Evidence of surface defects in ultrathin tetrahedral amorphous carbon films probed by x-ray absorption spectroscopy

S. S. Roy, R. McCann, P. Papakonstantinou, G. A. Abbas and J. A. McLaughlin

Northern Ireland Bioengineering Centre- Nanotechnology Research Institute, University of Ulster at Jordanstown, Northern Ireland, United Kingdom. (s.roy@nibec.ulster.ac.uk)

ABSTRACT

The tetrahedral amorphous carbon (ta-C) films with thickness 1-10 nm were obtained by filtered cathodic vacuum arc deposition and investigated by near edge X-ray absorption fine structure (NEXAFS) and Raman spectroscopies. The C K (carbon K) edge NEXAFS spectra clearly revealed that the C=C bonds are more or less same for the film above 2 nm thickness. The evidence of surface defect was clearly visible for films with 1 nm thickness. The C K edge NEXAFS analysis further showed that the content of the surface defect (mainly C–H bonds) decreased with the increase thickness in the films. The intensity of the Raman G peak increased with the increase of thickness. The X ray reflectivity measurements revealed the increased of film density with thickness.

Keywords: Tetrahedral amorphous carbon, ultrathin film, Electronic structure, Surface defect, Raman spectroscopy

1 INTRODUCTION

Ultra-thin diamond-like carbon films [1-5] are extensively used as protective coatings for instance, on magnetic and optical storage disks. The thickness of the air-bearing-surface protection film plays important role in those devices. Tetrahedral amorphous carbon coatings are used due to its unique mechanical and corrosion resistance properties. Ultra smoothness of diamond like carbon films have been explained recently by M. Moseler et al [2]. However the original bonding configurations and surface defect in ultra-thin films are not fully understood yet. In this study, using NEXAFS spectroscopy we aim to obtain novel information about the effect of thickness on the local bonding states of ultra-thin ta-C films deposited by FCVA techniques.

2 EXPERIMENTALS

The ultrathin ta-C films were deposited using a filtered cathodic vacuum arc (FCVA) technique. An arc current of 80 Ampere under floating conditions was used to synthesize films of a thickness range between 1 – 10 nm. Details of the deposition technique can be found in previous literature [6]. NEXAFS measurements were performed at station 1.1 of the synchrotron radiation source facility, at Daresbury Laboratory, UK. The spectra at the C K edge were recorded in the total electron yield mode and were normalized to the signal from a gold covered grid, recorded simultaneously. The resolution of the beam line was 0.1 eV at the C K edge. In order to obtain the π* and σ* peak areas, after subtracting the respective ionization jumps at both C K and N K edges, the resulting spectra were decomposed into several Gaussian peaks. Details of the fitting procedure can be found in literature [7]. In order to evaluate the density, layer thick-ness, x-ray reflectivity (XRR) measurements were performed. The Raman spectra were obtained with Argon laser excitation (514.5 nm) using a Labram confocal Raman microscope.

3 RESULTS AND DISCUSSION

Figure 1 shows *C K*-edge NEXAFS spectra of three representative ta-C films at various thicknesses. All normalized spectra were shifted upward for ease of comparison. A pre-edge resonance at 285.5 eV is due to transitions from the C 1*s* orbital to the unoccupied π^* orbitals ideally originating from sp^2(C=C) sites, and also from sp (C≡C) sites, if present. This peak is not visible in the spectrum of diamond, because diamond does not have any sp^2(C=C) sites. Therefore, the peak intensity of this resonance can be considered as an index of sp^2 content.

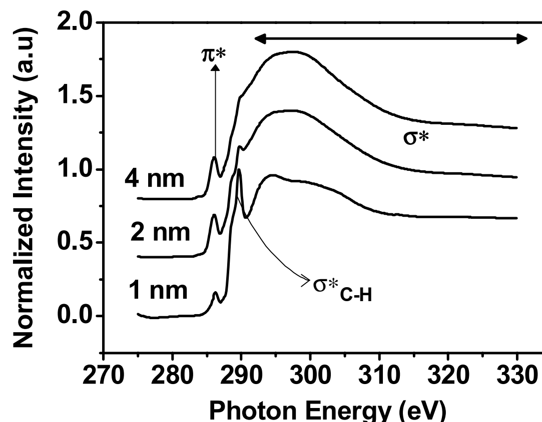

Figure 1: C K-edge NEXAFS spectra of three ultra-thin ta-C films.

It is clear from Fig. 1 that the intensity and area of π* peak (which indicates the sp^2 content in the film) at the C K

edge is significantly low in ta-C films with thickness 1 nm. The peak around 287.6 eV and 289.5 eV may originate from contamination related to 1s→π*(C=O) and 1s→π*(C-H) transitions respectively. The broad band between 290 and 310 eV results from overlapping C 1s → σ* transition at sp^2 or/and sp^3 sites. As we did not have any inherent C–H bonds those bonds are due to the surface contamination and absorption of hydrocarbon to the surface dangling bonds [6, 8].

