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Enhanced electron emission from oxidized regions on amorphous carbon films studied by X-ray spectro-microscopy.

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Photoemission electron spectro-microscopy with synchrotron radiation has been used to study the correlation between the chemical surface composition and electron emission properties of amorphous carbon films. Regions of about 4 micrometer diameter were found which exhibited up to 10 times higher secondary electron emission than the rest of the film. Near edge x-ray absorption fine structure spectroscopy of these regions showed that they contained highly oxidized carbon in the form of carboxylic and carbonate groups. These observations are directly linked to the field emission properties of the films.

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Amorphous carbon films can be grown with a high proportion of sp^3 hybridized atoms [1,2,3,4,5], and have mechanical and electronic properties close to those of diamond [6]. Such films have potential applications as electron emitters in electron field emission devices [6,7]. Diamond films deposited by chemical vapor deposition (CVD) are already promising candidates for field emission displays [7]. Amorphous carbon films have practical advantages over CVD diamond films because they are uniform, inexpensive to make and compatible with existing silicon technology. So far, however, their field emission properties [8, 9] are inferior to those of CVD diamond films [7,10]. High enough emission currents, useful for field emission displays technology, are only observed in localized regions of these films [11]. High field emission from localized regions has also been observed in non-hydrogenated amorphous carbon films [12], and it seems to be an intrinsic property of amorphous carbon surfaces. There is no clear understanding of the physical process leading to the field electron emission from such surfaces. A possible reason is the presence of contaminants on the carbon surface which lowers their work function. This has been observed in CVD diamond and diamond, whose electron field emission characteristics improve when their surfaces are treated with oxygen or hydrogen [10,13,14,15]. For all surfaces a microscopic chemical analysis is lacking owing to the difficulties of obtaining spectroscopic information for microscopic surface areas.

The combination of photoemission electron microscopy (PEEM) with synchrotron radiation is well suited for the study of field electron emission from carbon surfaces. PEEM provides images of the sample surface by collecting the photoemitted secondary electrons. It therefore gives a map of the secondary electron yield from the surface, laterally resolved at a submicron scale. In a photoemission experiment a high secondary electron yield is evidence for a low vacuum barrier and it can be correlated with the field emission characteristics of the emitting surface [13,14]. By using x-ray excitation and scanning of the x-ray energy the secondary electron yield, which is proportional to the x-ray absorption coefficient of the sample, also provides spectroscopic information through the near edge x-ray absorption fine structure (NEXAFS) [16]. The combination of NEXAFS spectroscopy and PEEM thus provides elemental and chemical characterization of the surface with a lateral resolution given by the PEEM optics. NEXAFS spectroscopy is particularly powerful for carbonaceous materials since the detailed spectral resonances at the carbon K-edge

identify the bonding environment of the carbon atoms in the sample, e.g. the presence of C-O bonds and their hybridization[16].

The x-ray spectromicroscopy studies of amorphous carbon films reported here revealed inhomogeneities in the secondary electron emission from their surface. We identified small areas, of about 4μm diameter, with an up to 10 times enhanced electron yield over the rest of the film. The number of these regions across the amorphous carbon surface was about 20 per cm^2. NEXAFS analysis of the regions showed that they contained oxidized carbon, in particular, carbonate ($-CO_3$) groups. The oxygen concentration outside the regions was considerably lower and mostly consisted of saturated C-O (i.e. alcohol (-C-O-H) and ether (-C-O-C-)) and carbonyl (–C=O) groups. The increased oxidation of the local regions is argued to be the origin of their enhanced field emission.

Samples were grown by cathodic arc deposition on silicon wafers. The deposition parameters were chosen to obtain the highest concentration of sp^3 hybridized carbon atoms in the film. Details of the deposition process and the characteristics of the films are published elsewhere [1,17]. Samples were exposed to air before introduction into the microscope chamber. The pressure in the chamber during measurements was $2x10^{-9}$ mbar. A technical description of the PEEM microscope used in the experiment can be found in reference 19. For the present studies the microscope had a resolution of 0.4 μm. The highest accelerating field strength was 5 V/μm. This electrical field was below the field strength necessary to obtain a measurable field emission current from the sample [8,11], as was tested by turning off the x-ray beam. Experiments were carried out at the Stanford Synchrotron Radiation Laboratory, using soft x-ray radiation from the spherical grating monochromator on beam line 10.1. The x-ray angle of incidence was 30 degrees from the sample surface and the size of the x-ray beam spot at the sample was $0.2x1mm^2$. The x-rays were linearly polarized with the polarization vector in the plane of the sample. NEXAFS spectra were recorded with a resolution of 0.15eV at the carbon K-edge and 0.3 eV at the oxygen K-edge. The photon energy was calibrated using the π^* resonance position in the carbon K edge spectrum of graphite (285.4 eV) [18]. For the oxygen K-edge, photon energy calibration was done using the π^* resonance position of carbonate (534 eV) within the high emitting regions [22]. The intensity of the spectra was normalized to the incident photon flux by recording the current from a

