Structural changes in diamond and amorphous carbon induced by low-energy ion irradiation

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In the present work we describe an investigation of the influence of low-energy ion irradiation (1-keV Ar^+) on the surface structure of polycrystalline diamond and amorphous carbon films with various degrees of graphitization. Photoelectron spectroscopy (PES) with excitation energies in the ultraviolet and x-ray regime is employed to monitor the radiation-induced modification of the electronic structure of the surface which is closely linked to the local bonding environment of the carbon atoms. A comparison of the mean photoelectron escape depth and the thickness of the irradiation affected layer also illustrates the suitability of PES for this investigation. For the chemical vapor deposition (CVD)-diamond film a gradual change from typical diamond features to amorphous carbon is observed for ion doses surpassing 6×10^{14} cm^{-2}. The structural changes in the diamond lattice are expressed in a broadening of the C $1s$ core-level peak, and increasing contributions from p-π states around 3–4 eV in the valence-band spectra. Likewise the peak located at 13 eV (He II, $h\nu=40.82$ eV), characteristic of diamond, is no longer apparent for ion doses exceeding 3×10^{15} cm^{-2}. The diamond surface clearly shows a tendency to amorphize rather than graphitize under ion irradiation. To complement the results for the diamond film, we irradiated two amorphous carbon films with different microstructures: (A) a predominantly amorphous film, and (B) a film with graphitic inclusions. The destruction of graphitic structures in film (B) is apparent even for the lowest ion dose (1.5×10^{14} cm^{-2}), and expressed in an increase in the width of the C $1s$ core-level peak and a smearing out of the valence-band spectral features. The resultant valence-band and core-level spectra (total ion dose: 3×10^{15} cm^{-2}) are very similar to the one obtained for the amorphous film (A), which, on the other hand, does not show any significant changes in its structure upon irradiation. The irradiation of both diamond and graphitic structures with low-energy Ar^+ ions leads to the formation of a predominantly amorphous surface layer. [S0163-1829(96)07934-9]

I. INTRODUCTION

Diamond, owing to its unique properties and since the development of CVD deposition methods for thin polycrystalline films, has been of considerable interest for a variety of potential applications.[1] Aside from its use as protective coatings or heat sinks, the modification of the electronic and surface properties of this wide-band-gap material by the incorporation of dopants promises interesting applications.[2–5] Among the techniques suggested to achieve n doping are thermally activated diffusion or ion implantation with or without additional annealing to minimize defect densities.[6,7] All these methods are well known and established in semiconductor processing, but encounter numerous difficulties in the case of diamond, such as graphitization or amorphization of the diamond lattice.[8,9] It has even been suggested recently that lattice defects, respectively sp^2-hybridized carbon atoms, might themselves act as n dopants, rendering a foreign doping material unnecessary.

The two most common crystalline allotropes of carbon, exhibiting strikingly different properties are diamond and graphite. Apart from the crystalline forms of carbon there exists a variety of amorphous structures with varying contributions of sp^3- and sp^2-hybridized carbon atoms, spanning the range from tetrahedral amorphous carbon (90–100 % sp^3, ta-C) to carbon films produced by evaporation or sputtering with about 90% sp^2-hybridized carbon (a-C).[10–12] In contrast to most metals, the ion irradiation of an insulator or semiconductor can lead to the irreversible destruction of the lattice structure, a so-called metamict transformation, and subsequent formation of an amorphous material.[13,14,25] It has already been demonstrated by several authors that such a phase transition upon irradiation is indeed observed for diamond, although the resultant structure of the irradiated layer is still a subject of discussion.[15–17]

Raman spectroscopy and ion channeling, which probe the structural changes in the bulk material, have been the major tools to investigate the effect of ion irradiation in a wide energy range and for a variety of projectiles.[8,9,18–20] Low-energy ion irradiation (below about 5 keV), however, affects only a shallow surface layer with a thickness of at most 100 Å, and therefore more surface-sensitive analytical techniques, such as photoelectron, secondary electron emission, or Auger spectroscopy, are appropriate.[17,21,22]

