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Structural transformation of diamond induced by 1-keV Ar-ion irradiation as studied by Auger and secondary-electron spectroscopies and total-secondary-electron-yield measurements

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Secondary-electron emission and Auger spectroscopies and total-secondary-electron-yield measurements have been employed to monitor the transformation of type-IIa diamond (110) induced by 1-keV Ar irradiation for a dose range between 7×10^{12} and 6.2×10^{17} ions/cm^2. The irradiations and the analysis were carried out *in situ* in a UHV chamber. The C(KLL) Auger line shape provides evidence of the increasing graphitelike nature of the surface as a function of the ion dose. The total secondary-electron yield was found to decrease from the unirradiated value of 0.9 to a value of 0.58 for doses exceeding 1×10^{16} ions/cm^2. The most unusual result was the observation of an abrupt and extreme charging of the surface [as measured by a shift in the C(KLL) line position] which occurred at a critical dose of between 1.7×10^{15} and 2.5×10^{15} ions/cm^2. Above this critical dose, the charging was observed to decrease gradually over about a decade of ion dose. This unusual charging can be understood in terms of the production of an amorphous, but still insulating layer at the critical dose, which upon further irradiation gradually transforms into a graphitelike structure. The results are consistent with a model for the ion-beam-induced transformation of diamond involving three distinct dose regimes. Below a certain critical dose, the diamond remains essentially single crystalline, albeit with increasing levels of disorder. At the critical dose, the damaged structure suddenly transforms into an amorphous, but still highly insulating material whose properties appear to be similar to those of amorphous carbon with local tetrahedral (i.e., sp^3) bonding but without any long-range order. Further irradiation results in the transformation of sp^3 to sp^2 bonds with a concomitant rise in the conductivity. At very high doses, there is spectroscopic evidence for the formation of sp^2-bonded microcrystallites.

I. INTRODUCTION

The two most common crystalline allotropes of carbon are graphite and diamond. Graphite consists of carbon atoms bonded into hexagonal sheets (sp^2-type bonding) with only weak forces between the sheets, while, by contrast, diamond displays fourfold sp^3-type bonding. The different bonding configurations give rise to very different physical and chemical properties, with graphite being soft, opaque, and electrically conducting, while diamond is extremely hard, transparent over a wide range of wavelengths, and electrically insulating.

At room temperature diamond is metastable with respect to graphite. One of the most interesting methods of inducing a transformation from diamond into graphite is ion irradiation which allows the observation of this transformation as a gradual function of ion dose. Furthermore, since ion implantation is the method of choice for the introduction of dopants into diamond, it is important to understand the nature of ion-beam-induced damage in this technologically important material.

Since graphite is electrically conducting and diamond is insulating, it is not surprising that many authors have used the ion dose dependence of the conductivity to monitor the ion-induced transformation of diamond. The results of many studies[1-3] show an amazing similarity of the ion-induced changes in the conductivity for a wide range of implanted ion species (C, Ar, Xe, Sb). For example, Fig. 1 shows the data for irradiation with 100-keV C ions which are typical of those obtained also for the other ions. Three dose regimes are identifiable. For $D<D_1$ the irradiation causes an increase in the conductivity, presumably due to the production of isolated defects. In the region $D_1<D<D_2$ the conductivity decreases as a function of increasing ion dose for reasons not yet understood. For $D>D_2$ a very rapid increase in the conductivity is observed, which is associated with the production of continuous graphitelike pathways.

The values of D_1 and D_2 are found to be dependent on ion species and ion energy. However, if these values are transformed to the nuclear energy imparted by the projectile per carbon target atom, remarkable agreement is obtained in the density of nuclear energy deposited in the transformed layer at these transition doses. Table I

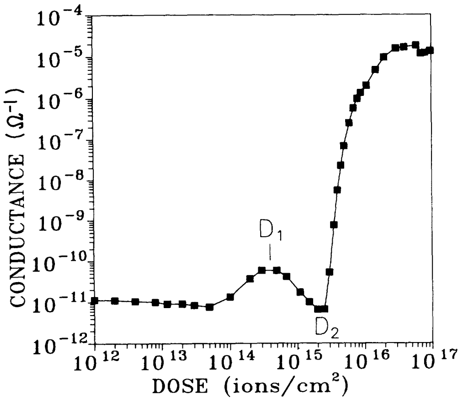

FIG. 1. Conductance of type-IIa diamond as a function of ion dose for 100-keV C ions. The irradiation was performed at room temperature. Note the two critical doses D_1 ($=4.2\times10^{14}$ C$^+$/cm^2) and D_2 ($=2.5\times10^{15}$ C$^+$/cm^2).

shows that D_1 is equivalent to about 1 eV/target atom, while D_2 is equivalent to about 5 eV/target atom for all cases studied so far. The level of agreement is remarkable considering the range of ion masses and energies used in the different experiments and strongly suggests that the transformation is damage driven. Nevertheless, many puzzles remain in understanding the nature of the ion-beam-induced diamond-graphite transition, particularly in the region $D < D_2$.

Recently it has been shown that secondary-electron emission (SEE) spectroscopy is very sensitive to crystalline damage in diamond and to the bonding state of carbons in general.[4,5] The secondary-electron emission spectrum can in fact be used as a fingerprint for the different carbon allotropes.[5] In the present paper SEE and Auger spectroscopies and total secondary-electron yield are used to study in detail the ion-induced transformation of diamond to graphite. It is shown that the transformation proceeds from damaged, but essentially single crystalline diamond to a form of polycrystalline graphite via an amorphous sp^3-bonded structure. We suggest that a critical dose exists at which the damaged diamond suddenly transforms into this amorphous structure.

In the present work the diamond samples were irradiated with 1-keV Ar ions *in situ* under UHV conditions in the same chamber in which the Auger and SEE measurements were carried out. This energy was chosen because the ion-beam-affected depth [about 20 Å as estimated from TRIM (Ref. 6)] is about the same as the skin depth of the SEE and Auger probing techniques.

