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X-ray absorption spectroscopy (XAS) study of dip deposited a-C:H(OH) thin films

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Abstract

This work measures the C and O K-edge x-ray absorption near-edge structure (XANES) spectra of hydrogenated amorphous carbon (a-C:H) films deposited at various baking temperatures T_b ($T_b = 300\text{--}500\text{ }^\circ\text{C}$ at $50\text{ }^\circ\text{C}$). The C–H σ^* peak related to the content of the sp^2 graphite-like bonding in the C K-edge spectra was found to yield to the C–H π^* peak related to the sp^3 diamond-like bonding at high temperature ($500\text{ }^\circ\text{C}$). We find that the intensities of both the sp^2 and sp^3 features in the C K-edge XANES spectra decrease with increase of T_b , which suggests an increase of the defect concentration with T_b . The intensities of the O K-edge XANES spectra are found to decrease with increase of T_b , which suggests thermally induced decomposition of carbonyl contaminants on the surface. The elemental analysis C/O (or O/C) ratio was obtained from XPS spectra and indicates that films are not hydrogenated amorphous carbon but rather oxyhydrogenated amorphous carbon thin films.

1. Introduction

Hydrogenated amorphous carbon (a-C:H) films have attracted interest in view of the potential use in many applications, for example as chemically inert, low-friction and hydrophobic coatings [1], resist masks for lithography [2] and optical devices protecting against wear [3].

Investigations of a-C:H focused on the capability of changing the optical, electronic and mechanical properties by tuning the content of fourfold sp^3 and threefold sp^2 states of carbon atoms as well as the shape and/or size of the olefinic/aromatic chains/rings in which the sp^2 sites

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tend to cluster [4, 5]. Knowledge of the sp^2/sp^3 ratio and hydrogen content was considered sufficient for classifying amorphous carbon (a-C) films [6]. Measurements, including the Raman and Fourier transform infra-red (FTIR) spectra [7], of the sp^2 and sp^3 (and/or sp^2/sp^3 ratio) contents present in the films were often used to determine the carbon phases. In a previous report a range of a-C:H films were deposited at various baking temperatures and were studied by thickness (≈ 0.3 – $1.2 \mu\text{m}$), Raman spectroscopy, FTIR, electron spin resonance and other methods [8]; the results showed that the carbon phase changed with the temperature during deposition. X-ray absorption near-edge structure (XANES) spectra are convenient and useful for accurately determining the sp^2 and sp^3 contents in the film's surface, because graphite and diamond phases yield very different spectra. However, XANES (NEXAFS) is an useful technique for categorizing the nature of a-C:H films. The aim of this work is to elucidate the nature of carbon in various dip deposited a-C:H films with the x-ray absorption spectra. To our knowledge, no report of XANES analysis of 'dip deposited' a-C:H films has been published. In this work, our C and O K-edge XANES measurements provide new information on the nature of the carbon phases in the a-C:H films.

2. Experimental details

C and O K-edge XANES measurements were performed for a-C:H films and highly oriented pyrolytic graphite (HOPG), which was used as a reference, using a high-energy spherical grating monochromator beamline, operated at an electron energy of 1.5 GeV and a maximum stored current of 200 mA at the National Synchrotron Radiation Research Centre (NSRRC), Hsinchu, Taiwan. The C and O K-edge XANES spectra were measured using the total yield mode by recording the sample drain current mode. Simultaneously, the signal from a gold grid located upstream in the x-ray path was recorded and the spectra were normalized using the incident beam intensity I_0 , keeping the area under the spectra fixed over an energy range between 315 and 335 eV for the C K edge and between 552 and 569 eV for the O K edge. All measurements were taken at room temperature. The compositions of the films were determined by x-ray photoelectron spectroscopy (XPS), using an XSAM 800 (Kratos) spectrometer. Films were grown by the dip technique on glass substrates at various deposition baking temperatures T_b , in open atmosphere, using ethanolic ($\text{C}_2\text{H}_5\text{OH}$) solutions of sucrose ($\text{C}_6\text{H}_6(\text{OH})_6$). The films are highly uniform and chemically stable. The films prepared at lower baking temperatures are comparatively soft. The details of the preparation of a-C:H film and their characterization have been described elsewhere [8]. The samples used in this study were prepared at various T_b ($T_b = 300$ – 500°C at 50°C).