We employed photoelectron spectroscopy to investigate *in situ* the transformation of a polycrystalline boron-doped diamond film under 1-keV Ar-ion bombardment as a gradual function of ion dose. To complement the results obtained for diamond, we also studied the effect of irradiation on amorphous carbon, prepared by evaporation of graphite. In addition to the observation of the C $1s$ peak and its loss region by x-ray photoelectron spectroscopy (XPS), the influence of irradiation on the valence-band density of states was studied with ultraviolet photoelectron spectroscopy (UPS).
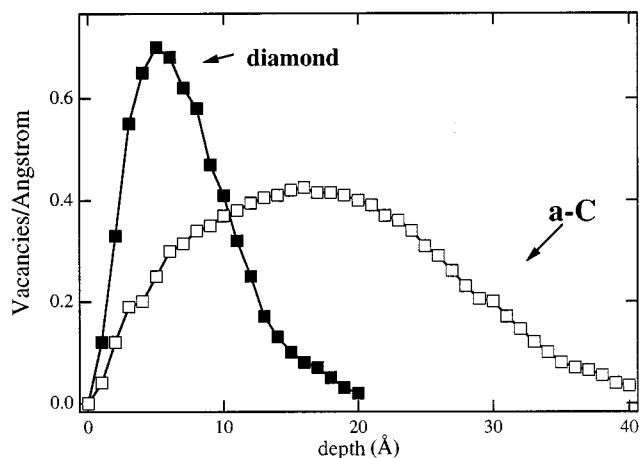
FIG. 1. Vacancy distributions in diamond and amorphous carbon created by ion irradiation with 1-keV Ar$^+$ ions. The angle of ion incidence was 50° for diamond, and normal to the sample surface for the amorphous carbon films. The program TRIM 92 was used for the calculation of the distribution.

II. EXPERIMENT

A. Interaction of low-energy ions with diamond and amorphous carbon

The computer program TRIM (Refs. 9, 23, and 24) (version TRIM 91.00) was employed to calculate the depth distribution of vacancies in diamond and a-C created by irradiation with 1-keV Ar ions, and therefore to ascertain the suitability of photoelectron spectroscopy for this analysis. For the calculation of the primary vacany distribution in the chemical vapor deposition (CVD)-diamond and a-C films the following energies in agreement with data from literature,[26,27] were used: CVD-diamond (ρ=3.5 g/cm^3): E_b=1.5 eV, E_d=40 eV; and for a-C (ρ=2.0 g/cm^3): E_b=1.5 eV, E_d=25 eV. The vacancy distributions for both materials created by irradiation with 1-keV Ar$^+$ are depicted in Fig. 1. The maximum of the distribution is for diamond located at about 6 Å, whereas for a-C the maximum is shifted to a depth of 15–20 Å and is due to the reduced angle of incidence and the lower density of the amorphous material, considerably broader. The sputtering yields are 2.1 and 0.9 atoms/ion for diamond and a-C, respectively. A comparison of the thickness of the irradiation affected layer and the mean photoelectron escape depth (5–8 Å for UPS, and 12–20 Å for XPS analysis[28]) illustrates the suitability of photoelectron spectroscopy to study the effect of low energy ion irradiation on diamond and a-C.

B. Diamond

A semiconducting, boron-doped polycrystalline diamond film was used as substrate. The boron doped diamond film was fabricated by W. Hänni, CSEM, Rue Jacquet-Droz I. CH-2007 Neuchâtel, Switzerland. The film was deposited by means of hot filament chemical vapor deposition (HF-CVD) in a mixture of 1% CH$_4$ in hydrogen at a substrate temperature of 830–850 °C. In order to achieve sufficient doping levels 1 ppm BF$_3$ was added to the process gas. The film does not exhibit a preferential orientation of the diamond

TABLE I. Summary of the irradiation doses (1-keV Ar ions) used for irradiation of the polycrystalline CVD-diamond film and the amorphous carbon films.