It will be shown that despite the very low-energy ions (1 keV) used in this study to induce the structural transition, the picture to emerge from the electron spectroscopies of the present study using an energy of 1 keV is consistent with that which emerges from previous studies using ion energies of many tens of keV. However, the present work adds important new information about the nature of the amorphous sp^3 structure which precedes the transformation of the diamond into graphitelike carbon.

II. EXPERIMENTAL

Samples

For calibration purposes the carbon allotropes used in this study were type-IIa diamond, highly oriented pyrolytic graphite (HOPG), amorphous sp^2- and sp^3-bonded carbons, and glassy carbon. SEE, and Auger spectroscopies and total-secondary-electron-yield measurements were taken on each of these allotropes and compared to the results of measurements on Ar-irradiated diamond. The samples used for the irradiations were also type-IIa diamond, supplied by Drukkers International (Amsterdam) as slabs $3\times3\times0.25$ mm^3. The orientation of the slabs was within 10° of the [110] direction. The slabs were polished optically flat and contained no visible inclusions.

The distinction between the structure of the different noncrystalline allotropes of carbon used as "calibration" standards is central to the interpretation of the results presented below and hence some detail of each of these allotropes is now presented.

Two forms of amorphous carbon were used in this study. The first was a thin film obtained by *e*-beam evaporation of carbon. Such films consist primarily of sp^2-bonded carbon.[7] Herein this form of carbon will be referred to as *a*-sp^2, to signify short-range sp^2-type bonding in the absence of long-range order. The second form of

TABLE I. Range, straggling, and damage parameters for ion-beam irradiation of diamond with various species. The critical doses were converted from ions/cm^2 to eV/target atom by dividing the total nuclear energy deposited at the critical dose by the atomic density of diamond (1.76×10^{23} atoms/cm^3) and the thickness of the affected layer (taken to be $R_p+\Delta R_p$).

Ion	Energy (E) (keV)	Ref.	Range (R_p) (nm)	Straggling (ΔR_p) (nm)	Nuclear energy loss (n) (%)	Critical doses (ions/cm^2)		Nuclear energy deposited $\left[\frac{EnD}{(R_p+\Delta R_p)\times1.76\times10^{23}}\right]$ (eV/target atom)	
						D_1	D_2	D_1	D_2
C	100	3	133	26	6.0	4.2×10^{14}	2.5×10^{15}	0.90	5.4
Ar	40	1	22	6	19.7	1.9×10^{14}	3.7×10^{14}	3.2	6.3
Sb	340	2	82	17	16.7	4.7×10^{13}	1.7×10^{14}	1.6	5.4
Xe	320	3	55	8.5	13.0	2.7×10^{13}	1.2×10^{14}	1.0	4.5

amorphous carbon used was a thin film produced by the filtered vacuum arc technique.[8] The radial distribution function of this material shows that the nearest-neighbor interatomic distance is 1.53 Å which is very close to the spacing for diamond of 1.54 Å.[8] This value of 1.53 Å is significantly different from the graphite interatomic distance of 1.42 Å. Hence the radial distribution function provides convincing evidence of short-range sp^3-type bonding in the absence of any long-range order. This material is sometimes referred to as "amorphous (or amorphic) diamond" but for the purposes of this paper carbon with no long-range order which nevertheless displays short-range sp^3-type bonding will be referred to as a-sp^3 carbon. As one might expect, a-sp^2 carbon is electrically conducting, while a-sp^3 carbon is insulating.

Glassy carbon consists of a tangle of graphitelike ribbons.[7] There is a good ordering of the carbon atoms into hexagonal sheets within the planes, but very poor registry between the planes.[7,9] This material is best described as micropolycrystalline graphite with crystallite sizes of the order of 30–100 Å, which displays the so-called "turbostatic" structure.[9] The bonding is almost exclusively sp^2, and in this paper such a material will be referred to as μc-sp^2 (i.e., micropolycrystalline sp^2-bonded carbon). Glassy carbon is produced by the slow, controlled thermal degradation of certain polymers. The surfaces of the samples of glassy carbon (obtained from Atomergic Chemetals Corp.) were prepared by polishing with 1-μm diamond paste.

All samples (with the exception of HOPG) were ultrasonically cleaned in acetone and rinsed in deionized water prior to insertion in the UHV system. The HOPG specimen was freshly cleaved using the standard scotch peeling technique prior to insertion in the vacuum system.

The experiments were all performed in an ultrahigh-vacuum chamber equipped with a cylindrical mirror analyzer. The primary electron energy used in the Auger and SEE measurements was 1 keV, which was established by measuring the reflected electron beam in the electron analyzer. The electron energy was measured with respect to the vacuum and is independent of the sample potential. The primary current for Auger measurements was 0.2 μA while the current used for SEE measurements was only half this value in order to avoid saturation of the electron multiplier. The Auger and SEE spectra were recorded in the $d[EN(E)]/dE$ vs E mode using a 5- and 2-V peak to peak modulation, respectively. This measurement mode enhances the fine structure in the spectrum. The electron-beam diameter was 100 μm. All measurements were performed at room temperature.

The 1-keV Ar-ion irradiation was performed *in situ* in the UHV chamber using the ion gun normally employed for sputter profiling. The ion energy was independent of the sample potential. The angle of incidence of the ion beam to the sample normal was 63°, and the diameter of the ion beam was approximately 5 mm. Both the ion dose and electron current densities were measured by placing a Faraday cup in the sample position.

Charging effects were minimized by performing the Auger and SEE measurements as close as practicable to the metal clip which was used to hold the specimen to the carousel. Nevertheless, as will be shown below, charging effects continued to play a large role in the analyses of insulating materials.

