

Accepted Manuscript

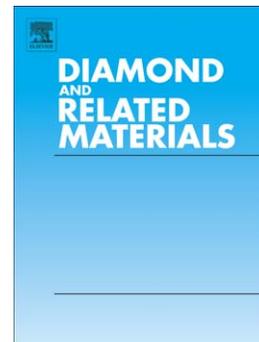
Ultraviolet and visible Raman analysis of thin a-C films grown by filtered cathodic arc deposition

J. Wasyluk, T.S. Perova, D.W.M. Lau, M.B. Taylor, D.G. McCulloch, J. Stopford

PII: S0925-9635(10)00039-7
DOI: doi: [10.1016/j.diamond.2010.01.019](https://doi.org/10.1016/j.diamond.2010.01.019)
Reference: DIAMAT 5402

To appear in: *Diamond & Related Materials*

Received date: 30 November 2009
Revised date: 20 January 2010
Accepted date: 21 January 2010



Please cite this article as: J. Wasyluk, T.S. Perova, D.W.M. Lau, M.B. Taylor, D.G. McCulloch, J. Stopford, Ultraviolet and visible Raman analysis of thin a-C films grown by filtered cathodic arc deposition, *Diamond & Related Materials* (2010), doi: [10.1016/j.diamond.2010.01.019](https://doi.org/10.1016/j.diamond.2010.01.019)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**Ultraviolet and visible Raman analysis of thin a-C films grown by filtered
cathodic arc deposition**

J. Wasyluk¹, T. S. Perova^{1*}, D.W.M. Lau², M.B. Taylor², D.G. McCulloch², J.
Stopford³

¹*Department of Electronic & Electrical Engineering, University of Dublin, Trinity
College, Dublin 2, Ireland*

²*Applied Physics, School of Applied Sciences, RMIT University, GPO Box 2476V
Melbourne 3001, Australia*

³*Department of Electronic Engineering, Dublin City University, Dublin 9, Ireland*

Abstract

Amorphous carbon thin films with a wide range of sp^2 fraction from 20 to 90% grown by filtered cathodic arc deposition have been examined by ultraviolet (UV) at 325 nm and visible Raman spectroscopy at 457 nm excitation wavelength. The comprehensive study of behaviour of G, D and T band with sp^2/sp^3 content has been carried out. The upwards shift of the G peak with sp^3 content was observed for both excitation wavelengths. It was also found that the I(D)/I(G) ratio decreases with sp^3 content for UV and visible excitations, and for high sp^3 content I(D)/I(G) tends to zero. The dispersion of the G peak is also investigated in this work as a function of sp^2 content.

* Author for correspondence, tel.: +353 1 896 1432; FAX: +353 1 677 2442; e-mail: perovat@tcd.ie

1. Introduction

Amorphous carbon (a-C) films have been extensively investigated by researchers due to their hardness, chemical stability, and its electronics properties [1]. The a-C films have widespread applications as protective coatings in areas such as magnetic storage disks, biomedical coatings, and as microelectromechanical devices. The amorphous carbon films have wide range of structural configuration due to sp^2 and sp^3 sites. Diamondlike carbon (DLC) is defined as a-C or an hydrogenated amorphous carbon (a-C:H) with a significant fraction of sp^3 bonds [2]. The DLC films with highest sp^3 content are called tetrahedral amorphous carbon (ta-C) [2]. There are four key parameters determine the structure and properties of a-C, the fraction of sp^3 bonded carbon sites, hydrogen content, ordering and clustering of sp^2 sites. Different characterisation methods are used to determine the structural parameters of a-C films. For instance, the sp^3 content is usually measured by nuclear magnetic resonance (NMR) or electron-energy-loss spectroscopy (EELS), but these are time consuming and destructive methods. Raman spectroscopy is a very popular, non-destructive tool for the structural characterisation of a-C films. Visible Raman spectroscopy is 50-230 times more sensitive to sp^2 sites, as photons with wavelength in visible range preferentially excite π -states. UV Raman, with its higher photon energy, excites both the π and the σ states and so it is able to probe both the sp^2 and sp^3 sites [3].