Diamond		Amorphous carbon	
	irradiation dose		irradiation dose
$D0$	as deposited	$A0$	as deposited
$D1$	5.8×10^{13} cm^{-2}		
$D2$	1.1×10^{14} cm^{-2}	$A1$	1.5×10^{14} cm^{-2}
$D3$	1.7×10^{14} cm^{-2}		
$D4$	2.5×10^{14} cm^{-2}		
$D5$	3.6×10^{14} cm^{-2}	$A2$	4.3×10^{14} cm^{-2}
$D6$	5.8×10^{14} cm^{-2}		
$D7$	9.6×10^{14} cm^{-2}		
$D8$	1.3×10^{15} cm^{-2}	$A3$	1.3×10^{15} cm^{-2}
$D9$	1.8×10^{15} cm^{-2}		
$D10$	2.3×10^{15} cm^{-2}		
$D11$	2.8×10^{15} cm^{-2}		
$D12$	3.2×10^{15} cm^{-2}	$A4$	3×10^{15} cm^{-2}
$D13$	4.3×10^{15} cm^{-2}		
$D14$	5.4×10^{15} cm^{-2}		
$D15$	6.5×10^{15} cm^{-2}		
$T16$ (3 keV)	1.1×10^{16} cm^{-2}	$B5$	annealing for 10 min, 800 °C

crystals if regarded with scanning electron microscopy. No contamination with the filament material could be detected with x-ray photoelectron spectroscopy and contamination levels are therefore well below 1%. The contamination with oxygen is about 1%.

The photoelectron spectra were measured on a Fisons ESCALAB 210. Monochromatized Al $K\alpha$ (1486.6 eV) radiation was used to record the core-level spectra (MXPS), and the corresponding plasmon loss region on the low-energy side of the C 1s peak. A helium gas discharge lamp emitting light in the ultraviolet region (He I, $h\nu$=21.22 eV, and He II, $h\nu$=40.82 eV) was used to determine the valence-band spectra (UPS). The typical resolution was 0.1–0.2 eV for UPS and 0.2–0.5 eV for MXPS measurements. The spectra have been recorded using a constant retardation ratio for the UPS and a constant pass energy for the MXPS measurements. Except when otherwise stated, the spectra here are presented without background or satellite subtraction. The energies of the discussed spectral features are given with respect to the Fermi level (E_F) and the Au $4f_{7/2}$ core-level line (positioned at 84.0-eV binding energy) of a clean gold sample.

The ion irradiation was performed in situ, and the angle of incidence between the surface normal and the ion beam was 50°. The total ion current to the substrate mounting stage was measured and the beam area was about 1 cm^2, and located in the center of the substrate. The samples were analyzed as a gradual function of ion dose: each irradiation step was followed by a photoelectron spectroscopy analysis, and subsequently the next irradiation step was performed. The accumulated ion doses for each irradiation step are summarized in Table I. For $D1$ to 15 the ion energy was 1 keV, for the last irradiation step an ion energy of 3 keV was used. It was assumed that the area analyzed with photoelectron spectros-

copy was located well inside the ion-beam-affected region. No charging of the film was observed for UPS as well as MXPS measurements.

C. Amorphous carbon

The microscopic structure of these amorphous carbon (a-C) films, which were mostly prepared by sputter deposition or electron-beam evaporation without additional ion bombardment, has been the subject of a number of recent publications.[10–20] It is generally agreed upon that a-C consists of a disordered network built of mainly sp^2-hybridized carbon atoms with less than 15% of the fourfold-coordinated sp^3-hybridized carbon. The carbon network, although called amorphous, does exhibit a certain degree of local order, forming ring structures (graphitic clusters) and olefinic chains. The size of graphitic clusters in the mostly disordered sp^2 network of a-C increases with the substrate temperature and can thus be adjusted by choosing the appropriate deposition conditions,[5,29,30] but a complete graphitization cannot be expected for temperatures below 1500 °C.[9] It should also be mentioned that the graphitic component is much more prominent in a-C films deposited at high substrate temperatures than in films which were annealed at the same temperature.[30]