The total normalized electron yield Y, given as

$$Y-(I_p-I_{\text{sample}})/I_p \ , \tag{1}$$

was also measured for each of the allotropes mentioned above and as a function of ion dose for the irradiated diamond. Here I_p is the primary electron-beam current measured with a Faraday cup and I_{sample} was the sample current to ground measured with an electrometer. No bias potential was placed on the sample for the measurement of Y. The primary electron-beam energy, diameter, and current were the same as those used for the Auger measurements (i.e., $E_p=1000$ eV, $I_p=0.2$ μA, and spot size 100 μm).

Since the sample current is given by

$$I_{\text{sample}}=I_{\text{backscattered}}+I_{\text{true secondaries}}-I_p \ ,$$

it follows from Eq. (1) that

$$Y=\frac{I_{\text{backscattered}}+I_{\text{true secondaries}}}{I_{\text{primary}}} \ , \tag{2}$$

where $I_{\text{backscattered}}$ refers to backscattered (both elastic and inelastic) electrons from the surface and $I_{\text{true secondaries}}$ refers to the low-energy secondary electrons. Due to the lack of a bias potential, Y is not quite the secondary-electron yield as it includes a backscattered electron contribution. However, it is an exact measure of the balance between the incoming and outgoing electron fluxes. Even for highly insulating samples a value of Y equal to 1 will result in the absence of charging effects as the net impinging electron flux is exactly balanced by the total electron current (which includes backscattered and true secondary electrons) emitted from the surface. A value of less than unity will result in negative charging of the surface and therefore an increase in the observed kinetic energy of the Auger and secondary electrons. The degree of charging depends on the balance between I_p and the rate of discharge, with the latter primarily dependent on the sample resistivity.

III. RESULTS

A. SEE signatures of the carbon allotropes

As the use of SEE in the analysis of carbon surfaces is a relatively new technique, we briefly summarize here the major findings from our previous results.[4,5,10–12] In general secondary electrons are emitted from a solid in response to primary excitation with photons, electrons, or ions. The energy dependence of the secondary-electron yield consists of a slowly varying function peaking at a few eV. The integrated intensity of these secondary electrons is commonly used in order to image surfaces in the scanning electron microscope. Superimposed on the slowly varying background is a fine structure which has been shown to reflect features in the empty density of states above the vacuum level.[11,12] For example, for diamond peaks at 15.5 and 26 eV were observed (Fig. 2) which were found to be associated with transitions from the valence band to unoccupied high-energy conduction-band states.[12] Not surprisingly, these states are sensitive to crystalline perfection and bonding configurations. It is this sensitivity which can be exploited in using SEE to provide signatures for each of the different carbon allotropes.

Figure 2 shows the SEE spectra of five different carbon allotropes. In Fig. 3 the fine structure is emphasized by displaying the spectra at a higher magnification. Clearly each allotrope possesses a unique SEE signature and these signatures are used below to assess the ion-beam-induced structural transformation of diamond. Details of peak assignments for diamond and graphite corresponding to peaks in the empty density of states can be found elsewhere.[11,12] It is noteworthy that the spectra from a-sp^3 and a-sp^2 carbon are distinguishable from each other, demonstrating that SEE is sensitive to the difference in the short-range order between these materials. This is an important result, as Auger spectroscopy is not capable of this distinction, as it exhibits very similar line shapes for a-sp^2 and a-sp^3 carbon, at least within the resolution of our measurements. It is also important to note that although the SEE spectra from diamond and a-sp^3 carbon are different, the overall broad envelopes are similar. The broad envelopes for HOPG (graphite), glassy carbon, and a-sp^2 are also similar to each other, but quite different from those of diamond and a-sp^3 carbon. The comparison between diamond and a-sp^3 on the one hand, and HOPG, glassy carbon, and a-sp^2 carbon on the other, suggest that the broad envelope in the SEE spectrum is characteristic of bond type (i.e., sp^2 or sp^3) whereas the fine structure is characteristic of long-range order (i.e., degree of crystallinity).

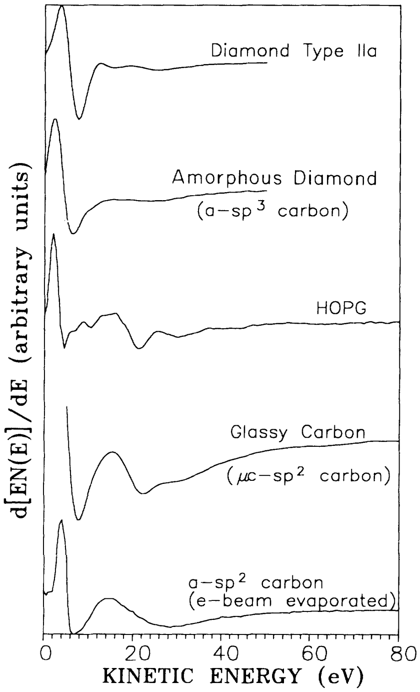

FIG. 2. Secondary-electron emission spectra of differnt allotropes of carbon: Natural type-IIa diamond (110); amorphic diamond produced by the filtered vacuum arc technique and referred to in the text as a-sp^3 carbon; highly oriented pyroltic graphite (HOPG); glassy carbon, referred to in the text as μc-sp^2 carbon; and amorphous carbon produced by e-beam evaporation of a carbon target and referred to in the text as a-sp^2 carbon.

B. SEE of Ar-irradiated diamond

Figures 4 and 5 show the SEE spectra of diamond irradiated with increasing doses of 1-keV Ar ions from 7×10^{12} to 6.2×10^{17} ions/cm^2. It is clear that doses as low as 7×10^{12} ions/cm^2 are sufficient to cause a noticeable change in the spectra, i.e., a change in the relative intensity of the two main peaks in the spectrum. The unirradiated signature is only observed for very high quality material. Above doses of about 1×10^{14} ions/cm^2 the fine structure is gradually washed out, while retaining the envelope typical of sp^3-bonded carbons. At doses of about 7×10^{14} ions/cm^2 the spectrum is similar to that observed for a-sp^3 carbon. Above this dose charging starts to become severe, an effect which will be explained below in greater detail, so that the line shapes for doses between 1×10^{15} and 7×10^{15} ions/cm^2 may yield unreliable measures of the bonding state. The spectra for doses of 2.8 and 4.1×10^{15} ions/cm^2 have been translated by 77 and 35 eV, respectively, in order to be able to plot them on the same scale as the remaining data. At doses exceeding 1×10^{16} ions/cm^2 the line shape is typical of a-sp^2 or μc-sp^2 carbon, evidencing the transformation of the surface layer of the diamond into a highly disordered sp^2 region.