3. Results and discussion

Figure 1 shows the normalized C K-edge XANES spectra of a-C:H films and the reference HOPG. The HOPG spectrum shows that π^* and σ^* bands are located at 285.5 and 292.5 eV, respectively. The spectra of all a-C:H samples have two main features, near ~ 285.5 and 293 eV, which were assigned to the unoccupied π^* and σ^* bands respectively as observed by different researchers [9–11] for different carbon related materials. The π^* feature at ~ 285.5 eV is typical of the C=C bond (sp^2) [12, 13], while the σ^* feature at ~ 293 eV is typical of the tetrahedral C–C bond (sp^3) [14, 15]. Two additional peaks (near 287.2 and 289.2 eV) marked by \mathbf{a}_1 and \mathbf{a}_2 in figure 1 are observed between π^* and σ^* features. The \mathbf{a}_1 (287–288 eV region) peak was observed by Alonso *et al* [16] and Kikuma *et al* [17] for different polymer materials (polystyrene, poly- α -methyl styrene etc) and is attributed to the C–H σ^* band. By analogy we

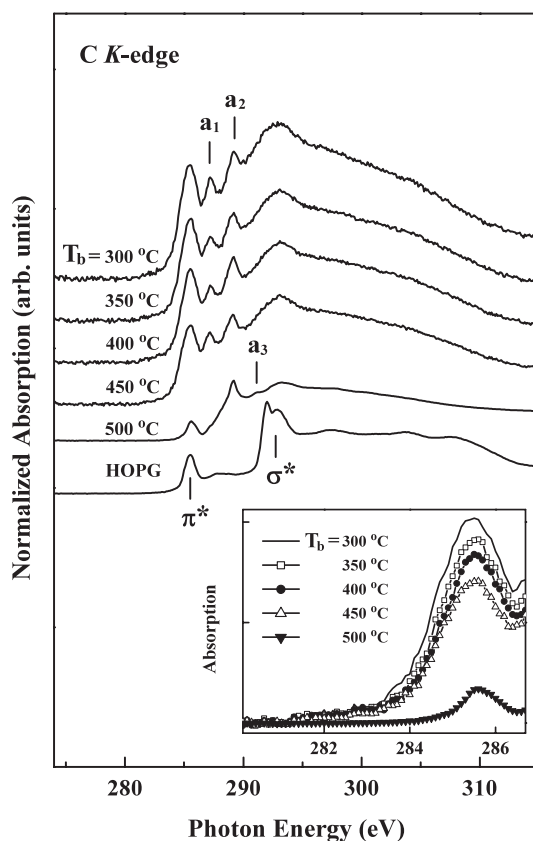


Figure 1. Normalized C K-edge absorption spectra of the a-C:H films. The inset shows the π^* region magnified.

assigned this \mathbf{a}_1 peak to the C–H σ^* band and as due to the bonding between the H atom and a diamond-like-bonded C atom. In peak \mathbf{a}_1 there may be some contribution from the oxygen content due to the thermal treatment and that might be related to O–C=C bond. The peak \mathbf{a}_2 (288–290 eV region) observed for our all films was attributed to the C=O π^* bond [18] and also observed in a XANES study in on nylon polymer by Kikuma *et al* [17]. The spectrum of the films deposited at 500 °C is quite different from those for other samples. In this spectrum a very weak peak is observed at ~ 291.2 eV (marked as \mathbf{a}_3), which is attributed to the C–H π^* band due to the bonding between the H atom and a graphite-like-bonded C atom. Kikuma *et al* [17] also observed this \mathbf{a}_3 peak in XANES studies of poly-vinyl pyrrolidone (PVP). At 500 °C, the sp^3 -bonded (σ^*) hydrocarbon (C–H σ^*) was found to yield sp^2 -bonded (π^*) hydrocarbon (C–H π^*) [19, 20] as indicated by the disappearance of feature \mathbf{a}_1 and the emergence of \mathbf{a}_3 . This \mathbf{a}_3 peak (291.2 eV) could also be assigned to a C–C σ^* bond (in the C–C σ^* region), but we have assigned it to the C–H π^* band by analogy (without calculation) with observations by other researchers [19, 20]. This change occurs at higher baking temperature (sp^3 - to sp^2 -bonded hydrocarbon), and was also observed in FTIR studies, as discussed in detail in our previous report [8]. It is also observed that the intensity of the sp^2 peak (at 285 eV) of the film prepared at 500 °C baking temperature is significantly reduced; this may be due to the formation of comparatively more compact film [8] or may be due to the formation of defect-rich