The amorphous carbon (a-C) films used in this study were prepared by electron-beam evaporation of graphite onto Si(100) substrates. Two different a-C films were deposited: one at ambient temperature [a-C(aT)] and the other one at a substrate temperature of 790 °C [a-C(790°)] (measured by a thermocouple below the substrate). The deposition was performed in a preparation chamber, and the samples subsequently transferred to the analysis chamber without breaking the vacuum. The base pressure was in the low 10^{-9}-mbar region in both chambers, and oxygen concentrations in the films of less than 2% were achieved. The irradiation with 1-keV Ar^+ ions was performed simultaneously for both samples in the preparation chamber, with a Penning ion source (Leybold IPQ/10/63) and the angle of ion incidence was normal to the sample surface. The ion dose could be determined with a Faraday cup placed at the sample position. The irradiation doses, labeled $A1-A4$, are summarized in Table I. The sample which was deposited at elevated substrate temperature was, following the irradiation, subjected to an annealing at 800 °C for 10 min.

The photoelectron spectra were measured on a Leybold EA11/100 ESCA (electron spectroscopy for chemical analysis) system. For the XPS analysis we employed Mg $K\alpha$ radiation (1253.6 eV), and for the UPS spectra a helium gas discharge lamp was used, similar to the one described above. The resolution for the XPS measurements is about 0.9–1.0 eV.

III. RESULTS

A. Diamond

The UPS spectra, for both He I and He II excitations, of the CVD-diamond film are depicted in Figs. 2(a) and 2(b) as a function of ion irradiation dose. The UPS spectra for the untreated film [the bottom of Figs. 2(a) and 2(b)] are dominated by a peak centered at 7.0±0.1 eV, which can be attrib-

uted to excitation from two bands with p character in σ-bonding states.[31–33] The total width of the diamond valence band, however, amounts to about 24 eV, and can therefore not be observed in its entirety by UPS. This is not disadvantageous for our experiment, since the photoelectron excitation cross section for valence bands with p character is enhanced compared to those with s character if the photon energy lies below 130 eV. UPS spectroscopy is therefore especially sensitive to changes in the bonding environment of carbon atoms like the formation of π bonds. For both excitation energies He I and He II, a significant increase in the density of states in the energy range between 3 and 4 eV is observed, and the main peak is shifted to higher binding energies of 8.0±0.2 eV if the ion dose surpasses about 6×10^{14} cm^{-2} ($D7$). The shoulder around 3.5 eV is related to the emergence of p-π states, or, on the molecular level, to the formation of π bonds between sp^2-hybridized carbon atoms. The spectra obtained for the maximum irradiation dose resemble the ones obtained for amorphous carbon deposited at ambient substrate temperature, which are shown in Fig. 5. An estimate of the change in contributions from π states can be given by fitting the He I spectra with three Gaussians centered at ≈12.5, 7.5-, and 3.5-eV binding energy. This procedure, due to the cross section differences for π and σ states, does not yield absolute concentrations of sp^2 and sp^3-hybridized carbon atoms, although it allows a qualitative description of irradiation-induced structural changes. The result of the fitting procedure is summarized in Fig. 3. The contribution from the p-π states or sp^2 carbon atoms remains small and nearly constant for ion doses below about 6×10^{14} cm^{-2} (critical dose), then increases steeply and reaches a constant level of about 0.15. The He II spectra depicted in Fig. 2(b) exhibit an additional peak at 13.2-eV binding energy which is characteristic of diamond. The intensity of this peak begins to decreases at the critical dose, and disappears completely for ion doses exceeding 2×10^{15} cm^{-2}. A further increase in the p-π contributions and the closure of the gap between the valence-band maximum and the Fermi level, which is about 0.3 eV for $D0-D15$, is observed only for the last irradiation step ($T16$).

