

Enhancement of sp^3 -bonding in high-bias-voltage grown diamond-like carbon thin films studied by x-ray absorption and photoemission spectroscopy

S C Ray¹, C W Pao¹, H M Tsai¹, J W Chiou¹, W F Pong^{1,5}, M-H Tsai²,
T I T Okpalugo³, P Papakonstantinou³ and T W Pi⁴

¹ Department of Physics, Tamkang University, Tamsui 251, Taiwan

² Department of Physics, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

³ NIBEC, School of Electrical and Mechanical Engineering, University of Ulster, County Antrim, BT37 0QB, Northern Ireland, UK

⁴ National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

E-mail: wfpong@mail.tku.edu.tw

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Abstract

X-ray absorption near-edge structure (XANES) and valence-band photoemission spectroscopy (VB-PES) were used to elucidate the electronic and mechanical properties of diamond-like carbon (DLC) thin films deposited by the plasma-enhanced chemical vapour deposition method at various bias voltages (V_b) using a C_2H_2 vapour precursor in an Ar^+ atmosphere. The increase of V_b is found to increase and decrease the contents of sp^3 - and sp^2 -bonded carbon atoms, respectively, i.e. the films become more diamond-like. The Young's modulus measurements show increases with the increase of the presence of sp^3 -bonded carbon atoms in the structure of the DLC films.

1. Introduction

For both economical and technological reasons, diamond-like carbon (DLC) films have attracted the interest of many researchers because of their excellent physical and chemical properties, including chemical inertness, electrical insulation, hardness, optical transparency, surface smoothness, resistance to wear and electron emission [1–4]. The plasma-enhanced chemical vapour deposition (PECVD) process is one of the well established methods of deposition, which allows the properties of films to be tuned by changing the process parameters such as the bias voltage (V_b), precursor gas, gas pressure and others [1, 3, 4]. V_b has the most significant effect on the mechanical, optical and electrical properties [1, 4]; a change in V_b causes structural variations of the DLC films during deposition. Previous studies have focused on the various properties of DLC films deposited by different methods [5–8]. This work,

⁵ Author to whom any correspondence should be addressed.

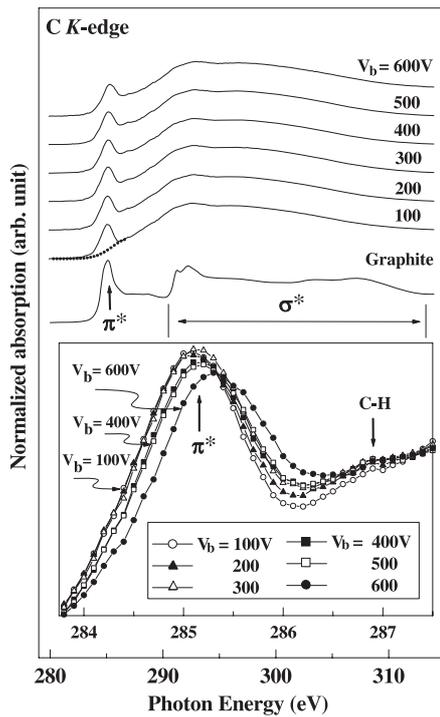


Figure 1. C K-edge XANES spectra of DLC films deposited at various V_b from 100–600 V. Inset magnifies the π^* and C–H bonds.

however, focuses on the dependence of the electronic structure and the mechanical property of the DLC thin film on V_b by studying the C K-edge x-ray absorption near-edge structure (XANES) and the valence-band photoemission spectroscopy (VB-PES).

2. Experimental details

C K-edge XANES and the VB-PES spectra were measured using a high-energy spherical grating monochromator and low-energy spherical grating monochromator beamlines, respectively, at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan. The XANES data were obtained in sample drain current mode, whereas VB-PES spectra were obtained at an excitation of 90 eV, with a typical resolution of 0.1 eV at a base pressure of $\sim 5 \times 10^{-10}$ Torr, after the sample surface was cleaned by Ar^+ bombardment. The DLC films were synthesized on the Si(100) substrate by RF PECVD with an electrode self- V_b in the range 100–600 V, using C_2H_2 in Ar^+ plasma. The thicknesses of the films are 150 ± 15 nm, determined by the deposition time. The deposition of these films and their characterizations have been described elsewhere [9]. Additionally, Fourier transform infrared (FTIR) and photoluminescence (PL) spectra were also measured using spectrophotometers, while the Young's modulus was measured using a nanoindenter. All measurements were made at room temperature.