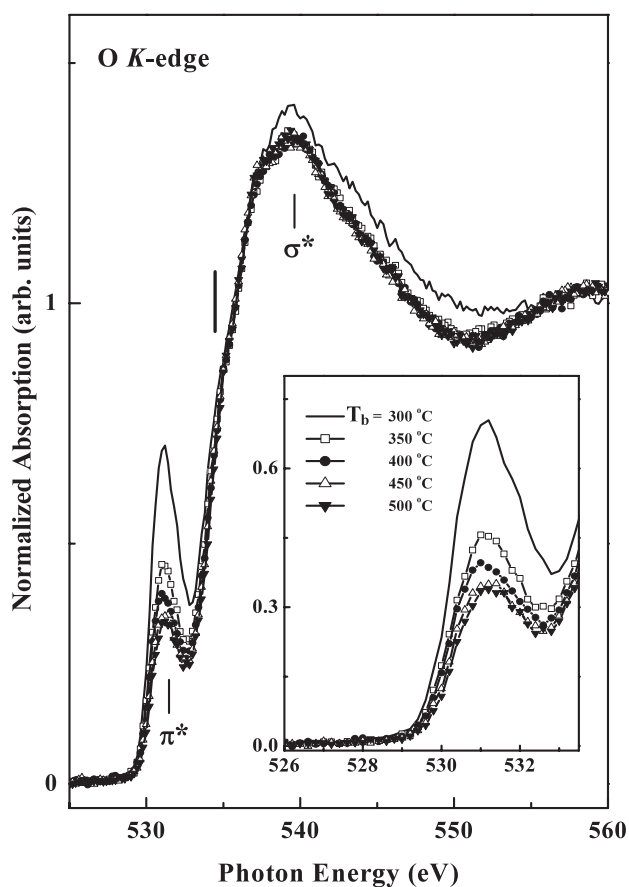


Figure 2. Normalized O K-edge absorption spectra of the a-C:H films. The inset shows the magnified π^* region.

film as we discuss later. Since the intensity is approximately proportional to the density of the unoccupied C 2p-derived states, this result indicates a decrease in the absorption intensity as T_b for the films increases, not only for those associated with the unoccupied π^* bands but also for those associated with the σ^* bands (the π^* part is clearly shown in the inset of figure 1). The π^* bands are composed of C 2p_x and 2p_y orbitals, whereas the σ^* bands contain the C 2p_z orbital. The sp²- and sp³-bonded carbon contents of each sample were estimated from the relative heights of the π^* and σ^* features at 285.5 ± 0.1 and 293.2 ± 0.1 eV, respectively. We took their ratio (i.e. sp²/sp³) and discuss this below in comparison with the π^* O K-edge case (see figure 3), as the sp²/sp³ ratio of the films indicates the graphitization and allows one to classify the different carbon phases [7].

Figure 2 displays the normalized O K-edge XANES spectra of a-C:H films and shows that the content of oxygen in the film decreases with the baking temperature (T_b). Jiménez *et al* [21] also observed this phenomenon during the annealing of the boron carbide films; when the annealing temperature was relatively high (>1500 K), oxygen was no longer detectable in the sample. The peak at ~ 531.2 eV (enlarged in the inset of figure 2) and the relatively weak shoulder features at ~ 535 eV (labelled with a vertical bar) are related to the C=O π^* bands, which were argued to indicate the presence of carbon oxide contaminants

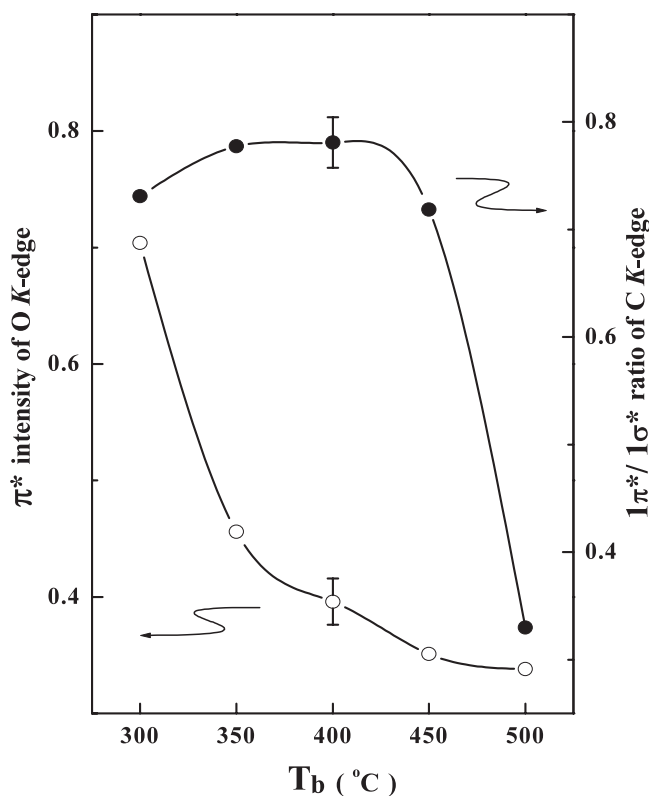


Figure 3. The intensity ratio $1(\pi^*)/1(\sigma^*)$ at the C K edge and the intensity of the π^* resonance feature at the O K edge for the a-C:H films, as a function of T_b .