The Raman spectra of the a-C films show several common features in the 800-2000 cm^{-1} region: the G and D peaks at around 1570 and 1400 cm^{-1} observed for visible and UV excitation and the T peak $\sim 1100\text{ cm}^{-1}$ detected only for UV excitation [2,4]. The G and D peaks are due to sp^2 sites only [3]. The G peak is due to the bond stretching of all pairs of sp^2 atoms in both rings and chains, and the D peak is due to the

breathing modes of sp^2 rings [3]. The T peak is contributed to the C-C sp^3 vibrations [2,3].

In this paper, we report on application of Raman spectroscopy at 325 and 457 nm excitation wavelengths to distinguish between the a-C and ta-C films and to assess their structural properties. A possible explanation for the position of the G peak and its linewidth is discussed in this paper. There are reasonable arguments in the literature about the origin of upwards shift of the G peak with sp^3 content. Some conjectures indicate, that shift can be due to compressive stress in ta-C films [5], while other investigators show, that the G peak position does not decrease when the stress is removed by annealing [6]. Present paper underlines the importance of the D and G peaks intensity ratio ($I(D)/I(G)$) and intensity of the T peak in analysis of a-C films.

2. Experiment

A) a-C samples

Carbon thin films with sp^2 content between ~20% to ~90% were deposited onto silicon wafers using a dual bend filtered cathodic arc deposition (FVCA) system operating with a 99.9 % pure graphite target, an arc current of 56 A and a base pressure of better than 10^{-5} Torr. Three different flow rates of Ar (0, 7, and 15 ml/min) were used with the different deposition parameters. Silicon (100) substrates were cleaned prior to deposition in an ultrasonic bath, with acetone, ethanol and distilled water before being air dried. The substrate holder was connected to a regulated DC power supply, allowing films to be deposited over a range of bias

voltages from -25 V to -1000 V. The stress was determined from substrate curvature using Stoney's equation and the film thickness (from 20 to 80 nm) was determined by step height measurements obtained using a Tencor P-16 profilometer [7,8]. The film density and fraction of sp^2 bonded carbon atoms was estimated from an EELS measurements [8]. Samples were also prepared with a thin Cu under layer approximately 2 nm thick sputter deposited onto the substrate prior to the carbon deposition.

B) Raman spectroscopy

For the study of a-C films Raman spectroscopy with visible and UV excitations has been used. Unpolarized visible Raman spectra were excited at the backscattering geometry using 457 and 514 nm lines of an Ar^+ laser as well as 633 nm line of a HeNe laser. Spectra were collected using RENISHAW 1000 micro-Raman system equipped with a CCD camera and a Leica microscope. An 1800 lines/mm grating was used for all measurements, providing a spectral resolution of $\sim 1 \text{ cm}^{-1}$. A laser output of 10 mW was used and the laser spot was focused on the sample surface using 50x objectives with short-focus working distance. UV Raman spectra were collected using micro-Raman system HR800 model supplied by Horiba Jobin Yvon. As an excitation source the He-Cd laser at 325 nm with power of 22 mW was used. The laser spot was focused on the sample surface using 40x objectives with short-focus working distance. The Raman spectra were fitted with mixture of Gaussian and Lorentzian function to obtain the position, intensity, and linewidth of detected peaks.

3. Results and discussion

The shape of Raman spectra of a-C films depends on a number of different factors. These factors are a clustering of the sp^2 sites, bond disorder, presence of sp^2 rings or chains and the sp^2/sp^3 ratio [3]. Fig. 1 shows Raman spectra acquired at wavelengths 457 nm and 325 nm, respectively. The following Raman features are observed for both excitation wavelength: a TO Si phonon at $\sim 970\text{ cm}^{-1}$ due to the second order phonon scattering from the silicon substrate, and the carbon D and G bands at about 1400 and $\sim 1570\text{ cm}^{-1}$, respectively. The TO Si phonon mode is more pronounced for visible excitation (457 nm) due to a larger depth of laser light penetration than in case of UV excitation (325 nm). In addition to that, a weak T band at $\sim 1100\text{ cm}^{-1}$ is observed for UV excitation (see Fig. 1(b)). For visible excitation, the sp^2 sites have a high cross section and they dominate the spectra. In the same time, the sp^3 sites can not be detected and the spectrum corresponds only to the configuration or order of the sp^2 sites. At the higher excitation energy (in the UV range), the sp^3 sites are clearly shown in Raman spectra, due to resonant enhancement of the σ states of C-C bonds [2], (see Fig. 1(b)).