3. Results and discussion

Figure 1 presents the normalized C K-edge XANES spectra of DLC films and the reference graphite. These spectra following pre-edge background subtraction were normalized to the incident beam intensity I_0 , and the area under the spectra was fixed in the energy range

Table 1. The sp^2 -content and (π^*/σ^*) intensity ratios from XANES; (π/σ) intensity ratios, peak II (p_σ) and peak III (presumably C–H bonds) intensity from VB-PES, and the C–H-content determined from FTIR; the PL intensity and Young’s modulus (E) of DLC thin films deposited at various V_b .

Bias voltage, V_b (V)	Measurements from XANES (arb. unit)		Peak intensity from VB-PES (arb. unit)				C–H-cont. (arb. unit) from FTIR	PL Int. (arb. unit)	Young’s modulus, E (GPa)
	sp^2 -cont.	(π^*/σ^*) Int. ratios	Peak I (p_π)	Peak II (p_σ)	Int. ratios (p_π/p_σ)	Peak III (C–H)			
100	1.34	0.63	3.0	13.6	0.22	5.05	1.08	1.89	173.25
200	1.20	0.61	2.8	14.1	0.20	4.15	0.82	1.31	179.54
300	1.18	0.60	2.8	14.8	0.19	3.68	0.74	0.92	187.12
400	1.05	0.60	2.6	15.0	0.17	3.21	0.67	0.87	197.02
500	1.04	0.59	2.3	15.2	0.15	2.72	0.51	0.58	207.02
600	0.95	0.57	2.7	15.7	0.17	2.67	0.43	0.49	205.32

315–325 eV. The graphite spectrum demonstrates that π^* and σ^* bands are located at 285.0 and 292.2 eV, respectively, whereas these bands (π^* and σ^*) of the DLC films deposited at $V_b = 100$ V are observed near 285.1 and 292.8 eV, respectively. When V_b is increased to 600 V, these bands shift to higher energies of 285.3 and 293.0 eV, respectively, and may be due to the formation of more DLC films. The π^* feature is typical of the C=C bond (sp^2) whereas the σ^* feature is typical of the tetrahedral C–C bond (sp^3) [7, 10, 11]. A very weak C–H feature is also observed in all films at ~ 287 eV [7, 10, 11], as shown in the inset of figure 1, which suggests that the content of C–H bonds is relatively low compared to those of sp^2 and sp^3 bonds. The content of sp^2 -bonded carbon atoms of each sample was estimated from the integrated area between a Gaussian fit of the spectrum and the baseline in the 282.2–286.2 eV range. The baseline is indicated in figure 1 as a dotted line for the sample grown at $V_b = 100$ V only. The curve reveals that the sp^2 -content (π^*) decreases as V_b increases. The sp^2 -contents are also tabulated in table 1. The (π^*/σ^*) intensity ratio obtained from the corresponding peak heights also decreases as V_b decreases. The results clearly indicate that the increase of V_b enhances the sp^3 C–C bond content in DLC films.