Figure 2 and Figure 3 illustrates decomposed C K edge spectra for 1nm and 4 nm films respectively**.** The spectra were decomposed by six Gaussian peaks. We observed (Fig. 2 and Fig. 3) as the thickness increased the intensity of the first peak ($\pi^*_{C=C}$ resonance) increased. The second resonance (C=O), did not show any significant change with thickness. The third resonance (C-H) dropped dramatically with thickness. On the other hand broad σ* feature were observed at higher film thickness.

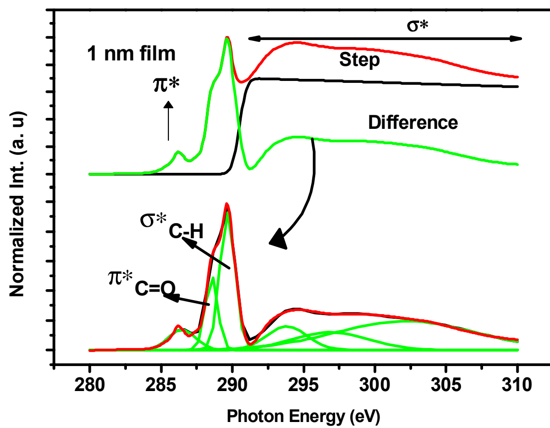

Figure 2: Deconvoluted C K edge peaks of a ta-C film.

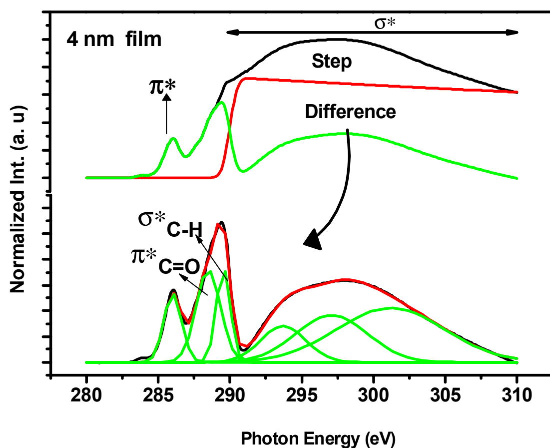

Figure 3: Deconvoluted C K edge peaks of a ta-C film.

The intensity of π* (C=C) and σ*(C-H) peak at the C K edge, as a function of film thickness, is shown in the Fig. 4. The π*/σ* ratio in the C K edge presents the relative contribution from C=C, C≡C (if present) to the all possible σ* states. This ratio is used to estimate the sp^2 domain configurations in amorphous carbon network. For films having thickness greater than 2nm the π*/σ* ratio did not change significantly. However, for films with thickness 1nm, we noticed a low π* (C=C) and high σ*(C-H) value.

It appears that for 1 nm films the surface defects (oxygen and hydrogen related) are more pronounced. In fact, at the 1nm films, both the sp^2 cluster size and distribution of sp^2 domain in the sp^3 matrix are quite complicated. The decrease of σ*(C-H) resonance and the enhancement of the σ*(CC) feature with film thickness, is a signature of the formation of sp^3 C sites. We can also observe (Fig. 4) that the π* peak increases rapidly, when the thickness increased from 1 to 2 nm. However that intensity fall down and saturate above 4 nm, indicating an initial rise and fall of sp^2 bonding configuration. It seems there is some critical value of thickness above which both sp^3 C distorted sp^2 C structures is stable.

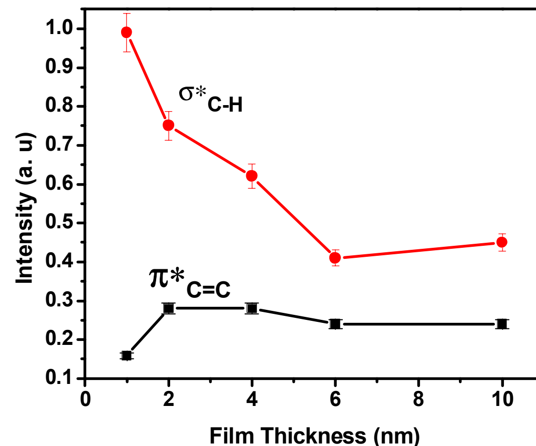

Figure 4: The intensity of π* (C=C) and σ*(C-H) peak of ta-C films at different thicknesses.

Figure 5 shows the Raman spectra of ta-C films in the ultrathin region. Depending on the sp^3/sp^2 ratio of carbon bonds, the visible Raman spectra of DLC films always show a single G peak or two peaks (G peak and D peak) in the 1100-1800 cm^{-1} region [9,10]. The G peak is connected to the presence of all sp^2 structures, both olefinic (chains) and aromatic (rings) while the D peak is related to the presence of aromatic rings only [9]. The D peak was not prominent in all ta-C film indicating a higher sp^3 content in the films. The ta-C film, showed a very small baseline slope in the entire ultra thin region with the diamond like carbon (DLC) component dominating, which suggests superior film properties. It is quite difficult to distinguish D and G band for ultrathin film. The spectra were fitted with two Gaussian peaks for G and D bands.

