

Z-contrast imaging and electron energy-loss spectroscopy analysis of chromium-doped diamond-like carbon films

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(Received 30 April 1999; accepted for publication 31 August 1999)

Metal-doped diamond-like carbon films were produced for the purpose of an electrochemical nanoelectrode. In this study we use Z-contrast scanning transmission electron microscopy to directly observe metal cluster formation and distributions within the chromium-doped carbon films. At low doping (~ 6 at. % Cr), Cr is uniformly distributed within the C matrix; at high doping (~ 12 at. % Cr), Cr-rich clusters are formed. Analyzing electron energy loss spectroscopy Cr $L_{2,3}$ white line ratios, we find that the Cr tends to be metallic-like when it is uniformly distributed in the C matrix and carbide-like in the Cr-rich clusters. The carbon is more diamond-like at low doping and more graphite/carbide-like at high doping according to the sp^2/sp^3 electron percentage measurements.

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Diamond-like carbon (DLC) is a very promising material with a wide variety of potential applications due to its unique diamond-like properties.¹ Doping with metals could create a two dimensional array of metal clusters within the diamond-like carbon matrix. Such composite structures are of interest for use as nanoelectrodes in electrochemistry.² The formation and distribution of the metal clusters within the carbon film are fundamentally important for the physical properties of the material. Here we study the structure and chemistry of chromium-doped DLCs using Z-contrast electron imaging and electron energy loss spectroscopy (EELS). We assess the structure of the diamond matrix by quantifying the percentage of sp^2 bonding from the EELS C K edge, and we investigate the distribution and bonding of Cr within the DLC matrix.

In this work we employ the Z-contrast electron imaging method because it is more directly interpretable than conventional phase contrast imaging.³⁻⁵ Using an annular dark-field detector in the scanning transmission electron microscope (STEM), only the high angle scattering of electrons are collected, where the total scattering intensity is proportional to the square of the atomic number, Z . The Z-contrast image can directly reveal atomic positions as the brighter spots correspond to the positions of heavier atoms. The EELS data can be collected simultaneously through the hole of the dark-field detector allowing direct correlations between the images and spectra.

Diamond-like carbon films of 0.1–5.0 μm thickness were grown on alumina substrates using a plasma chemical deposition technique described elsewhere.⁶ The doping of chromium was performed by coevaporation of chromium

into the reactor volume while growing the carbon film.^{7,8} The carbon film was prepared for transmission electron microscopy by mechanical dimpling from the substrate side and ion beam milling to electron transparency. Two samples doped at low (~ 6 at. % Cr) and high levels (~ 12 at. % Cr) were examined by Z-contrast imaging in a VG HB603 STEM and a VG HB501. The EELS data were collected on VG HB501 STEM and Philips CM200 transmission electron microscopes.

Figure 1 is a phase contrast image of highly doped sample which is similar to a typical amorphous structure.^{7,8} The Cr is not readily distinguishable. Figure 1(b) is a dark-field Z-contrast image of the same area. Since Cr atoms are heavier than C, the brighter areas directly correspond to Cr-rich regions. The average Cr-rich cluster size is estimated to be 2 nm with a separation of 3.5 nm between clusters. The low-doped sample does not show any Cr-rich regions, indicating uniform Cr distribution throughout the DLC matrix (picture not shown).

The EELS spectra of carbon the K edge and Cr L edge were collected from both samples, as well as from reference samples of chromium carbide Cr_3C_2 , metallic Cr and synthetic graphite. Spectra, shown in Figs. 2(a)–2(e), were taken in image mode from a scanned area of approximately 100 nm^2 . Since the highly doped film has uneven Cr distribution, spatially resolved EELS were also collected on the VG HB501 with a probe size less than 3 Å from both Cr-rich regions and Cr-deficient regions, as shown in Fig. 3. The probe position was determined from the Z-contrast image taken simultaneously with the EELS spectra. Using the intensity ratio of I_C and I_{Cr} and calibrating with the reference sample Cr_3C_2 , the concentrations of Cr are found to be an average of 6% for the low doped sample. For the highly doped sample, bright regions show 7–17 at. % Cr whereas dark regions show 1–3 at. % Cr.