The considerable modifications of the surface structure induced by ion irradiation, which are expressed in the changes of the density of states in the valence band as observed with UPS, are also apparent in the MXPS spectroscopy of the C 1s core-level peak. The MXPS spectra of the C 1s peaks are depicted in Fig. 4. The bottom curve corresponds to the untreated diamond surface: the symmetric C 1s peak is located at 283.8 eV, and has a full width at half maximum (FWHM) of 1.2 eV, a typical value for a CVD-diamond film. For low ion doses no broadening or shift in the position of the C 1s peak is apparent. For an ion dose of 9.6×10^{14} cm^{-2} the peak maximum is shifted to 284.6 eV and the FWHM has nearly doubled to 2.25 eV. For doses of 2×10^{14} cm^{-2} and higher an upward shift to 285 eV and a slight decrease in the FWHM to 2.05 eV is observed. No further changes are apparent with the last irradiation step $T16$. The C 1s peaks for ion doses ≥9.6×10^{14} cm^{-2} appear to be composed of two components which accounts for the assymmetry and increasing FWHM of the peak. We assume that those two peaks, located at about 285 and 283.8 eV, represent the majority components of the film: first, amor-
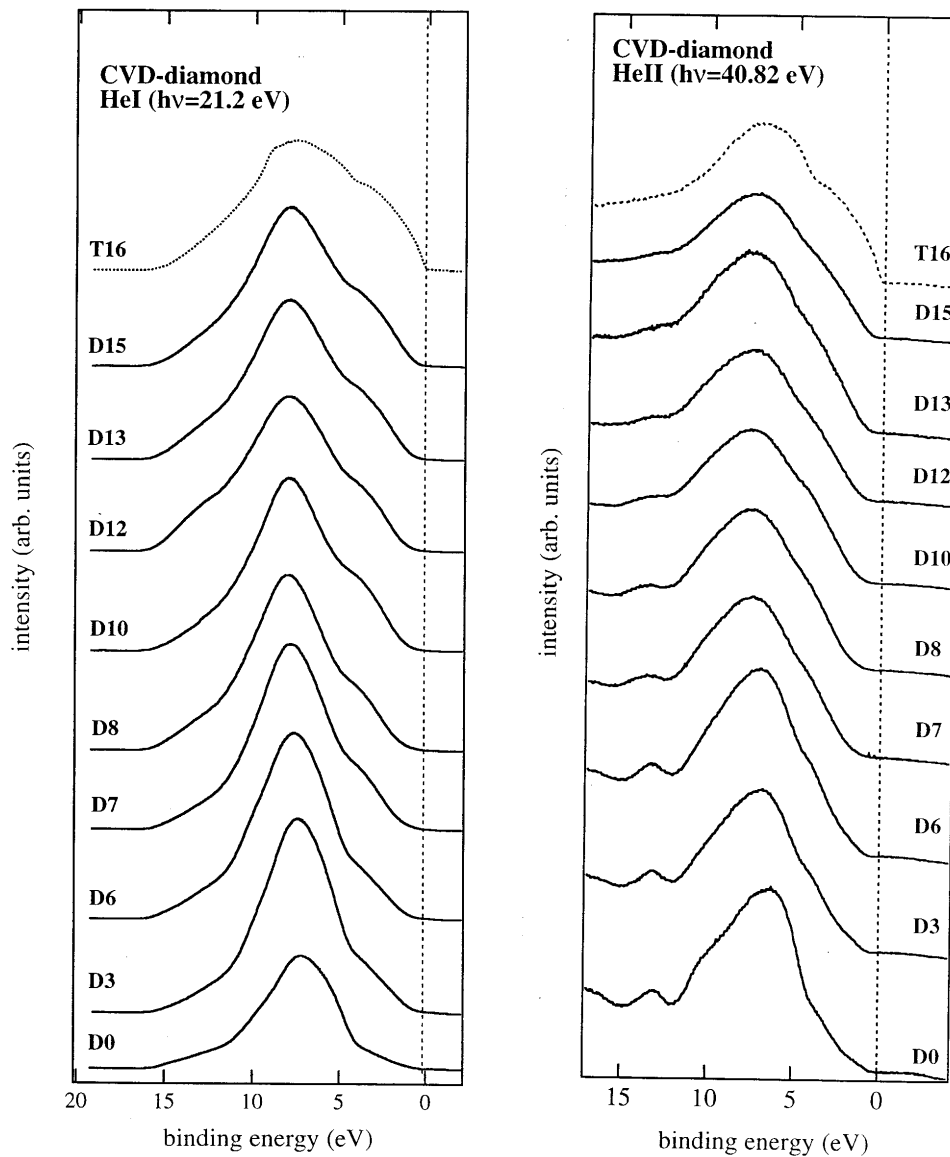
FIG. 2. UPS spectra of the diamond film as a gradual function of ion dose (see Table I).