of carbonyl groups [21]. These two $\pi_{C=O}^*$ levels are predicted to have localized non-interacting π^* characteristics [22]. They were regarded as quasi-degenerate because of their large spatial separation [22]. Analogy with multiple C $1s \rightarrow \pi^*$ transitions in transition metal carbonyl complexes [23] indicates that the oxygen core hole localizes the excitation at a single carbonyl and strongly enhances the lower-energy O $1s \rightarrow \pi_{C=O}^*$ excitation. In contrast, the higher-energy $\pi_{C=O}^*$ band and a possible second $\sigma_{C=O}^*$ resonance are strongly overshadowed by the broad $\sigma_{C=O}^*$ resonance at 539 eV, as shown in figure 2. These C=O features in the O K-edge XANES spectra of all the samples are similar except that the intensities of features $\pi_{C=O}^*$ and $\sigma_{C=O}^*$ both decline with increase of T_b due to outgassing of oxygen [19].

Figure 3 summarizes the effect of the oxygen ion on the surface damage ($1\pi^*/1\sigma^*$ ratio C K edge) and on the concentration of carbonyl groups on the film surface. In this figure, only the π^* feature intensity of the O K edge is considered, because the σ^* feature intensity does not significantly vary with temperature, unlike the π^* feature intensity. It was observed that $1\pi^*/1\sigma^*$ increases with temperature up to 400 °C, slightly decreasing at 450 °C and then dropping abruptly at 500 °C. This result indicates that the graphitization increases up to 400 °C due to increase of the sp^2/sp^3 ratio, as observed by many researchers [7, 8], and then, due to irradiation of the surface by oxygen ions from the surroundings (open atmosphere), the surface is damaged above 450 °C and the graphitization rapidly decreases at 500 °C, because of the formation of sufficient carbonyl groups at the film surface. The bond strength energy of the carbonyl group is ~ 3.36 eV [18], which is much higher than the energy associated with the

Table 1. C (at.%), O (at.%) and their ratios obtained from XPS compositional analysis.

Baking temperature, T_b (°C)	C (at.%)	O (at.%)	C/O ratio	O/C ratio
300	66.82	33.18	2.01	0.50
350	68.25	31.75	2.15	0.46
400	69.42	30.58	2.27	0.44
450	70.05	29.95	2.34	0.43
500	71.44	28.56	2.50	0.40

temperature ($k_B T \leq 0.066$ eV) during film deposition. This energy is insufficient to break the bond in the carbonyl group, so the reduction in the surface damage can be attributed to a chemical reaction that involves the incoming oxygen ions from the surroundings, preferably with sp^2 -bonded carbon atoms ($C=C$), and the subsequent removal of the volatile reaction products from the starting solution during film deposition [8]. Accordingly, the oxygen does not contribute to the accumulation of more oxide groups on the film surface and the consequent formation of defect-rich films. Reinke *et al* [24] also examined the same mechanism at the same temperature during the interaction of a polycrystalline diamond film with water and oxygen and the ratio of the heights of the π^*/σ^* features was used to measure the extent of the damage. However, in this case, the films deposited at 500°C ($k_B T \approx 0.066$ eV) developed a defect-rich surface layer due to a large drop of the $1\pi^*/1\sigma^*$ ratio of the C K edge [24], which is structurally similar to that of an a-C film [8] but does not exhibit a long-range graphite-like ordering. The damage layer includes a high concentration of sp -hybridized carbon atoms and dangling bonds, which can subsequently serve as reaction centres on the surface of the films [24]. However, the mechanism is not completely clear for the formation of defect-rich film and needs further study. The elemental analysis (C (at.%) and O (at.%)) of π for these films is given in table 1. The C and O contents (at.%) and their ratios were calculated from the XPS data analysis. The results show that the film having the highest C/O ratio (or lowest O/C ratio) is at 500°C , which is consistent with the results discussed above, though we cannot compare XPS results directly with the XANES results because of the differences between XPS and XANES. The XPS measurement extends to only a few ångströms at the top of the films, whereas XANES measurements in total yield mode extend over the whole film present on the substrate.