For the low dose irradiations shown in Fig. 4, it is clear that the high-energy peak (about 26 eV) is more sensitive

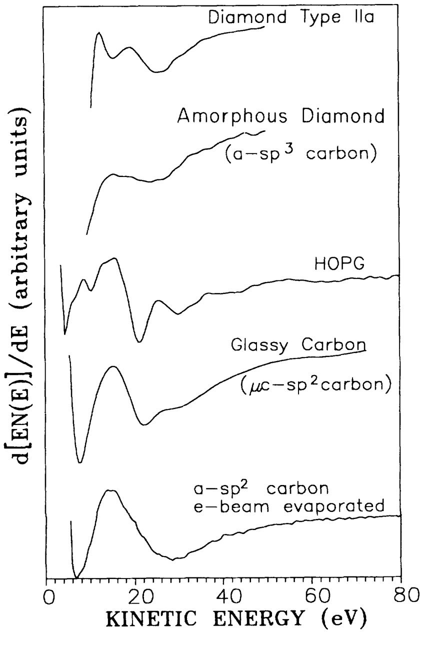

FIG. 3. Secondary-electron emission spectra of different allotropes of carbon as in Fig. 2 but shown at a higher magnification to emphasize the fine structure.

to crystalline damage than the lower-energy peak (at about 15 eV) since the high-energy peak shows a preferential decrease in intensity and broadening as a function of ion dose as compared to the low-energy peak. This is probably due to the fact that the mean free path for electrons decreases as a function of electron energy up to about 30 eV. Such a decrease would result in an increase in surface sensitivity for higher-energy SEE peaks. While this is the most likely explanation for the relative sensitivity of the two observed SEE peaks another factor which may be relevant is the relative sensitivity to crystalline damage of the electronic states from which the observed peak in the SEE spectrum originates. In general, higher-energy bands will be more delocalized in direct space and thus more sensitive to disruption of crystalline order.

Even though more work needs to be done to quantify the SEE technique, it is clear from the extreme sensitivity of the SEE double structure typical of unirradiated diamond (Fig. 4) to even low levels of crystalline damage that the SEE signature can be used as a sensitive probe of the bonding state of the diamond surface.

C. Auger measurements

Figures 6 and 7 show the C(KLL) Auger line for ion doses ranging from 7×10^{12} to 6.2×10^{17} ions/cm^2. For unirradiated diamond the C(KLL) line occurs at an energy of 276 eV. As the dose is increased the double structure characteristic of diamond is lost and the line moves

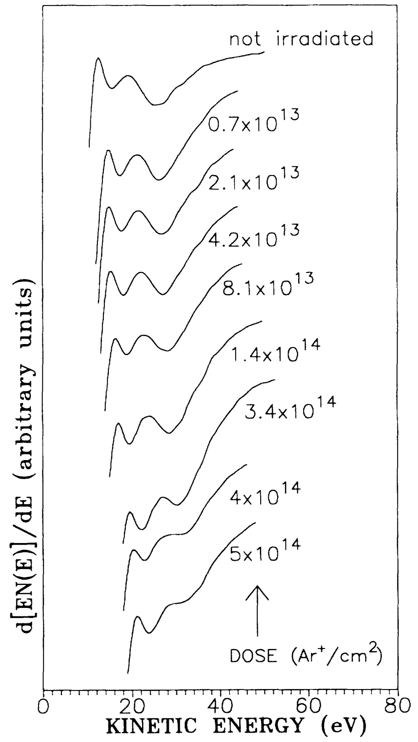

FIG. 4. Secondary-electron emission spectra of type-IIa diamond irradiated with 1-keV Ar ions under UHV conditions for ion doses between 7×10^{12} and 5×10^{14} ions/cm^2.

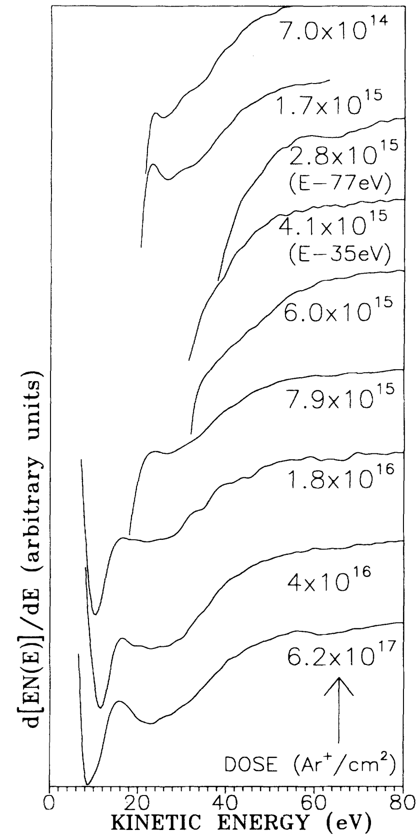

FIG. 5. Secondary-electron emission spectra of type-IIa diamond irradiated with 1-keV Ar ions under UHV conditions for ion doses between 7×10^{14} and 6.2×10^{17} ions/cm^2. Note that the spectra for doses of 2.8×10^{15} and 4.1×10^{15} ions/cm^2 have been displaced by 77 and 35 eV, respectively, in order to be able to plot them on the same scale as the remaining spectra.

