Secondary electron emission and photoemission studies on surface films of carbon nitride

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The secondary electron emission yield of fullerene, graphite, and diamondlike carbon after low-energy N_2^+ ion bombardment was studied for antimultipactor applications. Nitrogen incorporation into the carbon thin films decreases their secondary emission yield, contrary to the hydrogen or oxygen effect. Carbon nitride surface textured to a nanometric scale had the property of hindering secondary electron emission. Valence bands obtained from photoemission spectroscopy using synchrotron radiation were correlated with secondary electron emission measurements. Multipactor threshold power for carbon nitride was 7.5 kW. © 2006 American Institute of Physics. [DOI: [10.1063/1.2173307](https://doi.org/10.1063/1.2173307)]

I. INTRODUCTION

The multipactor effect is a resonant radio-frequency (rf) electron discharge in vacuum sustained by secondary electron emission from the walls of radio-frequency devices.^{1–7} Multipactor discharge is caused by electron multiplication due to emission of secondary electrons from surface materials, due to the impact of rf energized electrons. It is an important problem in high-power rf devices in vacuum, such as telecommunication and remote sensing equipment in satellites, rf cavities in particle accelerators, and rf plasma heating devices in nuclear fusion experiments.^{3–7} Usually, several conditions have to be fulfilled for the apparition of the multipactor effect, namely, (a) a phase resonance must exist, (b) primary electrons accelerated by the rf field must have an energy such that the secondary electron emission yield of the impacted surface must exceed unity, and (c) the product of operating frequency by gap spacing (fd) must fall within a range which ensures that the electron transit time is in the order of an odd multiple of one-half rf cycle.

The search for reliable low secondary electron emission materials, which would reduce the feedback necessary for the electron avalanche, is an important technological issue. The main objective of this research is to find a stable and inert surface with respect to secondary electron emission properties, or, at least, one that evolves favorably under the initial stages of multipactor discharge, i.e., upon low-energy electron and ion bombardment. In this work we present results about the relationship between the secondary electron emission and multipactor properties. The materials studied were fullerene, diamondlike carbon, and graphite before and

after the nitridation process. Surface physics spectroscopic and microscopic techniques were used in combination with secondary electron emission measurements.

Oblique incidence angles imply a longer part of the penetration range of the primary electron being inside a near-surface region from which secondaries can escape from, therefore leading to higher secondary electron emission yield (SEY). However, there are also shadowing effects of the protruding surface structures over the concave zones that hamper their SEY. These effects are different for emitted true secondary electrons (low-energy, cosine-law emission in all directions) than for backscattered electrons (higher-energy, more specular reemission). This seems to produce a shift to lower energies of the SEY from rough surfaces. In this sense, low-energy ion bombardment can level rough surfaces or create topographical structures in a smooth surface. For instance, although most calculations⁸ seem to indicate a general increase of SEY with surface roughness, one of the methods to reduce secondary emission electrons on copper surfaces is by using an ion-beam process or bake out at atmospheric pressure that produces deeply textured surfaces.^{9,10} In this work, the results on the relationship between the surface nanomorphology and SEY are also shown. Low-energy ion beams were used as a surface-processing tool. Two main types of surface changes of the thin film materials induced by low-energy ion bombardment were studied, namely, modification of the electronic structure and modification of the morphology.

II. EXPERIMENT

Amorphous hydrogenated carbon ($a\text{-C:H}$) of the type called diamondlike carbon (DLC) and fullerene (C_{60}) were deposited by CH_n^+ ion bombardment and sublimation of C_{60}

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powder, respectively, onto (100) silicon wafers in an ultra-high vacuum chamber, directly attached to the photoemission analyzer. The background pressure was 2×10^{-9} mbar. Carbon nitride was synthesized by low-energy N_2^+ ion bombardment at 750 eV in C_{60} , a -C:H, and pyrolytic polycrystalline graphite.^{11,12} The ion source was of the Penning cold-cathode type, producing an ion flux of $10 \mu A$ on a surface of 1.5 cm^2 ($\sim 8 \times 10^{13}$ ions/ $\text{cm}^2 \text{ s}$). The samples were also bombarded by Ar^+ ions of 500 eV at a dose of 0.12 C/cm^2 .