Figure 2 displays the VB-PES spectra of DLC films deposited at various V_b obtained using incident photon energy of 90 eV. The spectra are very smooth and exhibit basically a prominent feature centred at ~ 7 eV and a leading shoulder at the top of the valence band near ~ 3 eV, which corresponds to p_σ and p_π contributions to the density of states of DLC films [12, 13], respectively. These spectra are decomposed into four Gaussian peaks (right-hand column in figure 2) after a base line, represented by a dotted line (in the left column in figure 2), is subtracted to better illustrate the effect of V_b . The decomposed peaks have been assigned to p_π (peak I) at $\sim 3.1 \pm 0.2$ eV, p_σ (peak II) at 7.2 ± 0.3 eV and surface plasmons of the sp^2 states (peak IV) at 17.5 ± 0.4 eV [7, 12, 13]. Surface plasmons are confined to the surfaces and they interact strongly with the incident light. Peak III at 12.2 ± 0.5 eV is presumably associated with C–H bonds [7] or perhaps with a mixture of s and p bands of carbon atoms [14]. Here, p_π and p_σ represent sp^2 - and sp^3 -bonded carbon, respectively. The integrated peak areas of p_σ (peak II) and p_π (peak I) increase and decrease, respectively, with the increase of V_b . Thus, the integrated area ratio (p_π/p_σ) decreases with the increase of V_b . Peak III decreases with the increase of V_b . This observation is consistent with the decrease in the sp^2 -content and the (π^*/σ^*) intensity ratio obtained from C K-edge XANES spectra. The decrease of the C–H content, which corresponds to the C–H_n bonds [5], is consistent with the integrated

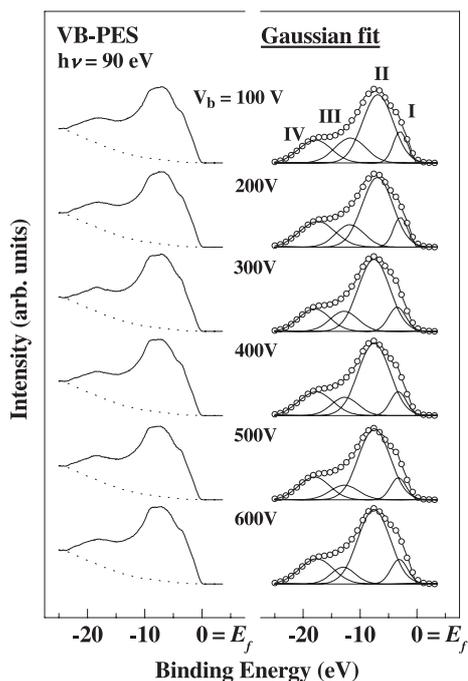


Figure 2. Left panel: VB-PES spectra; the base line is indicated by the dotted line. Right panel: VB-PES spectra are decomposed into four Gaussian peaks. In each panel, open circles represent the total fit whereas the four solid lighter lines represent the Gaussian fit.

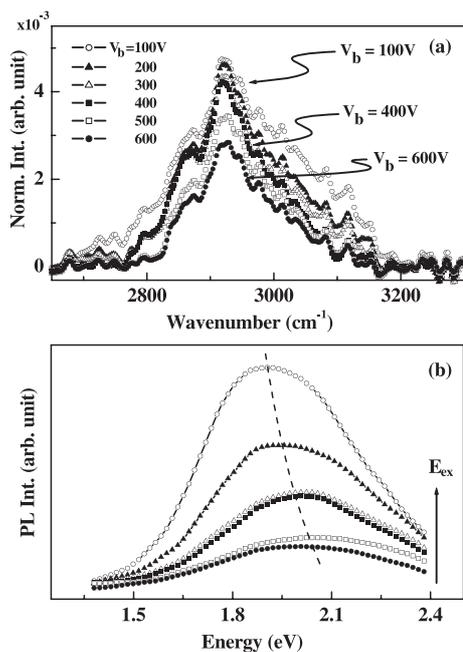


Figure 3. (a) FTIR spectra within the 2600–3300 cm^{-1} range for the C–H vibration mode and (b) PL spectra at various V_b . E_{ex} denotes the excitation energy.

area under the curve in the 2600–3300 cm^{-1} range of the FTIR spectra of the C–H vibration mode as shown in figure 3(a) and table 1. This result agrees with that of Lee *et al* [4]. The VB-PES spectra revealed no signature of the oxygen 2s core excitation typically observed at $\sim 23\text{--}25$ eV [15, 16], which is consistent with the absence of the C=O peak in the XANES