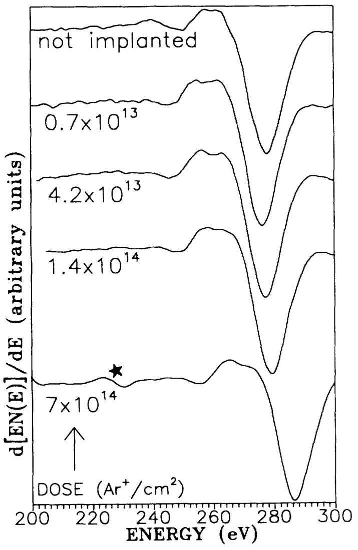

FIG. 6. Auger spectra of type-IIa diamond irradiated with 1-keV Ar ions under UHV conditions for doses between 7×10^{12} and 7×10^{14} ions/cm^2. The Ar (*KLL*) Auger line is marked with an asterisk.

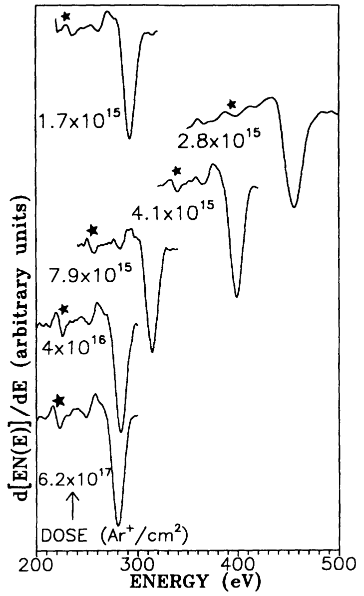

FIG. 7. Auger spectra of type-IIa diamond irradiated with 1-keV Ar ions under UHV conditions for doses between 1.1×10^{15} and 6.2×10^{17} ions/cm^2. The Ar(*KLL*) Auger line is marked by an asterisk. Note the extremely strong charging which occurs for doses bewteen 1.7 and 2.8×10^{15} ions/cm^2.

up in energy due to increased charging. Here again, as is clear from Fig. 7, very severe charging occur for doses exceeding 2×10^{15} ions/cm^2, reaching its maximum value for a dose of 2.8×10^{15} ions/cm^2. It is important to note the very sudden and abrupt nature of the charging effect. For a dose of 1.7×10^{15} ions/cm^2 the C(KLL) line energy position is 293 eV and this value increases very abruptly to 460 eV for a dose of 2.8×10^{15} ions/cm^2. Further irradiation actually causes a decrease in the charging until at doses exceeding 1×10^{17} ions/cm^2 the C(KLL) line saturates at a value of 282 eV. In Fig. 8(a) the position of the C(*KLL*) line is plotted as a function of ion dose showing this large rise and the gradual fall off of the charging.

Many authors have used the Auger C(*KLL*) line shape as a signature for different carbon allotropes.[13–15] The

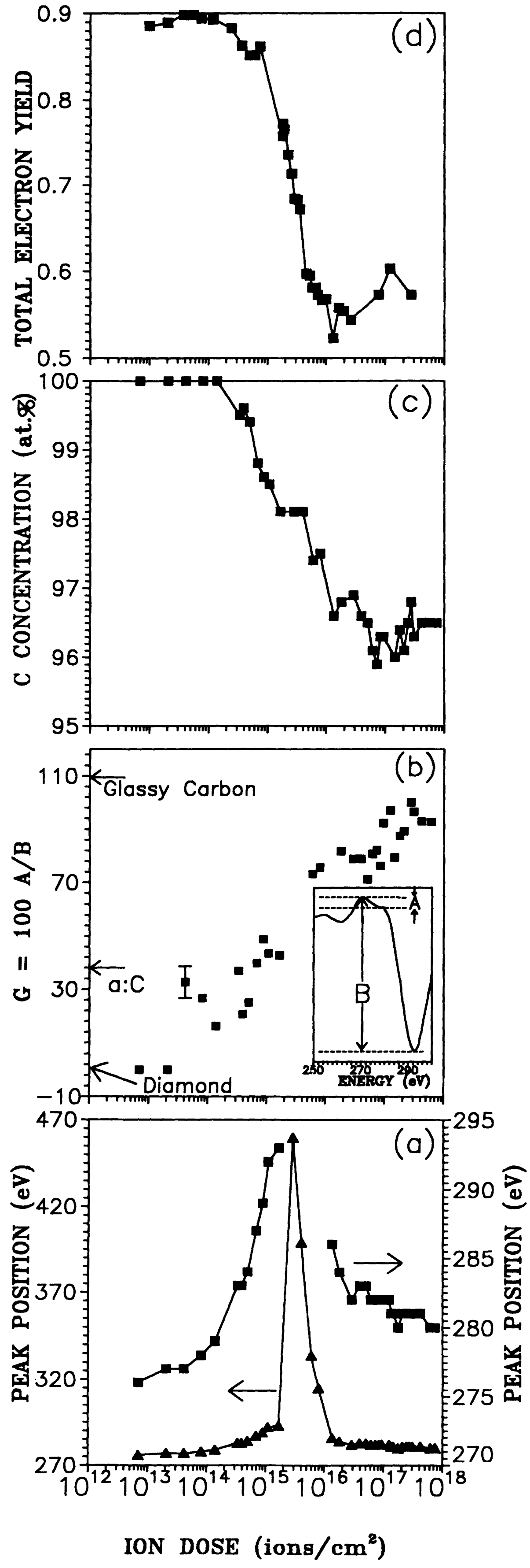

FIG. 8. (a) The position of the C(*KLL*) Auger line as a function of ion dose for irradiation with 1-keV Ar ions. The triangles are plotted using the left-hand axis, while the squares show the data at a higher magnification and have been plotted with reference to the right-hand axis. (b) The parameter *G* extracted from the C(*KLL*) line shape as a function of ion dose for irradiation with 1-keV Ar ions. The inset shows how *G* was extracted from the Auger line shape. The value *G* for amorphous carbon, glassy carbon, and diamond is marked on the plot. For HOPG, $G=210\pm10$. (c) The concentration of C as a function of ion dose for irradiation with 1-keV Ar ions. The decrease from a value of 100% is due to the increase in the Ar concentration in the irradiated volume. (d) The total secondary-electron yield (Y) as a function of ion dose for irradiation with 1-keV Ar ions. For unirradiated diamond $Y=0.9\pm0.1$ while for HOPG, a-sp^2 and a-sp^3 carbon, and glassy carbon $Y=0.65\pm0.1$.