Ultraviolet photoemission spectroscopy (UPS) was performed at the TGM2 beam line of the BESSY synchrotron of Berlin (Germany) using a VG ADES 400 system with a hemispherical energy analyzer with 4° acceptance angle. Valence band (VB) photoemission spectra in the 30–172 eV photon energy range were recorded. Combined energy resolution of the monochromator and the analyzer was found to be better than 0.4 eV. X-ray photoelectron spectroscopy (XPS) was performed in a VGS ESCALAB 210 instrument using a nonmonochromatic $Mg K\alpha$ x-ray source ($h\nu = 1253.6 \text{ eV}$). The combined resolution of the analyzer and the $K\alpha_{1,2}$ line was 0.75 eV. The total secondary electron emission coefficient σ , being $\sigma = \delta + \eta$, with δ as the true secondary electron yield and η as the backscattered electrons per primary electron, was measured *in situ* as a function of the primary electron beam energy E_p from 0 to 2000 eV by measuring the sample current to ground I_s while the electron beam was impinging normally on the sample surface. The sample was biased at -27 eV to repel secondary electrons. We have calculated the total secondary electron emission coefficient from the ratio $\sigma(E_p) = 1 - I_s/I_p$, where I_p is the primary current of the electron gun. I_p was obtained by applying a relative calibration method using the total secondary electron emission coefficient of platinum as a reference.

Atomic force microscope (AFM) measurements were performed with a Nanoscope IIIa equipment (from Digital Instruments, CA) at ambient conditions. Images were taken in both contact and tapping modes. For the contact mode, silicon nitride cantilevers were employed whereas for the tapping mode silicon cantilevers were used. Multipactor tests were performed at ESA/ESTEC test facilities using a dedicated vacuum chamber. The rf signal was chosen to be at 5.3 GHz using a pulse width of $37 \mu s$ and a duty cycle of 1.7% with a parallel plate sample geometry with a gap of 2.0 mm and a plate size of 30.0 mm length and 15.0 mm width. The breakdown event was monitored using spectrum analyzers, which are able to detect changes in the harmonic level and in the reflected signal when the discharge takes place. An electron detector and photomultiplier were also used as additional detection methods.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the SEY coefficient σ versus the primary electron energy E_p for a -C:H exposed to air before (curve i) and after Ar^+ ion bombardment (curve ii). Relevant parameters are the maximum values of SEY σ_m at the energy E_m , and both crossovers for $\sigma=1$, E_1 , and E_2 (marked in curve i). Table I presents the experimental values of these SEY parameters. After Ar^+ ion bombardment, σ_m decreases,

FIG. 1. Total SEY coefficient vs primary electron energy of (a) a -CH_x deposited by CH₄ plasma after air exposure (curve i) and after Ar^+ ion (500 eV and 10^{16} cm^{-2}) bombardment (curve ii); (b) C_{60} exposed to air (curve i) and after Ar^+ ion bombardment (curve ii); and (c) clean pyrolytic polycrystalline graphite (curve i), after N_2^+ (1000–250 eV and $2 \times 10^{18} \text{ cm}^{-2}$) bombardment (a -CN_x) (curve ii), after 6 days of air exposure (curve iii), and typical high V_{thres} Alodine (curve iv).

E_m and E_1 shift toward higher primary energies, and E_2 shifts toward lower primary energies. Figure 1(b) shows the $\sigma(E_p)$ curves of C_{60} fullerene exposed to air before and after Ar^+ ion bombardment of 500 eV, curves i and ii, respectively. Also, a decrease in σ_m is observed after Ar^+ ion bombardment. This decrease is related to the determinant step of the escape through the surface that is affected by low-energy ion bombardment and to the cleaning effect of the surface.

Figure 1(c) (curve i) shows the $\sigma(E_p)$ curve measured for clean pyrolytic polycrystalline graphite. The SEY curves of the amorphous carbon a -C (not shown) produced by low-energy Ar^+ ion bombardment of graphite are similar than those of pyrolytic polycrystalline graphite. However, a -C:H has a high relative σ_m [Fig. 1(a) (curve i)] as compared with graphite that can be attributed both to its diamondlike bonding (sp^3) and hydrogen content [in this case 30 at. % as we measured by elastic recoil detection analysis (ERDA)]. This could be explained by the formation of an energy band gap and surface states that help secondary electrons to diffuse and tunnel through the surface energy barrier. The presence of an energy gap can prevent low-energy sec-

TABLE I. Comparison of the SEY parameters of *a*-C:H, C₆₀, and graphite before and after low-energy ion bombardment.