clean silicon wafer for the carbon K-edge [16,20], and from a freshly evaporated gold grid for the oxygen K-edge. NEXAFS spectra of micron-sized regions were recorded with an energy step size of 0.2 eV and an integration time of 30 seconds per point.

Figure 1(a) shows a PEEM image of the surface of an amorphous carbon film. The image was taken with zero order radiation (white beam, non-monochromatic x-rays), which gave higher photon flux the monochromatized beam. The gray scale in the PEEM image is linear with the intensity of the secondary electron emission, it is black for no intensity, and white for the highest intensity. The image clearly shows a region of about 4 μm diameter, that is brighter than the rest of the film. The intensity profile across the image is displayed in figure 1(b), showing an almost ten times larger intensity in the bright region than outside the region. We observed no changes in the NEXAFS spectra, indicative of radiation damage, at the used flux densities of $3x10^{15}$ photons·sec^{-1}·cm^{-2}. The secondary electron yield from all regions of the sample changed linearly when the photon flux was reduced by monochromatization to about $5x10^{13}$ photons·sec^{-1}·cm^{-2}.

NEXAFS spectra at the carbon and oxygen K-edges were recorded for areas of similar diameter inside and outside the bright region by measuring the intensity within these areas as a function of the photon energy. The normalized spectra are displayed in figures 2 and 3. The carbon K-edge NEXAFS spectrum of the bright region (fig. 2 (a)) is clearly different from the spectrum taken outside the region (fig. 2 (b)). It exhibits prominent peaks A at 284.7 eV, C at 288.7 eV, and D at 290.1 eV. A broad intensity maximum E is centered around 300 eV. The spectrum recorded outside the region (figure 2(b)) only exhibits one sharp peak A at 284.7 eV and a broad peak centered at about 297 eV.

Strong differences between the spectra of each region are also observed at the oxygen K-edge. The spectra taken inside and outside the bright region are displayed in figures 3(a) and (c), respectively. Both spectra were obtained with the same acquisition time. The oxygen signal from the outside region is within the noise, indicating a much lower concentration of oxygen than in the bright regions. The spectrum displayed in figure 3(b) correspond to that of the total area illuminated by the x-rays. It shows better the kind of oxygen present outside the bright region, since the contribution from the bright areas to the total signal is negligibly small. The NEXAFS spectrum exhibits a π^* resonance centered at about 531 eV, and an asymmetric σ^*

resonance with a maximum near 538 eV. In comparison, the spectrum inside the bright region has more fine structure.

The various peaks in the NEXAFS spectra can be assigned by considering both the C and O K-edge spectra and comparing them to published spectra of different functional groups [16]. These assignments are summarized in table I. The C K-edge spectrum outside the bright region shown in figure 2(b) consists of a C=C π^* resonance at 284.7eV and a broad σ^* resonance centered around 297eV, characteristic for amorphous carbon. The O K-edge exhibits a C=O π^* resonance around 531eV and a broad σ^* resonance around 538eV. The spectral features indicate that O contamination in the films or on the surface is present in the form of carbonyl (C=O) and saturated groups such as alcohols (-C-O-H) or ethers (-C-O-C-).

The spectrum of the bright region contains the same structure as that taking outside the bright region plus additional fine structure. The peaks labeled C' and D' in figure 3(a) are assigned to transitions from the oxygen 1s level to π^* orbitals between carbon and oxygen in carboxylic and carbonate groups, respectively. This identification agrees with the presence of the corresponding resonances C and D in the carbon K-edge spectrum at 288.7 eV and 290.1 eV, arising from transitions from the carbon 1s level to the same π^* orbitals. Resonance E' at 545eV corresponds to a σ^* resonance associated with the carbonate group. The carboxylic group has two σ^* bonds associated with the C-O and C=O bonds, which should give rise to broad peaks around 539 eV (G') and 543 eV (H'), respectively. [16]. These peaks are superimposed on other structures and are only partly visible.