inset to Fig. 8(b) shows one method of semiquantitatively extracting a "graphitelike" parameter from the Auger spectra. The C(*KLL*) line shape for diamond displays a double structure so that $G=100^{*}A/B$ [see Fig. 8(b), inset] is 0±10. Using spectrometers with better energy resolution somewhat smaller (i.e., negative) values can be obtained.[14,15] The values of G for a-sp^2, glassy carbon, and HOPG were measured to be 38±10, 110±10, and 210±10, respectively. Hence the larger G, the larger the graphitic component of the material. The Auger line shape can therefore be used to semiquantitatively distinguish between sp^2-bonded carbons with different degrees of long-range order. In Fig. 8(b) the parameter G extracted from the Auger spectra in Figs. 6 and 7 is plotted as a function of ion dose. Up to a dose of 2×10^{13} ions/cm^2 G remains about zero, similar to the value obtained for unirradiated diamond. Above this dose there is a monotonic rise in G. For doses less than 1×10^{15} ions/cm^2 the value is typical of that obtained for a-sp^2 carbons. For doses exceeding 1×10^{16} ions/cm^2 G saturates at a value typical of that obtained for glassy carbon, suggesting that the ion-beam modification terminates with the production of a disordered sp^2 structure. There is no evidence for the production of large graphitic crystallites or layers which would be expected to give a value of G of about 210. Note that it is not possible to extract G from the Auger spectra for Ar doses between 1×10^{15} and 1×10^{16} ions/cm^2 due to distortion of the line shape due to the extreme charging.

Figures 6 and 7 also show the emergence of the Ar(*KLL*) peak for ion doses exceeding 7×10^{14} ions/cm^2. The relative sensitivity factor of Ar(*KLL*) to C(*KLL*) was taken from the literature to be 0.2.[16] If one assumes a homogeneous distribution of Ar in the implanted region, then the argon concentration in the implanted diamond, C_{Ar}, can be estimated to be

$$C_{\mathrm{Ar}}=0.2/(A+0.2)\ ,$$

where $A=I_{\mathrm{C}(KLL)}/I_{\mathrm{Ar}(KLL)}$ is the measured ratio of the relative intensity of the carbon to argon Auger peaks. In Fig. 8(c) the concentration of carbon, $C_{\mathrm{C}}=1-C_{\mathrm{Ar}}$, is plotted as a function of ion dose. There is no observed decrease in the C concentration until a dose of about 1×10^{14} ions/cm^2 after which the Ar concentration increases monotonically until it saturates at level of about 4% for doses exceeding about 5×10^{16} ions/cm^2. The saturation is presumably caused by sputtering limiting the maximum concentration of Ar in the modified layer. However, other factors could also account for the observed saturation such as Ar diffusion either into the bulk or out from the surface. Figure 8(c) is useful in that it shows that provided doses less than about 5×10^{15} ions/cm^2 are considered, sputtering is unlikely to be a major factor in the interpretation of the results, and that, at least to a first approximation, the damage introduced is likely to be proportional to the ion dose.

D. Total yield

The total electron yield Y was measured for a primary electron energy of 1 keV and primary current of 0.2 μA as a function of ion dose and the results are shown in Fig. 8(d). For unirradiated diamond, Y was measured to be 0.9±0.1, while for a-sp^2 and a-sp^3 carbon, and HOPG, Y was measured to be 0.65±0.1.[17]

Note that despite the very strong charging, it is possible to measure Y over the entire dose range since the charging only shifts the energy of the emitted electrons and these shifts do not affect the measurement of the total sample current. Y displays a monotonic decrease as a function of ion dose, saturating at a level of about 0.58 which corresponds to the value for the nondiamond carbon allotropes given above.

IV. DISCUSSION

Before commencing the discussion of the ion-beam-induced transformation of diamond it is prudent to stress the limitations on the sensitivity to long- and short-range order in carbons for Auger, SEE, and total-secondary-electron-yield measurements under the experimental conditions used in this study. Table II is an attempt to summarize these sensitivities in terms of the ability of the particular spectroscopy to reliably distinguish between different carbon allotropes. Clearly all of the three techniques are capable of distinguishing c-sp^2 from c-sp^3 (i.e., graphite from diamond). On the other hand, only SEE can distinguish a-sp^2 from a-sp^3 carbon. Auger spectroscopy returns the same value of G for these two allotropes.[18] However, it is difficult to use SEE to distinguish between a-sp^2 and glassy carbon (i.e., μc-sp^2) as the differences in the line shapes are very small, whereas the Auger G ratio is very useful for making this distinction. The total secondary-electron yield was measured to be 0.65 for a-sp^2, a-sp^3, glassy carbon, and graphite. Thus total yield measurements cannot distinguish between the different nondiamond carbon allotropes.

TABLE II. Ability of Auger, SEE, and total secondary-electron yield to distinguish between different allotropes of carbon.

	a-sp^2 vs a-sp^3	μc-sp^2 vs a-sp^2	c-sp^3 vs c-sp^2
Auger	N	Y	Y
SEE	Y	N[a]	Y
Yield	N	N	Y

[a] In Ref. 5 small, but significant differences in the SEE line shape between glassy carbon (μc-sp^2) and a-sp^2 carbon are reported. However, for the purposes of this study, these differences were found to be too small to be useful in helping to distinguish between μc-sp^2 and a-sp^2 following ion-beam irradiation.