Raman parameters, such as the I_D/I_G ratio and G peak position were evaluated for ta-C films. A little decrease of ID/IG ratio and a clear increase of G peak position towards higher wave number were observed. Increase of G peak position with film thickness denoted an decrease in the sp^2 fraction, as it is related to the bond angle disorder at sp^2 sites. Recently, Shin et al. [11] found the G peak of the Raman spectrum of amorphous carbon films shifts to higher wave numbers with the increase of compressive stress. The higher stress at higher thickness may be one of the reasons for the increase of G peak position in ta-C films. The previous NEXAFS study supports the formation of huge surface defect in ta-C film with thickness 1 nm. Also the lower G peak position in 1 nm film suggest the formation of amorphous carbon structures with reduced three dimensional cross linking.

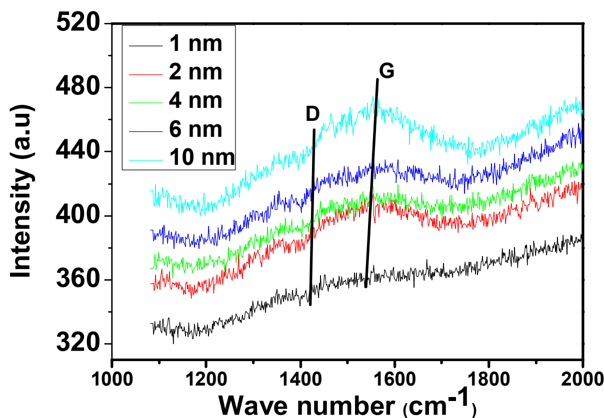

Figure 5: The normalized Raman spectra of five ultra thin films using 514-nm excitation wavelength.

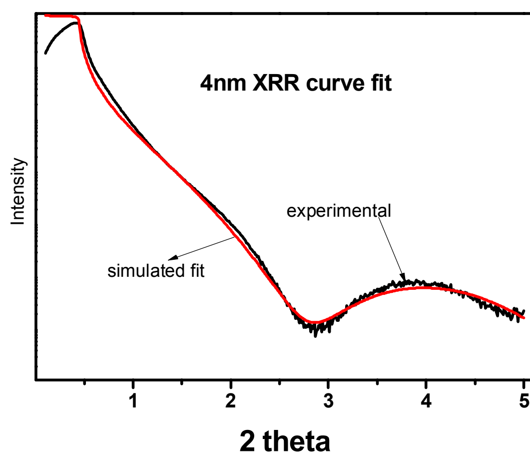

Figure 6: X-ray specular reflection profiles of a ta-C films illustrating the experimental and a model fit curves.

Figure 6 shows the XRR data for a 4 nm ta-C films versus scattering angle together with a model fit result. Simulation with a layer model including film-substrate interface and film surface layers gives a good fit as illustrated in the figure. The film density increased from 1.6, for film of 1nm thick to a value of 2.7 g/cm^3 for film of thickness 10 nm, indicating the formation sp^3 C-C rich structure at thicker film.

4 CONCLUSIONS

We demonstrate that the combined study of normalised NEXAFS, Raman and XRR spectra is very useful in determining the role of thickness in the structure of ta-C films. As the film thickness exceeds 1 nm the sp^3 C content and carbon density increased significantly. Also the surface dangling bond decreased with the increase of thickness. Raman spectra showed the evidence of enhance DLC component at higher film thickness.

REFERENCES

[1] D. J. Li, M. U. Guruz and C. S. Bhatia and Y.W Chung, Appl. Phys Lett., 81(6), 1113, 2002.
[2] M. Moseler, P. Gumbsch, C. Casiraghi, A. C. Ferrari and J. Robertson, Science, 309 (2), 1545, 2005.
[3] C. Casiraghi , A.C. Ferrari , R. Ohr , D. Chu and J. Robertson, Diamond and Relat. Mater., 13, 1416, 2004.
[4] M. G. Beghi, A. C. Ferrari, K. B. K. Teo, J. Robertson, C. E. Bottani, A. Libassi and B. K. Tanner Appl Phys Lett., 81, 3804, 2002.
[5] B. J. Chen, X. W. Sun, B. K. Tay, L. Ke and S. J. Chua. Appl Phys Lett., 86, 063506, 2005.
[6] G. A. Abbas, S. S. Roy, P. Papakonstantinou, and J. McLaughlin, Carbon, 43, 303, 2005.
[7] S. S. Roy, R. McCann, P. Papakonstantinou, J. A. McLaughlin, I. W Kirkman, S. Bhattacharyya, S. R. P. Silva, J. Appl. Phys., 99, 043511 (2006).
[8] C. S. Lee, J. K. Shin, K. Y. Eun, K. R. Lee, K. H. Yoon. J. Appl. Phys., 95, 4829, 2004.
[9] A. C. Ferrari, and J. Robertson Phys. Rev. B, 6, 14095, 2000.
[10] S. S. Roy, P. Papakonstantinou, R. McCann, G. Abbas, JP Quinn, J. McLaughlin. Diamond Relat. Mater., 13, 1459, 2004.
[11] J. K. Shin, C. S. Lee, K. R. Lee, K. Y. Eun. Appl. Phys. Lett., 78, 631, 2001.