phous carbon or a strongly distorted diamond lattice, and second, diamond or a weakly distorted diamond lattice. For an increasing ion dose the intensity of the peak associated with a strongly distorted lattice increases, while the contribution of undamaged diamond is diminished. This holds true for doses below $D12$ if the 285-eV peak is assigned to the strongly distorted lattice component. For higher ion doses the low-energy peak seems to gain in intensity again. Lau *et al.*[17] chose a different assignment, and suggested that the low-energy peak stems from the strongly distorted lattice (defect peak), and that the diamond peak is shifted to higher binding energies due to the band bending caused by the introduction of defects. A considerable band bending, as a reaction to the introduction of defects states in the band gap, cannot be discounted, but its magnitude is expected to depend on the nature and density of the defects which surely changes in the course of the experiment. We are, based on our experimental results, at present unable to solve these contradictions, but would suggest an alternative peak assignment as follows: the diamond peak originally positioned at 283.8 eV experiences a shift to higher binding energies whose magnitude varies in the course of the experiment, while the peak associated with a strongly distorted lattice or amorphous phase is located at an energy of about 284.5 eV and does only increase in intensity.

B. Amorphous carbon

Structural differences in *a*-C films deposited at different substrate temperatures [*a*-C(aT) and *a*-C(790 °C)] are readily apparent in the UPS spectra of not-yet-irradiated films which are depicted in Fig. 5 (bottom curves). A detailed discussion on the structural changes of *a*-C with substrate temperature can be found in a recent publication by Schelz *et al.*[30] The *a*-C(aT) spectrum, as a typical example for an amorphous material,[34] is dominated by two broad peaks centered at 3–4 eV (*p*-π) and at 8 eV (*p*-σ). The spectra of *a*-C (790 °C) exhibit a number of quite narrow peaks, which coincide with transitions at critical points in the band structure of graphite,[35,36] but appear to be smeared out as compared to polycrystalline graphite. Although the *a*-C(790 °C) film is certainly more graphitic in nature and
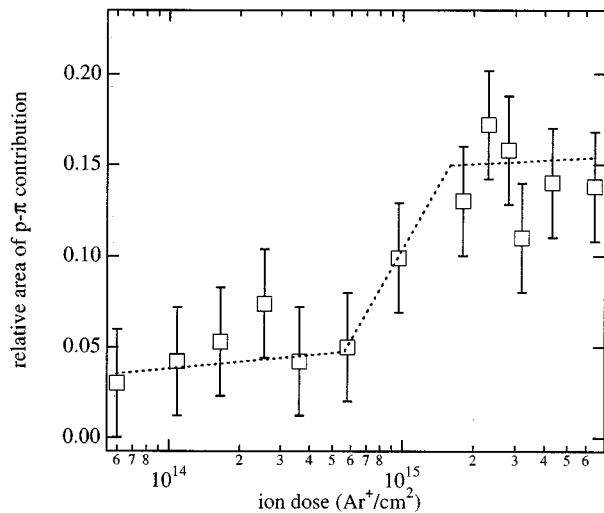
FIG. 3. Relative area of the p-π band contribution to the He I spectra of diamond as a function of ion dose.

FIG. 5. UPS spectra (He I) of the amorphous carbon films deposited at ambient substrate temperature [a-C(aT)] on the left-hand side, and deposited at elevated substrate temperature [a-C(790°)] on the right-hand side as a gradual function of ion dose (see Table I).

does contain distinct graphitic clusters, it still consists partially of an amorphous network.