Keeping the limitations of Table II in mind we can now proceed to interpret the results presented above. The Auger measurements show that up to a dose of 2×10^{13} ions/cm^2, the diamond structure is essentially preserved. Above this dose there is evidence for either a-sp^2 or a-sp^3 carbon or possibly simply heavily damaged diamond. Auger alone (within the resolution of our experimental arrangement) cannot distinguish between these possibilities. However, SEE suggests that a-sp^3 carbon is present in this dose range. Above 1×10^{16} ions/cm^2 there is evidence for the formation of a microcrystalline sp^2-rich structure, which is distinguishable from a-sp^2 carbon using the graphite parameter G. Between 10^{15} and 10^{16} ions/cm^2 the very strong charging prevents meaningful conclusions from being drawn from the Auger line shape.

By contrast, the total yield Y changes monotonically over the whole of the dose range. Up to a dose of 10^{14} ions/cm^2 no change in Y is observed. Between 1×10^{14} and 1×10^{16} ions/cm^2 a monotonic decrease is observed which saturates for doses in excess of 10^{16} ions/cm^2 at a value of Y comparable to that obtained from a-sp^2 or μc-sp^2. Although yield measurements cannot distinguish between these latter two possibilities, it is clear from the Auger measurements that in fact the surface is μc-sp^2 carbon for these doses. It is important to note that in contrast to the almost discontinuous dependence of the charging as a function of ion dose observed in the Auger measurements, the total yield is a much more gradual function of ion dose. This may be because the measured yield will in fact have contributions from both the modified surface and the unmodified underlying bulk. Auger electrons have skin depths of only 10–20 Å. However, the primary electrons have skin depths of at least an order of magnitude larger than this, and secondary electrons which originate from collisons much deeper than the thickness of the ion-irradiated layer (estimated to be 20 Å) may eventually contribute to the total observed yield via multiple collision cascades.

The most striking of the results presented above is the extremely sharp onset of charging as a function of ion dose. A slow rise in charging is observed up to a dose of 1.7×10^{15} ions/cm^2. Between 1.7 and 2.8×10^{15} ions/cm^2 there is a very sharp jump of the C(KLL) line position. Even though it was observed that the magnitude of this jump could be reduced by reducing the lateral separation between the point on the sample on which the electron beam was incident and the position of the grounded metal clip used to hold the sample to the carousel, the dose at which the strong charging was observed was found to be very reproducible and independent of the sample-electron-beam geometry.

The degree of charging is a convolution of two physical parameters of the sample under study. The first is the conductivity of the sample. No charging effect is expected in highly conducting, well grounded samples. The second, less well-known property is the yield Y. As has been explained above, Y represents the balance between the incoming and outgoing electrons from the surface. Hence even extremely insulating samples with a value of Y close to unity will practically not charge. Thus, for charging to occur, two conditions must be met simultaneously; Y must differ from unity and the sample must not be conducting.

In view of the above, the observation of strong charging must correspond to the production of a material which remains insulating, but whose total yield differs considerably from unity. The only possibility in terms of the materials examined in this study is a-sp^3 carbon, which is well known to be an excellent electrical insulator, but whose value of Y is 0.65, which is very different from the value of 0.9 obtained from single-crystal diamond.

The picture of emerge is then as follows. Up to a dose of 1×10^{15} ions/cm^2 the diamond remains essentially single crystalline albeit with evidence from Auger and SEE of the introduction of considerable levels of damage. Above this dose there is a very sudden transformation of the damaged crystalline structure to an a-sp^3 structure, which takes place over a narrow dose range. The change in Y concomitant with this transformation leads to an imbalance between incoming and outgoing electron fluxes and hence the observed extreme charging. The change in Y is not observed to be as sharp as the dose dependence of the charging because the former also includes contributions from the undamaged layers underneath the irradiated volume. After this transformation to a-sp^3 the material gradually transforms into conducting a-sp^2 under further ion impact and since the surface conductivity to the grounded clip increases, the charging gradually decreases as a pathway is built up allowing the excess electrons to find their way to ground. Charging terminates when a sufficiently conducting continuous surface layer is formed.

It is interesting to note that the critical dose for charging (2.8×10^{15} ions/cm^2) corresponds closely to the areal density of diamond. Hence at this dose each carbon atom on the surface has, on average, been "hit" at least once by an impinging ion.

If the above interpretation is correct it implies that diamond shares with silicon a well-defined critical dose (in terms of energy deposited per target atom) for a crystalline to amorphous transformation. For Si the transition at room temperature occurs at critical damage energy densities of 35–40 eV/target atom for irradiation with 150- and 300-keV Si ions.[19] In the present work the critical dose of 2.8×10^{15} Ar/cm^2 corresponds to an energy density of about 29 eV/target atom. The critical energy density for Si is temperature dependent,[19] with higher doses required for amorphization at elevated temperatures due to the annihilation of unstable individual defects prior to the formation of stable damage. Although the situation for diamond is less well researched, and the temperature dependence of the critical energy density is not known, it is clear, from resistivity versus ion dose data,[3,20] that the transformation is also very sensitive to implant temperature.

Finally, we attempt to compare the results of the present work to the work of other authors who have monitored the dose dependence of the conductivity (σ vs D). In the present work, it is very difficult, if not impossible, to directly measure σ vs D for 1-keV-irradiated surfaces due to the extreme thinness (<20 Å) of the modified region. However, the gradual decrease in charging (Fig. 8) gives an indirect measure of the surface conductivity. It can be seen that the increase in conductivity occurs over about one decade of ion dose (from 3×10^{15} to 2×10^{16} ions/cm^2). Previous work[2,3] using much more energetic ions, has also found that the change in the conductivity for room-temperature implantations also occurs over about one decade of ion dose. Indeed the charging versus dose curve of Fig. 8(a) is qualitatively very similar to Fig. 1 for $D>D_2$ if it is recalled that the decrease in charging in Fig. 8(a) corresponds to a decrease in the resistivity and therefore an increase in the conductivity.