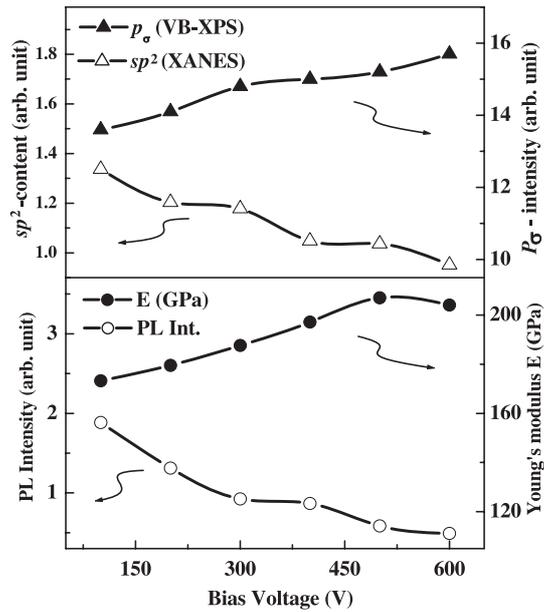


Figure 4. Top: the sp^2 -content and p_σ -intensity versus V_b ; bottom: the PL-intensity and Young's modulus versus V_b for DLC films.

spectra [17]. Figure 3(b) plots the PL spectra of these DLC films, which show a single broad band. The integrated PL intensities over the total area under the curve are tabulated in table 1. The full width at half maximum of the PL band is increased from about 0.57 eV ($V_b = 100$ V) to 0.71 eV ($V_b = 600$ V) and the position of the maximum intensity shifts from 1.9 to 2.0 eV. As V_b is increased, the PL intensity gradually decreases. This trend is similar to that observed by Rusli *et al* for the amorphous (a)-C:H film [18] and was argued to be caused by the radiative recombination of the electron-hole pairs that are confined to the π states of the sp^2 -bonded clusters in an sp^3 bonded amorphous matrix. According to this argument, the variation of the PL spectra in the present case suggests the existence of sp^2 -bonded clusters in the sp^3 -bonded matrix in DLC films. The reduction of the PL intensity correlates with the decrease of the concentration of sp^2 bonds as well as hydrogen content present in the films.

Figure 4 plots the V_b -dependent sp^2 -content, p_σ -intensity (sp^3 -bonded C), Young's modulus (E) and PL intensity, to better illustrate the effect of V_b on the mechanical property (Young's modulus) of the DLC films. The contents of sp^3 - and sp^2 -bonded carbon atoms determine, respectively, the hardness and softness of the materials [18, 19]. The present XANES, VB-PES measurements all consistently show the decrease and increase of the contents of sp^2 - and sp^3 -bonded carbon atoms, respectively, with the increase of V_b , which indicate the possible behaviour of an enhancement of the hardness by increasing V_b . The measured Young's modulus with respect to V_b as shown in figure 4 indeed confirms this trend. Lee *et al* [4] observed that the hydrogen content decreases as the residual stress increases with the increase of V_b gradually when the DLC film is deposited by RF PECVD using the gas precursor C_6H_6 . Similar results were found from the VB-PES and FTIR measurements in the present case as the hydrogen content decreases with increase of V_b , and this is also consistent with the decrease of PL intensity [20]. However, the PL intensity is an extremely sensitive function of the hydrogen content and hence is responsible for the Young's modulus and hardness of the hydrogenated amorphous carbon film. It was observed by many researchers that, with decrease of hydrogen content in the film, the PL intensity decreases [21–24] and the sp^3/sp^2 bond ratio increases [22]; as a result the Young's modulus/hardness increases [23], which is also observed in our case,

as shown in figure 4 and table 1. During the deposition process in the present case, the C_2H_2 vapour precursor is dissociated into hydrocarbon ions on the growth surface by Ar^+ ions, which results in small fragments such as C or CH, thereby forming an a-C and/or a-C:H film [4]. The high-energy Ar^+ ions and gas-phase C or CH fragments also transfer their energies to carbon atoms in the DLC films, which generates high local temperature that enables the formation of sp^3 -bonded carbon atoms. These processes are enhanced by the increase of V_b , which increases the kinetic energies of incoming Ar^+ ions and C or CH fragments.