Sample	σ_m	E_m (eV)	E_1 (eV)	E_2 (eV)	Ar ⁺ ion bombardment ^a	N ₂ ⁺ ion bombardment ^b	Air exposure ^c
<i>a</i> -C:H ^d	1.40	156	70	535	...	...	yes
<i>a</i> -C:H ^e	1.10	200	112	327	yes	...	...
C ₆₀ ^f	1.12	160	100	310	...	...	yes
C ₆₀ ^g	1.02	270	200	380	yes	...	...
Graphite ^h	1.00	290	...	...	...	...	yes
Nitrided graphite and C ₆₀ ⁱ	0.80	250	...	...	...	yes	...
Nitrided graphite and C ₆₀ ^j	1.08	190	110	330	...	yes	yes
Alodine ^k	3.10	220	100	...	...	...	yes

^aAfter Ar⁺ ion bombardment of 500 eV at a dose of 0.12 C cm⁻².^bAfter N₂⁺ ion bombardment of 750 eV.^cAfter 6 days of air exposure.^dFigure 1(a) (curve i).^eFigure 1(a) (curve ii).^fFigure 1(b) (curve i).^gFigure 1(b) (curve ii).^hFigure 1(c) (curve i).ⁱFigure 1(c) (curve ii).^jFigure 1(c) (curve iii).^kFigure 1(c) (curve iv).

ondary electrons from losing energy through electron-electron collisions, thereby resulting in a large diffusion length for the secondary electrons and a large secondary electron yield. In this sense, it is worth mentioning that the secondary electron yield of graphite increases after hydrogen implantation.¹³ Moreover, hydrogen has also been found to shift the conduction band minimum to energies close to, or even above, the vacuum level on diamond surfaces,^{14,15} that is to say, to create a negative electron affinity surface. In all cases, oxygen incorporation in carbon after air exposure (observed by XPS) increases its secondary electron emission.

Figure 1(c) also shows the SEY curves measured for graphite after nitridation (curve ii) and the subsequent air exposure (curve iii). The SEY results of Alodine alloy, originally the standard reference antimultipactor coating used in the aerospace industry, are also included for comparison purposes. In contrast to the effect induced by hydrogen and oxygen incorporations, a marked decrease in σ_m after the nitrogen incorporation in carbon (graphite, *a*-C:H, and C₆₀) is produced. CN_x surface ($x=0.35$, result obtained by the XPS analysis) has a value of σ_m lower than unity and, in consequence, no multipactor would be possible at any rf intensity. In addition, nitrogen bombardment is more efficient for the secondary emission reduction than bombardment by Ar⁺ ions. It is noteworthy that this low σ_m value had deteriorated to a very minor extent by exposure to air during 6 days (curve iii). Carbon is passivated by bonding to nitrogen and, therefore, does not absorb as much water and oxygen when exposed to air.

We have studied the relationship between the scale of surface roughness obtained by AFM and the secondary electron emission properties of C₆₀, *a*-C:H, and CN_x. Some representative results are shown in Fig. 2. The surface of the C₆₀ thin film deposited by evaporation onto a silicon substrate shows an aggregatelike morphology (bunches of grains) with

a root mean square roughness of 150 nm. The flatter regions not including the aggregates show an overall roughness of 35 nm [Fig. 2(a)]. The secondary emission curves $\sigma(E_p)$ [Fig. 1(b)] could be explained by the facts that (i) the pronounced maximum of σ for $E_p \sim 170$ eV can be due to the approximate coincidence of the penetration range of primaries of this energy with both the secondary diffusion length and characteristic length of the surface, and (ii) the low σ observed at large E_p is due to the low total electron density of the material (the C₆₀ molecule is an open structure and, moreover, the film shows an open morphology). After N₂⁺ ion bombardment, the surface of the C₆₀ thin film is modified to a smoother uniform surface with a roughness of 2 nm [Fig. 2(b)]. Correspondingly, the maximum σ_m smoothes out but σ increases at large energies (because the fullerene is compacted). Although the AFM images of the *a*-CH_x [Fig. 2(c)] reveal a very flat surface, the relatively high σ_m is explained by the presence of hydrogen that increases the secondary electron emission coefficient.