It is observed that for increasing ion dose the features associated with graphitic structures in the UPS spectra of the a-C(790 °C) film are broadened, or rather that the valleys between the narrow peaks are gradually filled. The peak
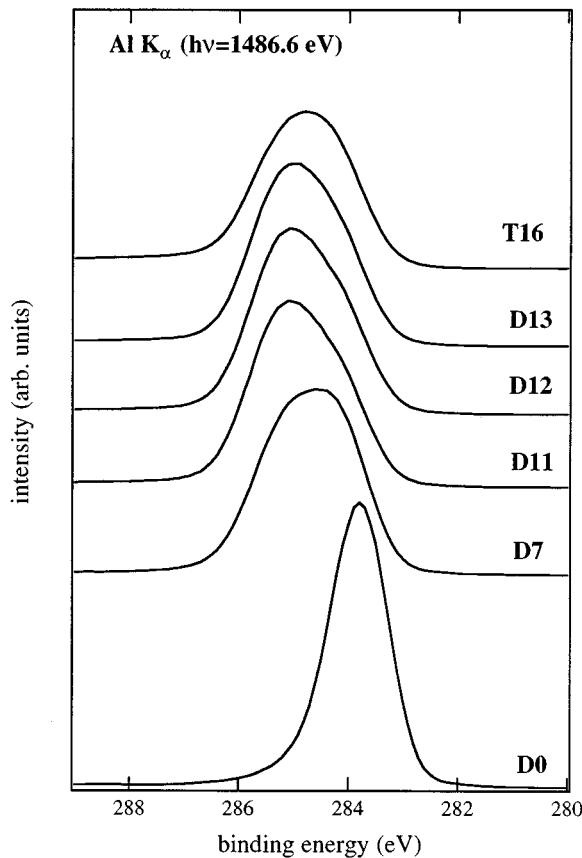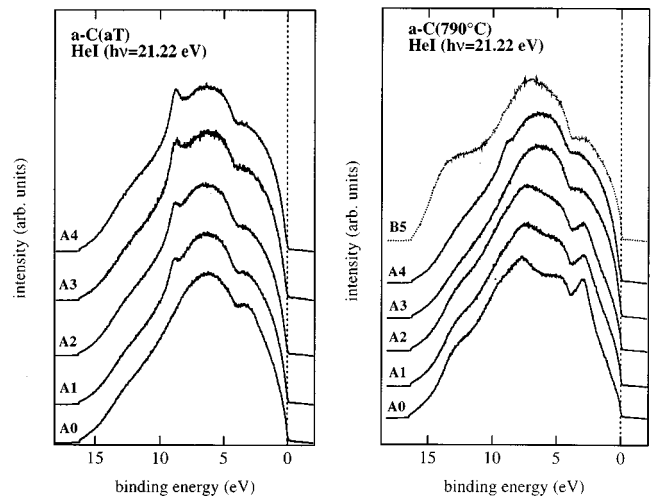
which appears at 8.7 eV binding energy is due to an excitation from the Ar $3p$ level, and thus illustrates the successive incorporation of Ar into the film in the course of the irradiation. The spectra obtained for the maximum ion dose of 3×10^{15} cm^{-2} are very similar to the ones obtained for the a-C film deposited at ambient temperature, and contrary to our findings for the CVD-diamond film no amorphization threshold or critical dose is observed. The damage introduced by the irradiation can only be partially reversed through the annealing step B5, a result already suggested in earlier experiments.[30]

No changes in the appearance of the UPS as well as XPS spectra are observed for the a-C(aT) film upon ion irradiation. Ar is again incorporated into the amorphous matrix, but the amount of Ar retained in the film matrix is smaller for the more graphitic film, at least before the ion irradiation leads to the destruction of the graphitic clusters.

The increasingly amorphous character of the a-C(790 °C) film is also apparent in the XPS spectra of the C $1s$ core level. The maximum of the C $1s$ peak is centered at 284 eV for the untreated film, and is shifted slightly to 284.15 eV for the maximum ion irradiation dose. The FWHM also increases with the ion dose from 1.4 to 1.9 eV, which is equivalent to the FWHM of the a-C(aT) film. Neither the position nor the FWHM of the a-C(aT) film changes significantly in the course of the ion irradiation.

IV. DISCUSSION

It is apparent from both UPS and MXPS analyses that the modification of the diamond surface layer which is affected by ion irradiation does not proceed continously from an undamaged to a predominantly amorphous structure. The onset of considerable structural changes in the diamond lattice, apparent in the diminished intensity of the peak at 13.2 eV (He II) increasing contributions from p-π states at 3–4 eV (He I, He II), and the broadening of the C $1s$ core-level peak (MXPS), is observed for a critical dose of about 6×10^{14} cm^{-2}.