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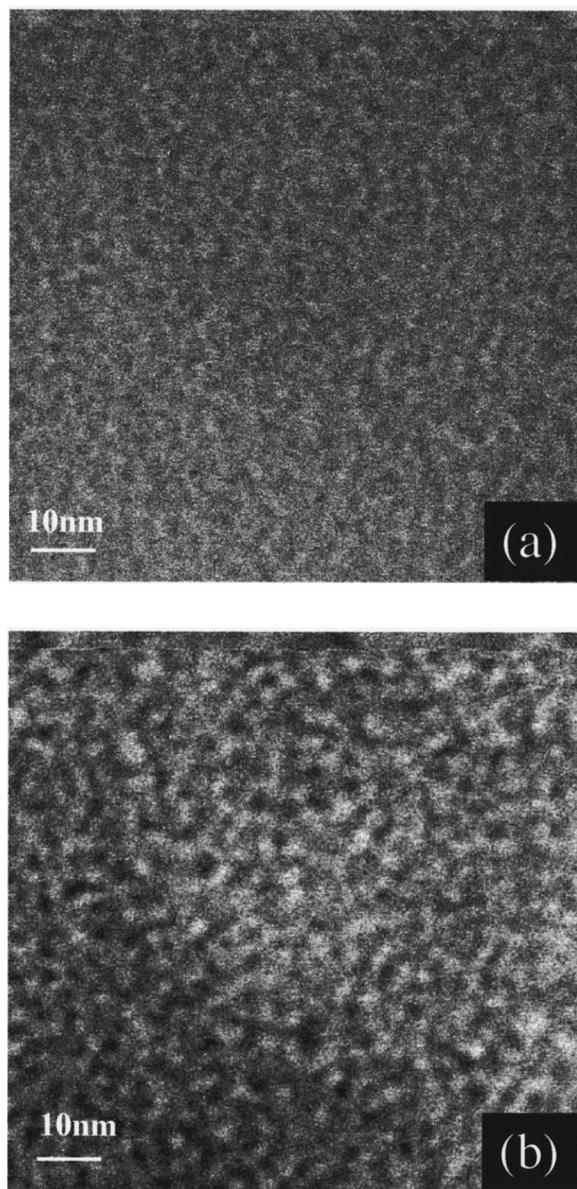


FIG. 1. Chromium doped diamond-like carbon. (a) Phase contrast image showing amorphous carbon matrix. (b) Z-contrast image showing Cr clusters.

All chromium L edges have similar features comprising two sharp peaks L_2 and L_3 , known as “white lines,” and a continuum background following the edge. The L_3/L_2 white line ratio, R_w , is correlated to the electron occupancy and spin pairing in $3d$ band.^{9–12} The variations of the white line ratio are due to the interaction between chromium and surrounding atoms. For example, a large increase of R_w in the chromium alloy $\text{Cr}_{20}\text{Au}_{80}$ reflects the dramatic increase of the magnetic moment.⁹ However, it is also found that the white line ratio is sensitive to Cr cluster size when deposited on a graphite substrate.¹⁰

In our case it is interesting to compare the Cr-doped DLCs with metallic Cr and chromium carbide. The white line ratios, R_w , calculated using the standard method,¹² are listed in Table I. The white line ratios in low-doped samples are close to metallic Cr. In the highly doped sample, they are close to carbide in the Cr rich region and metallic in the Cr deficient region. So, it appears that after a critical doping

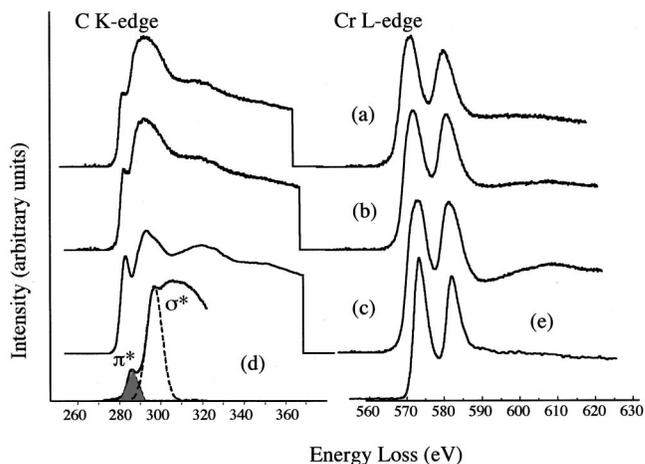


FIG. 2. EELS of carbon K edge (left) and Cr L edge (right). (a) Low doped DLC, (b) highly doped DLC, (c) chromium carbide, and (d) graphite. The σ^* peak is partially fitted by a Gaussian function as shown by the dashed curve. The shaded area is the π^* peaks obtained by subtracting the σ^* fitting. (e) Metallic Cr.

level, Cr-carbide clusters precipitate from the DLC matrix.

Since the introduction of chromium may change the structure of the carbon, it is also important to evaluate the electronic properties of the carbon. The major difference between a graphite-like carbon and a diamond-like carbon is the absence of π electrons in diamond-like material. This feature is shown in the EELS spectra in Figs. 2(a)–2(d) where the π^* peak is at about 284 eV. By measuring the intensity ratio of this peak against the following broad σ^* peak, and then calibrating with the known graphite structure, the percentage of sp^2 bonding in the many forms of pure carbon can be determined.