The electron photoemission from surfaces is related to the secondary emission process. The photoelectrons correspond to the elastically reflected and reemitted ones in secondary electron emission process, but photoelectrons carry the information of the binding energy, i.e., of the energy state they come from. Before being emitted to vacuum, the photoelectrons in the material can have energy losses and generate secondary electrons, just as in the secondary electron emission process. Figure 3 presents the photoemission spectra of both graphite and C₆₀ fullerene before and after N₂⁺ ion-beam bombardment. This measurement was performed with photons of 40 eV to ensure the minimum probe depth of two or three atomic layers. The curves i and ii show the UPS for polycrystalline graphite before and after N₂⁺ ion bombardment. Spectrum i also shows some structure in the density of states of the valence band due to the hexagonal sym-

FIG. 2. $6 \times 6 \mu\text{m}^2$ AFM images of (a) C_{60} fullerene evaporated on single crystal Si, (b) carbon nitride obtained by N_2^+ (500 eV and 10^{17} cm^{-2}) ion bombardment of C_{60} , and (c) $a\text{-C:H}$ obtained by CH_4 plasma on single crystal.

metry of its crystal structure. This structure is washed out by ion bombardment producing an amorphous material. However, the density of states close to the Fermi level, already high in graphite, remains very similar after bombardment by N_2^+ ions.

The photoemission spectrum of fullerene (curve iii) shows a marked structure in the range of 22–38 eV (kinetic

FIG. 3. UPS of N_2^+ ion bombarded pyrolytic polycrystalline graphite and C_{60} : (a) graphite, (b) last after N_2^+ (250 eV and $2 \times 10^{17} \text{ cm}^{-2}$) bombardment, (c) C_{60} , and (d) after N_2^+ (50 eV and $5 \times 10^{15} \text{ cm}^{-2}$) bombardment.

energy measured with respect to the Fermi level) corresponding to the valence levels of the highly symmetric C_{60} molecule. There are no energy levels just below the Fermi level (38–40 eV). Besides, the information on the escape process can be obtained from the part of the spectrum corresponding to low kinetic energies. No electron is emitted with energy below 5 eV, which is the work function of the material. Just above the vacuum level an intense and narrow peak is observed due to secondaries that escape through discrete energy levels of the surface states due to surface defects. After N_2^+ ion bombardment of C_{60} , this tunneling energy level disappears¹⁶ (spectrum iv) and, in general, the density of empty states close to the vacuum level decreases significantly. At the other extreme, the nearly discrete valence levels of the C_{60} valence band become wide solid-state bands extending up to the Fermi level with a density of states similar or greater than that of graphite. The material becomes a relatively good conductor at the surface upon ion bombardment. In a conductor, the diffusion length of secondaries is much smaller than that in an insulator and, therefore, the amount of electrons that can be emitted decreases.

The multipactor threshold power or multipactor breakdown power (MPT) for carbon nitride coatings tested at ESTEC was 7.5 kW, 10% higher than the previously measured on graphite before nitridation. In addition, the enhancement in multipactor threshold power by using CN instead of the standard antimultipactor coating, Alodine, is 20%. The relation between secondary electron emission properties and multipactor threshold (or multipactor breakdown voltage) V_{thres} is more complicated than expected because both measurements cannot be made simultaneously. In addition, the measurement of V_{thres} itself modifies the SEY of the film. From multipactor threshold tests and computer simulation studies,^{17,18} two parameters of secondary electron emission influencing V_{thres} appear to be dominant: σ_m and E_1 . In fact, a rough rule of thumb $\text{MPT} \propto (E_1/\sigma_m)^{1/2}$ seems to hold for $E_1/\sigma_m \leq 60 \text{ eV}$. Thus, in order to minimize or even reduce multipactor effects it would be interesting to increase V_{thres}

as much as possible. Therefore, for technical purposes, the value of E_1 should be maximized whereas σ_m should be minimized.

In summary, low-energy ion bombardment with N_2^+ of α -C:H, graphite, and C_{60} produces C–N bonding and reduces their SEY, and also deeply textures the surface to a nanometric scale with the property of hindering secondary electron emission. However, hydrogen or oxygen incorporation into the carbon coatings causes an increase in the SEY of the films. The decrease in secondary electron yield after nitridation of carbon was correlated with the valence band photoemission spectra. These results indicate that CN_x is favorable for low secondary electron emission applications since (a) the resulting material has low total (including core atomic orbitals) electronic density while maintaining a good conductivity similar to that of graphite, and (b) also, it exhibits a zero band gap as indicated by the valence band spectrum.

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