FIG. 4. MXPS spectra of the carbon $1s$ spectral region of the CVD-diamond film.

The observation of a similar threshold behavior has been reported in several publications, and is also apparent if the changes in film conductivity with ion dose are monitored.[22] The conductivity exhibits a small increase for ion doses around 10^{14} cm^{-2}, decreases again, and then finally for an ion dose around $5–10\times10^{14}$ cm^{-2} a steep increase is observed, which is connected to the higher level of damage in the lattice. Surprisingly similar values for the critical dose are reported for a variety of projectiles and energies.[8] However, only scarce information about the nature of the structural changes can be deduced from these measurements and the UPS analysis, as discussed in Sec. III is much more informative in this respect. The UPS spectra clearly show the tendency of the diamond lattice under irradiation to become amorphous rather than to graphitize. No indication of the formation of graphitic clusters can be seen in the UPS spectra, and even for the highest ion dose the spectra closely resemble the ones of a-C(aT). There is also no indication of the presence of a tetrahedral-amorphous component which was suggested by Hofmann, Prawer, and Kalish[22] as an intermediate configuration formed in the course of the irradiation experiment. But we have to concede that it might be quite difficult to distinguish a ta-C phase from diamond in the UPS spectra. However, the C $1s$ plasmon loss region, which was recorded for doses $D0$, $D7$, $D13$, and $T16$, does not exhibit the plasmon located at 30-eV energy loss, typical of a ta-C network.

We suggest that for an ion dose below the threshold value, only localized defects are present in the lattice, which have according to Prins,[37] the ability to recombine if appropriate annealing conditions are chosen. Further increase of the ion dose, and therefore of the level of damage in the lattice, leads to the formation of extended defect regions, with a structure similar to amorphous carbon; this transition is reflected in the UPS spectra. For an ion dose of more than 3×10^{15} cm^{-2}, no further increase in the p-π band contributions is observed, and it can be assumed that an equilibrium between the production of defects and the removal of surface atoms by sputtering is reached. A higher level of damage and a further destruction of the diamond lattice (amorphization) can only be achieved now with an increased ion energy.

The observation of the effect of ion irradiation on a-C films does complement the findings for the CVD-diamond film. It is apparent that the destruction of the graphitic clusters in the a-C(790 °C) film does take place even for the lowest ion dose used in this experiment. The resultant spectra are very similar to the ones obtained for diamond and for the as-deposited a-C(aT) film. This also explains the absence of distinctly graphitic features in the CVD-diamond film: even if graphitic clusters are formed in the diamond matrix, they would be immediately destroyed in the course of the subsequent irradiation, as they appear to be much more susceptible to damage than the original diamond lattice. The a-C(aT) film does not, as expected, undergo any considerable changes in its structure. This underscores that the a-C structure represents the most stable configuration which is reached under ion irradiation.

V. CONCLUSIONS

Three carbon films of different structure, namely, diamond, a-C [a-C(aT)], and an a-C film which contained graphitic clusters [a-C(790 °C)], were irradiated with 1-keV Ar ions. The changes in the electronic structure were monitored *in situ* with photoelectron spectroscopic methods (XPS and UPS), and were related to the modification or destruction of the diamond and graphite lattice. For diamond we observed considerable structural changes when the ion dose surpasses a critical dose of about 6×10^{14} cm^{-2}. The critical dose is characterized by a considerable increase in the contributions stemming from p-π states in the UPS spectra, a diminished intensity of the peak at 13.2 eV (He II), and the broadening of the C $1s$ core-level peak (MXPS). The spectra clearly show the tendency of the diamond film to form an amorphous rather than graphitic network under ion irradiation. In contrast to the observation of a critical dose for diamond the destruction of graphitic clusters in a-C(790 °C) is apparent in the spectra even for the lowest ion dose. The resultant film structure is indistinguishable from amorphous carbon, or respectively, the a-C(aT) film. The amorphous a-C(aT) film does not exhibit any changes in its electronic structure under ion irradiation. This supports the assumption that a-C represents the most stable structure which is reached under ion irradiation of carbon.

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