4. Conclusion

In summary, C and O K-edge XANES measurements of a-C:H deposited at various temperatures T_b ($T_b = 300\text{--}500^\circ\text{C}$ at 50°C) were conducted to identify the structural properties of these films. The C–H σ^* peak related to the content of the sp^2 graphite-like bonding in the C K-edge spectra was found to yield the C–H π^* peak related to the sp^3 diamond-like bonding at high temperature (500°C), which indicates reduction of graphitization of the film surface at high temperatures. We also find that the intensities of both the sp^2 and sp^3 features in the C K-edge XANES spectra decrease with increase of T_b , which suggests increase of the defect concentration with T_b . Significant changes in the XANES spectra were identified at a T_b of 500°C in the defects associated with the oxygen ions. The intensities of O K-edge XANES spectra are found to decrease with increase of T_b , which suggests thermally induced decomposition of carbonyl contaminants on the surface. Elemental analysis shows that the films are not hydrogenated amorphous carbon but rather oxyhydrogenated amorphous carbon thin films.

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References

- [1] Goglia P R, Berkowitz J, Hoehn J, Xidis A and Stover L 2001 *Diamond Relat. Mater.* **10** 271
- [2] Kragler K, Gunther E, Leuschner R, Falk G, Hammerschmidt A, Von Seggern H and Saemann-Ischenko G 1995 *Appl. Phys. Lett.* **67** 1163
- [3] Lettington A H and Smith C 1992 *Diamond Relat. Mater.* **1** 805
- [4] Robertson J 1995 *Diamond Relat. Mater.* **4** 297
- [5] Robertson J 1997 *Phil. Mag. B* **76** 335
- [6] Robertson J 1996 *Curr. Opin. Solid State Mater. Sci.* **1** 557
- [7] Fanchini G, Tagliaferro A, Messina G, Santangelo S, Paoletti A and Tucciarone A 2002 *J. Appl. Phys.* **91** 1155
- [8] Ray S C, Fanchini G, Tagliaferro A, Bose B and Dasgupta D 2003 *J. Appl. Phys.* **94** 870
- [9] Gago R, Jiménez I and Albella J M 2001 *Surf. Sci.* **482–485** 530
- [10] Fischer D A, Wentzcovitch R M, Carr R G, Continenza A and Freeman A J 1991 *Phys. Rev. B* **44** 1427
- [11] Batson P E 1993 *Phys. Rev. B* **48** 2608
- [12] Nithianandam J, Rife J C and Windischmann H 1992 *Appl. Phys. Lett.* **60** 135
- [13] Ziethen Ch, Wegelin F, Schönhense G, Ohr R, Neuhäuser M and Hilgers H 2002 *Diamond Relat. Mater.* **11** 1068
- [14] Morar J F, Himpfel F J, Hollinger G, Hughes G and Jordan J L 1985 *Phys. Rev. Lett.* **54** 1960
- [15] Ma Y, Wassdahl N, Skytt P, Guo J, Nordgren J, Johnson P D, Rubensson J E, Boske T, Eberhardt W and Kevan S D 1992 *Phys. Rev. Lett.* **69** 2598
- [16] Alonso F, Gago R, Jiménez I, Gómez-Aleixandre C, Kreissig U and Albella J M 2002 *Diamond Relat. Mater.* **11** 1161
- [17] Kikuma J and Tonner B P 1996 *J. Electron Spectrosc. Relat. Phenom.* **82** 53
- [18] Stöhr J 1991 *NEXAFS Spectroscopy (Springer Series in Surface Sciences vol 25)* (Berlin: Springer)
- [19] Bounouh Y, Spousta J, Benlahsen M, Zeinert A, Portemer F, Laurent A, Perriere J, Zellama K and Theye M-L 1996 *Diamond Relat. Mater.* **5** 453
- [20] Gielen J W A M, Kleuskens P R M, Van de Sanden M C M, Van Ijzendoorn L C, Schram D C, Dekempeener E H A and Meneve J 1996 *J. Appl. Phys.* **80** 5986
- [21] Jiménez I, Sutherland D G J, Van Buuren T, Carlisle J A, Terminello L J and Himpfel F J 1998 *Phys. Rev. B* **57** 13167
- [22] Francis J T and Hitchcock A P 1992 *J. Phys. Chem.* **96** 6598
- [23] Rühl E, Wen A T and Hitchcock A P 1991 *J. Electron Spectrosc. Relat. Phenom.* **57** 137
- [24] Reinke P, Knop-Gericke A, Hävecker M and Schedel-Niedrig Th 2000 *Surf. Sci.* **447** 229