4. Conclusions

In conclusion, a combination of XANES and VB-PES measurements consistently shows that the increase of the bias voltage during the growth process increases and decrease the contents of sp^3 - and sp^2 -bonded carbon atoms, respectively, in the diamond-like carbon thin films. Since the number of sp^3 -bonded carbon atoms increases with increase of the Young's modulus measurements, this confirms the possible increase of hardness; this finding is consistent with the FTIR and PL results.

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References

- [1] Jiang X, Zou J W, Reichelt K and Grunberg P 1989 *J. Appl. Phys.* **66** 4729
- [2] Robertson J 1992 *Surf. Coat. Technol.* **50** 185
- [3] Grill A and Patel V 1993 *Diamond Relat. Mater.* **2** 1519
- [4] Lee K-R, Baik Y-J and Eun K Y 1994 *Diamond Relat. Mater.* **3** 1230
- [5] Ray S C, Okpalugo T I T, Tsai H M, Chiou J W, Pong W F, Wang W J, Papakonstantinou P and McLaughlin J A 2004 *Mater. Res. Bull.* **40** 1757
- [6] Ray S C, Bose B, Chiou J W, Tsai H M, Jan J C, Krishna Kumar K P, Pong W F, Dasgupta D, Fanchini G and Tagliaferro A 2004 *J. Mater. Res.* **19** 1126
- [7] Ray S C, Bao C W, Tsai H M, Chiou J W, Jan J C, Krishna Kumar K P, Pong W F, Tsai M-H, Wang W-J, Hsu C-J, Okpalugo T I T, Papakonstantinou P and McLaughlin J A 2004 *Appl. Phys. Lett.* **85** 4022
- [8] Ray S C, Okpalugo T I T, Papakonstantinou P, Tsai H M, Chiou J W, Pong W F, McLaughlin J A and Wang W J 2005 *Thin Solid Films* **482** 242
- [9] Papakonstantinou P, Zhao J F, Lemoine P, McAdams E T and McLaughlin J A 2002 *Diamond Relat. Mater.* **11** 1074
- [10] Nithianandam J, Rife J C and Windischmann H 1992 *Appl. Phys. Lett.* **60** 135
- [11] Hoffman A, Comtet G, Hellner L, Dujardin G and Petravic M 1998 *Appl. Phys. Lett.* **73** 1152
- [12] Reinke P and Oelhafen P 1997 *J. Appl. Phys.* **81** 2396
- [13] Reinke P, Oelhafen P, Feldermann H, Ronning C and Hofsäss H 2000 *J. Appl. Phys.* **81** 5597
- [14] Mansour A and Ugolini D 1992 *Phys. Rev. B* **47** 10201
- [15] Francz G and Oelhafen P 1995 *Diamond Relat. Mater.* **4** 539
- [16] Ronning C, Schwen D, Eyhusen S, Vetter U and Hofsäss H 2002 *Surf. Coat. Technol.* **158/159** 382
- [17] Ray S C, Tsai H M, Bose B, Chiou J W, Jan J C, Krishna Kumar K P, Pong W F, DasGupta D and Tsai M-H 2004 *J. Phys.: Condens. Matter* **16** 5713
- [18] Rusli, Robertson J and Amaratunga G A J 1996 *J. Appl. Phys.* **80** 2998
- [19] Robertson J 2002 *Mater. Sci. Eng. R* **37** 129
- [20] Cui J, Rusli, Woon S F, Teo E J, Yu M B, Chew K, Ahn J, Zhang Q, Osipowicz T and Watt F 2001 *J. Appl. Phys.* **89** 2699
- [21] Jung H-S, Park H-H, Mendieta I R and Smith D A 2003 *J. Appl. Phys.* **94** 4828
- [22] Adamopoulos G, Robertson J, Morrison N A and Godet C 2004 *J. Appl. Phys.* **96** 6348
- [23] Li Z F, Yang Z Y and Xiao R F 1996 *Appl. Phys. A* **63** 243
- [24] Marchon B, Gui J, Grannen K, Rauch G C, Ager J W III, Silva S R P and Robertson J 1997 *IEEE Trans. Magn.* **33** 3148