The thickness of the oxidized carbon can be estimated assuming that the π^* resonance at 284.7 eV is associated only with C=C bonds in the amorphous carbon, which acts as a substrate to the oxidized layer. The thickness of the oxidized layer was determined by the following procedure. The spectrum for the outside region (fig. 2 (b)), multiplied by a weight factor f, was subtracted from the spectrum of the bright region (fig. 2 (a)) so that the intensity of the peak at 284.7eV is eliminated. The empirically determined weight factor f is determined by the attenuation of the amorphous carbon signal by the oxidized carbon layer of thickness t. It is given by $f=e^{-t/L}$, where L is the escape length of the secondary electrons through the oxidized layer. Taking the escape length of secondary electrons to be L=10 nm [21], the thickness of the oxidized layer was estimated to be 2.9 nm.

The oxidized regions on amorphous carbon films are likely formed when their surfaces are exposed to air. The same kind of bright regions appeared in amorphous carbon films deposited by laser ablation, with different sp^2 content and produced in a different laboratory. Although not detected, it can not be excluded that a low concentration of metallic impurities, created during deposition and/or sample manipulation, serve as nucleation points for these regions, or as anchoring sites for the carbonate radicals [22].

We identify the bright regions with the high field emission spots observed in these films because of their enhanced electron yield. Their concentration also matches the concentration of high field emission spots observed in other experiments [12]. We propose that the vacuum barrier is lower in the oxidized regions, in particular in the highly oxidized carbonate component. Our observations corroborate other observations on CVD diamond where increased field emission currents were observed after oxygen adsorption [10,13,23]. For these surfaces, the proposed mechanism consisted of a lowered vacuum barrier by dipole formation at the surface or band bending due to surface states created by the adsorption of oxygen [24]. Since carbonate is an insulator, another possible mechanism for lowering the vacuum barrier is by photocharging during x-ray illumination and consequent band bending of the oxide layer [25]. The estimated thickness of the oxide layer seems too small for stable charge accumulation. However, the presence of charge trapping is suggested by the fact that the spectra in the bright regions exhibited a larger noise than those recorded outside the regions. This indicates time dependent variations in electron yield due to charging [25,26].

In conclusion, we have demonstrated a spectro-microscopy method for the investigation of electron field emission surfaces which allows chemical characterization of submicron areas. The secondary electron yield from amorphous carbon surfaces illuminated by x-ray radiation was mapped. Regions of about 4μm diameter were observed whose electron yield was up to ten times higher than the rest of the film. These regions were shown to be enriched in carboxylic and carbonate groups. The highly oxidized carbon areas are shown to be responsible for enhanced electron emission. The present work suggests that the treatment of amorphous carbon surfaces with oxygen, in a way that the final surface is uniformly covered with highly

oxidized carbon, e.g. in a phase rich in carbonate, should increase the electron field emission currents from these films.

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Figure Captions

Figure 1. (a) PEEM micrograph of the surface of an amorphous carbon film. Accelerating field strength was 5 V/μm. (b) Intensity profile across the bright region.

Figure 2. Carbon K-edge spectra (a) inside, and (b) outside the bright region. Spectra were normalized to the intensity at 340 eV. Spectrum in (c) results from the subtraction of spectrum (b) from spectrum (a) as explained in the text.

Figure 3. Oxygen K-edge spectra (a) inside, and (c) outside the bright region. The spectrum in (b) corresponds to that of a macroscopic sample region and is dominated by the contributions from the areas between the bright spots.

Tables

Table I. Assignment of the resonances indicated in the NEXAFS spectra at the oxygen and carbon K-edges in figures 2 and 3.

