation of a highly insulative disordered \(sp^3\)-bonded carbon phase by the ion bombardment process.\(^5,14\)

The chemical composition of the near-surface region was determined by AES, measured in a broad kinetic energy range (180–600 eV). Oxygen was the only detected noncarbon component (with the exception of hydrogen, which cannot be measured by Auger). Its concentration was estimated to be in the range of 0.4–2 at. %, and it was somewhat higher for the heavily implanted sample than for the film exposed to the low dose ion bombardment. Oxygen concentration in the unimplanted sample was extremely low (less than 0.1 at. %).

For elucidation of the effect of ion bombardment on QPY, we conducted SEE measurements of the implanted films, of which the results are shown in Fig. 2. The SEE spectrum of the unimplanted diamond film shows a sharp low energy peak at 5.5 eV kinetic energy. Considering the reference level used in our electron spectroscopic measurements and the band gap of diamond, this peak corresponds to the emission of electrons thermalized to the conduction band minimum. Such emission may occur only in the case when the vacuum level is located below the conduction band minimum, indicating NEA.\(^11,15\) The SEE spectra of implanted films are characterized by: (1) a positive shift of the emission threshold to 6.6–6.7 eV, thus placing the position of the vacuum level more than 1 eV above the conduction band minimum; (2) a decrease of the emission intensity by a factor of 2.5 for the sample implanted to the low ion dose, and by a factor of 5 for the diamond samples irradiated at higher ion flux. The positive shift of the emission threshold indicates the conversion of the electron affinity from negative to positive. The decrease in secondary electron emission intensity was found previously to be associated with ion beam damage of diamond surfaces.\(^15,16\)

It is clear that the shift of the electron affinity from negative to positive is responsible for the degradation of the QPY properties of diamond. We may account the following three reasons which can explain this effect: (1) ion bombardment may result in the desorption of hydrogen from the diamond surface thus leading to elimination of the surface dipole responsible for NEA; (2) adsorption of oxygen may occur on the ion bombarded film either due to hydrogen desorption, resulting from the presence of oxygen traces in the ion bombardment chamber, or due to increased activity of the defects that cause the desorption yield; (3) formation of the disordered carbon layer in the near-surface region. Our AES measurements showed hydrogen on the sample surface in concentrations of 0.6–2 at. %. In the previous studies we found that diamond films with such concentration of oxygen have QPY values in the range of 5%–8% at 140 nm.\(^10\) Therefore, we can rule out the possibility that adsorption of oxygen has a dominant effect on the photoemission properties of the ion bombarded diamond films.

Considering the ion doses and energies used in our experiments, we do not expect ion implantation to result in any significant reduction in the amount of adsorbed hydrogen. This assumption is supported by \(H^+\) photodesorption studies\(^17\) which showed that the \(H^+\) desorption yield is similar for the unimplanted and different implanted diamond films. Therefore, in our opinion, the reason for the decrease in the secondary yield and reversal in the electron affinity.
CVD DIAMOND FILMS IMPLANTED BY Xe$^+$
(30 keV, ROOM TEMPERATURE)

![Graph showing QPY values for diamond films](image)

FIG. 3. Absolute QPY of the implanted (lines 1–3), and rehydrogenated implanted (lines 1H–3H) diamond films.

induced by implantation is driven by defects created by the ion irradiation process.

In our previous work we have reported that low dose ion implantation results in the formation of an electronic state 0.2 eV above the valence band maximum.\(^{14}\) This state was attributed to clusters of unsaturated, i.e., having dangling bonds, disordered \(sp^3\)-bonded carbon. The formation of such structures may result in a substantial decrease of the electron diffusion length.\(^{18}\) On the other hand, \(p\)-type electronic states produced by ion bombardment can result in the downward band bending, which increases the energy barrier between the surface conduction band minimum and the vacuum level, producing positive electron affinity. In addition, conversion of diamond to amorphous carbon results in changes in the optical absorption coefficient. It was shown that the functional form of the QPY as a function of photon energy is very similar to the bulk optical absorption coefficient.\(^{10,19}\) Indeed, it may be observed from Fig. 1, that the line shape of the QPY spectra for ion damaged diamond films differs from that measured for the unimplanted film, especially for the samples implanted to medium and high ion doses. All these factors result in degradation of the photoemission properties of diamond and a strong decrease in its QPY.

To examine the possibility of the removal of the ion induced damage, we exposed ion bombarded diamond films to MW hydrogen plasma for 1 h and measured their QPY after that treatment. We utilized such a procedure earlier to regenerate the photoemission properties of diamond films, where a decrease in QPY occurred as a result of oxygen adsorption and aging.\(^{10}\) It is also well known that atomic hydrogen produced in MW plasma results in rapid etching of graphite and amorphous phases.

The results of the QPY measurements of the ion implanted films exposed to the MW hydrogen plasma are shown in Fig. 3. It can be observed that the QPY values at 140 nm of the films implanted to low and medium ion doses increase to \(\sim 10\% – 11\%\) and are very close to those of the unimplanted sample (see Fig. 1, line 1). On the other hand, only partial enhancement of the photoemission properties is obtained for the diamond film implanted to the high Xe$^+$ dose after hydrogenation. For this film the QPY of \(\sim 3\%\) was measured at 140 nm. AES (\(KLL\)) measurements of all ion bombarded samples, after MW plasma treatment, showed line shapes corresponding to pure undamaged diamond. The Auger wide energy scan detected only traces of oxygen (0–0.2 at.%) on the sample surface. Such low oxygen concentration cannot be responsible for the low QPY of the high dose implanted diamond film after hydrogenation.\(^{10}\) It follows that high dose ion bombardment produces a carbon phase which is not completely etched by atomic hydrogen. Further experiments are being performed to elucidate this effect.

In summary, ion damaged diamond films have positive electron affinity and exhibit poor photoemission properties, even when the ion bombardment induces point defects only and does not result in a substantial deterioration of the diamond crystal structure. The photoemission properties of diamond films implanted to low and medium Xe$^+$ ion doses can be recovered by exposure to MW hydrogen plasma. The QPY of heavily damaged diamond films cannot be fully regenerated by such treatment.

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