One of the most comprehensive analyses of the dose dependence of σ was carried out by Kalish *et al.*,[2] who examined the applicability of various models for the transformation of diamond. they found that σ vs D was not sharp enough to be consistent with either a percolative transition or with a critical energy density amorphization model for the transition. An explicit assumption of their work was that the crystalline diamond is electrically insulating whereas amorphous carbon is conducting, and hence if the critical energy density amorphization model is correct, a very sudden rise in the conductivity is to be expected. Since this was not observed this model was discounted.

In the present work, we have suggested that the sudden transformation into an amorphous structure is not accompanied by a large increase in the conductivity. If this is true, then the changes in the conductivity observed above D_2 correspond, not to amorphization, but rather to a gradual transformation of a-sp^3 to a-sp^2. The dc conductivity measurements are therefore relatively insensitive to the critical dose required for amorphization. By contrast, in the present work, the crystalline to amorphous transition is observed, because although a-sp^3 is insulating, its secondary yield is quite different from that of diamond, resulting in very severe charging.

The above data are also consistent with the proposal that the transition from sp^3- to sp^2-bonded carbon is inhibited until the sudden crystalline to amorphous transformation occurs. Support for this proposition is found in the annealing studies of irradiated diamond. For example, for 100-keV C irradiation $D_1=4.2\times10^{14}$ ions/cm^2 and $D_2=2.5\times10^{15}$ ions/cm^2 (see Table I). Annealing studies[21] have shown that a critical dose of between 2 and 3×10^{15} (i.e., very close to D_2) exists for C-irradiated diamond below which the material can be almost completely annealed by furnace heating, but above which furnace annealing results in graphitization. Similar results are available for Sb$^+$ implantation for which it was found that D_2 is 1.7×10^{14} ions/cm^2 (Table I) and the dose above which the material graphitizes rather than anneals on furnace heating is 1.8×10^{14} ions/cm^2.[22] From these two annealing studies it is clear that D_2 closely corresponds to the critical dose above which furnace heating results in relaxation to graphite rather than in annealing of defects. Thus the nonannealable limit is reached at doses less than those required for the very large increase in the conductivity. This observation is consistent with our hypothesis that amorphization occurs at or below D_2, while increases in conductivity occur for $D>D_2$ as sp^3 bonds are gradually converted into sp^2 bonds if one makes the reasonable assumption that the damaged diamond is annealable, but that amorphized material is more likely to relax to graphite. A possible explanation for this is that the sp^3 to sp^2 transformation involves a large increase in C-C bond distances and would generate enormous pressures inside the diamond lattice were it to occur. It is possible that the diamond lattice is rigid enough to inhibit this expansion. Presumably, once the diamond is amorphized, expansion can occur unconstrained by the lattice.

Finally, we note that the results of this study, and indeed all studies to date, leave open the question of the origin of the very peculiar nonmonotonic behavior of the conductivity for doses below D_2. As Table I indicates the behavior appears to be damage driven and is ion species independent. The results of this work suggest that the diamond remains essentially single crystalline in this region, albeit with a considerable degree of introduced disorder. However, a more comprehensive understanding of this dose regime may have to await TEM studies of irradiated diamond which are currently in progress to unambiguously identify the defect structures present in the dose vicinity close to D_1.

V. SUMMARY

Secondary-electron emission and Auger spectroscopies, and total secondary-electron yield have been employed to assess the transformation of diamond under bombardment of 1-keV Ar ions under ultrahigh-vacuum conditions. The SEE and Auger line shapes for different carbon allotropes (diamond, HOPG, a-sp^2, a-sp^3-bonded carbon, and micropolycrystalline graphite) were measured and used in order to act as "calibration standards" for the assessment of the nature of the near surface region of the irradiated diamond. The results of the study may be summarized as follows.

(1) Up to a dose of 1×10^{15} ions/cm^2, the Auger C(*KLL*) line shape and the SEE spectrum show that the ion beam has introduced considerable disorder into the near surface region. The SEE line shape for a dose of 7×10^{14} ions/cm^2 is similar to that obtained from a-sp^3 carbon.

(2) Between 2 and 3×10^{15} ions/cm^2 extreme and very abrupt charging occurs as evidenced by the observed shift in the Auger C(*KLL*) line position. For doses exceeding 3×10^{15} ions/cm^2 the charging gradually decreases over about a decade of ion dose.

As extreme charging can only occur from a material with (i) a secondary-electron yield which differs considerably from unity *and* (ii) which is electrically insulating, the observation of charging is evidence for the formation of material which is not crystalline diamond, but is still electrically insulating. The most likely allotrope of carbon which meets these requirements is a-sp^3-bonded carbon.

(3) The total secondary-electron yield displays a monotonic decrease from a value of 0.9 for unirradiated dia-

mond to a value of 0.58 for doses exceeding 1×10^{16} ions/cm^2 All the nondiamond allotropes studied were observed to have secondary yields of 0.65.

The results are consistent with a model for the transformation of diamond involving the following stages.

(1) For doses below 1×10^{15} ions/cm^2 the ion beam introduces damage into the diamond, but the material remains essentially single crystalline. Comparison to other work suggests that furnace annealing is effective in annealing this degree of damage.

(2) At a critical dose of between 2 and 3×10^{15} ions/cm^2 the damaged diamond suddenly transforms into an amorphous structure, in which the carbon atoms are locally tetrahedrally bonded (i.e., sp^3 bonding). For this dose the material remains electrically insulating, but its secondary yield drops from 0.9 to 0.6 giving rise to extreme charging.

(3) Above this critical dose the a-sp^3 structure is gradually transformed into a-sp^2 carbon with a concomitant rise in the conductivity. For high doses a micropolycrystalline graphitelike layer is produced.

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[18] It should be noted that using a spectrometer with greater resolution may well result in the measurement of G to greater precision and if this is accomplished Auger spectroscopy may well be able to distinguish a-sp^2 from a-sp^3 carbon. However, this has not been accomplished to date.

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