Peak Position C-K edge	Peak Position O-K edge	Assignment
A 284.7 eV	-	π^* C=C
B 286-287 eV	B' 531-532 eV	π^* C=O
C 288.7 eV	C' 533 eV	π^* C=O (-COOH)
D 290.1 eV	D' 534 eV	π^* C=O (-CO3)
E 300. 5 eV	E' 545 eV	σ^* C-O (-CO3)
-	F' 537.4 eV	σ^* C-O (-C-OH)
-	G' 539.4 eV	σ^* C-O (-COOH)
-	H' 543 eV	σ^* C=O (-COOH)

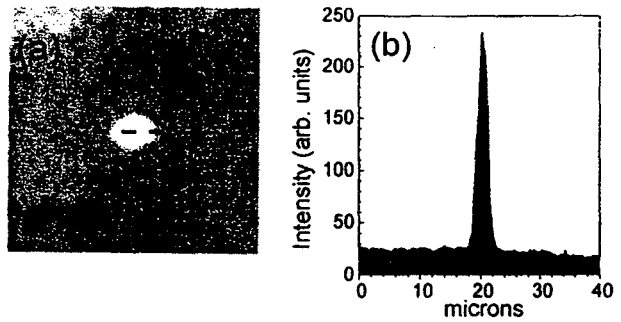
(a)
(b)
Intensity (arb. units)
250
200
150
100
50
0
0
10
20
30
40
microns

Figure 1(a) & (b)

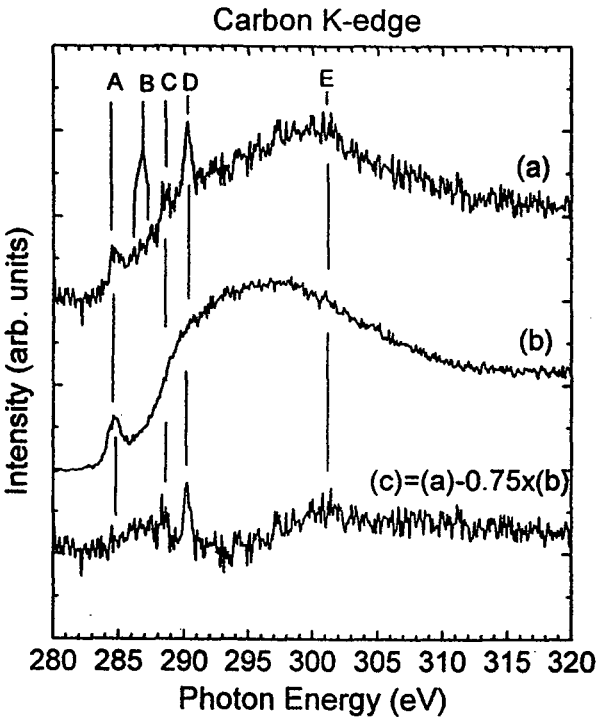
Carbon K-edge
A
B
C
D
E
(a)
(b)
(c)=(a)-0.75x(b)
Intensity (arb. units)
280
285
290
295
300
305
310
315
320
Photon Energy (eV)

Figure 2

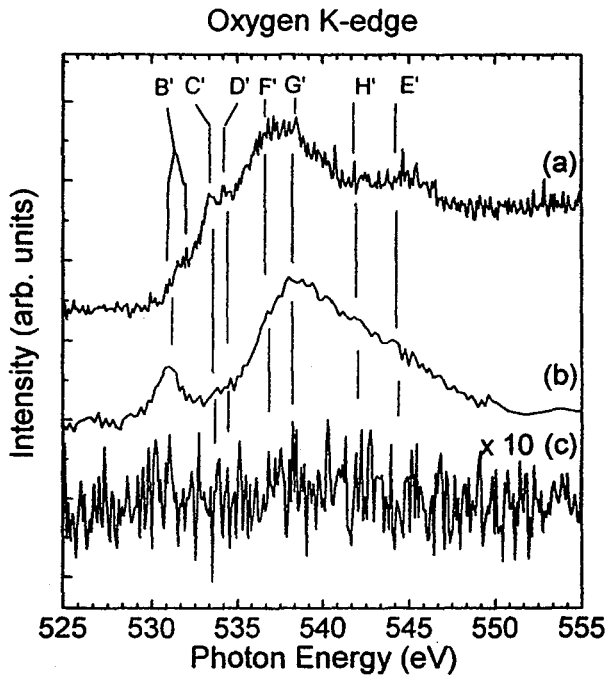
Oxygen K-edge
B' C' D' F' G' H' E'
(a)
(b)
x 10 (c)
Intensity (arb. units)
525 530 535 540 545 550 555
Photon Energy (eV)

Figure 3

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