Several methods have been used to measure the sp^2 percentage from the EELS $C K$ edge which involve selection of a fixed window for the π^* peak integrated intensity.^{13,14} We find these methods to be insufficient for our study because they do not take into account potential contributions to π^* integrated intensity from the overlapping σ^* peak. As can be seen, some of our spectra have higher relative intensity in the π^* peak region than that of graphite. This leads to the unrealistic result of higher sp^2/sp^3 ratio than graphite. It is believed that the broadening of the σ^* peak causes the increased intensity at π^* peak region. It was therefore

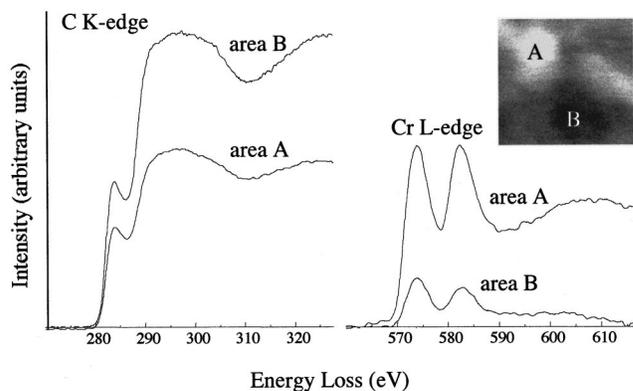


FIG. 3. The inset is a portion of the Z-contrast image. Spatially resolved EELS spectra of the $C K$ edge and Cr L edge were collected at bright area A and dark area B, respectively.

TABLE I. The Cr concentration % Cr, peak intensity ratio $I_{\pi}/I_{\pi+\sigma}$, sp^2 percentage and Cr white line ratio R_w , obtained from low doped (DLC-1), highly doped (DLC-h) at Cr rich area (A), and Cr deficient area (B), the reference samples chromium carbide (Cr_3C_2), metallic Cr and graphite.

	at. % Cr	R_w	$I_{\pi}/I_{\pi+\sigma}$	% sp^2
DLC-1	6%	1.7	0.047	56%
DLC-h(A)	7%–17%	1.4	0.13	...
DLC-h(B)	1%–3%	1.7	0.11	100%
Cr_3C_2	60%	1.35	0.15	...
metallic Cr	100%	1.63
graphite	0%	...	0.11	100%

necessary to use a modified version that takes into account this broadening effect.¹⁵ We demonstrate this method for the case of graphite in Fig. 2(d). The front edge of the σ^* peak is partially fitted with a Gaussian function as indicated by the dashed curve. The π^* function is obtained by subtracting the σ^* function in the π^* region, resulting as the shaded small peak. Then the relative peak ratio $I_{\pi}/I_{\pi+\sigma}$ is defined as the total intensity of the π^* peak divided by the total intensity of a fixed energy window in the original spectrum. We choose this range from 280 to 300 eV consistently for all the spectra. For pure carbon materials, the actual sp^2/sp^3 ratio can be determined by calibrating with pure graphite for which the percentage of sp^2 is 100%.

Our measurements on DLC samples are summarized in Table I. The low-doped sample shows about 56% sp^2 , i.e., 44% sp^3 bonding. In the highly doped material we have the additional complication of carbide formation. The Cr_3C_2 standard shows a $C-K$ edge structure with a strong peak at about 284 eV, the same energy as the π^* electron peak in graphite [see Fig. 2(c)]. Therefore, the sp^2/sp^3 ratio cannot be determined in Cr-rich regions where the Cr edge indicated carbide formation. The Cr-deficient region shows no evidence of carbide formation, the Cr edge indicating metallic bonding. Here the sp^2/sp^3 ratio could be analyzed, and the percentage of sp^2 bonded carbon is found to be almost 100%. We do not believe beam broadening to be a significant factor limiting our spatial resolution; we estimate beam broadening in a 20-nm-thick film to be only ~ 2 nm, which is comparable to the size of the Cr-rich and Cr-deficient regions. However, if the Cr signal from the Cr-deficient region was actually due to beam broadening into the adjacent Cr-rich area, the white line ratios would be identical in the two areas. In fact, the white line ratio indicates a change in bonding type, implying we do have the necessary spatial resolution.

In summary, we have directly imaged the Cr distribution in Cr-doped diamond-like carbon films by Z-contrast imaging. There is a critical change in Cr distribution from low to high level doping. The carbon in a low doped sample maintains its diamond-like features; the Cr is uniformly distributed throughout the matrix and maintains metallic bonding. This implies no strong interaction between carbon and Cr. High Cr doping leads to the formation of chromium carbide clusters. The residual Cr in between the clusters remains metallic-like, however the C loses its sp^3 -type bonding. Therefore the diamond-like carbon network breaks down at high Cr doping.

This research was sponsored by the NSF-MRSEC Advanced Carbon Materials Center under Grant No. DMR-9809686, and by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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