Figure 2 presents the dependence of Raman frequency of the G band versus the sp^3 content for visible and UV excitations. As can be seen from this figure, the G peak behaves differently for a-C films with low sp^3 content (up to 20%) in comparison with that for ta-C films with higher sp^3 fraction. For both excitation wavelengths, the G peak position decreases as sp^3 increases up to 20%. For the sp^3 content in the range from 20% to 80%, the position of G peak significantly shifts to the higher Raman frequencies. This is in agreement with previously published papers on a-C films [3,5]. The large shift of the G peak position (around 30 cm^{-1}) to the higher frequencies is

observed for UV excitation wavelength (see Fig. 2 (b)). The range of behaviour of G peak can be understood within the three-stage model for different wavelengths introduced by Ferrari [3]. In passing from a-C to ta-C, the sp^3 content rises from 20% to 85%, while the sp^2 sites change gradually from rings to chains. The π states become increasingly localized on olefinic sp^2 chains and, eventually, sp^2 pairs embedded in the sp^3 matrix. Olefinic C=C bonds are shorter than aromatic bonds, so they have higher vibration frequencies and consequently they have a larger contribution at UV excitation wavelength [3,9,10]. It has been discussed in the literature if the high frequency of the G peak has also been attributed to the larger compressive stress in ta-C films [5,6]. At present time we could not make definite conclusion on the influence of stress on the G peak position. Further research has to be carried out.

Fig. 3(a) shows the full width at half maximum (FWHM) of the G peak as a function of sp^2 content for 457 nm and 325 nm excitation energy. The FWHM of the G peak decreases linearly with sp^2 fraction for both excitation wavelengths. The a-C films with lower sp^2 content has the largest G linewidth as they are more disorder. This is in agreement with the fact that the linewidth of G peak at any excitation increases as the disorder increases [5-7]. The linewidth of G band is around 180 cm^{-1} for a-C films and approximately 230 cm^{-1} for ta-C, which is in agreement with Ref. [3]. We did not observe any significant changes in the linewidth of G peak between 457 nm and 325 nm excitation wavelengths. This can be due to the reason that excitation wavelengths used in this work are quite close to each other.

Fig. 3(b) presents the variation of the G peak position with excitation wavelength for ta-C and a-C samples. The G-peak dispersion occurs only in disordered carbon and it is proportional to the degree of disorder of the sp^2 clustering [2,3,11]. As it can be

seen from Fig. 3(b), the G peak position decreases with the excitation wavelength for both a-C and ta-C films. For ta-C films the G peak position decreases from 1615 cm^{-1} at 325 nm excitation wavelength to 1529 cm^{-1} at 633 nm excitation wavelength. A smaller dispersion is observed for a-C films with high sp^2 content when the G peak position shifts from 1600 cm^{-1} to 1556 cm^{-1} at 325 nm and 633 nm excitations, correspondingly. This is consistent with results obtained in Ref. [2].

Fig. 4(a) presents the intensity ratio of the D and G peaks as a function of sp^3 content. The ratio of $I(D)/I(G)$ decreases with increase of sp^3 fraction. This confirms the three stage model introduced by Ferrari [3], which shows that $I(D)/I(G)$ ratio decreases with sp^3 content for a-C films and for ta-C films with high sp^3 content the $I(D)/I(G)$ tends to zero. As the sp^3 content increases, the sp^2 content decreases and sp^2 bonded clusters become smaller. The carbon rings are more distorted, open up and break into segments with chains of C=C groups. The D band, which is due to the breathing mode of aromatic sp^2 rings, is vanished and for very high sp^3 values the G band is nearly symmetrical, which is in agreement with spectra presented in Fig. 1.

Fig. 4(b) shows that the intensity of T peak at 1060 cm^{-1} increases with increase of sp^3 fraction, which is in agreement with published data [2,12,13]. This confirms a statement that T peak is identified with sp^3 -bonded carbon. The T peak is sensitive to small changes in sp^3 content in particularly at high sp^3 fraction.

4. Conclusion

We have presented a systematic analysis of the Raman spectra measured at 457 and 325 nm excitations for a-C films with sp^2 content varies from ~20% to ~90%. We have shown how the UV Raman spectra can provide a direct evidence for the presence of sp^3 bonds based on T peak, while visible Raman spectra present a powerful way to follow the evolution and ordering of the sp^2 sites based on the G and D peak. Within the three-stage model of the Raman spectra of the carbon films [3], in passing from a-C to ta-C, the sp^2 sites change gradually from rings to chains and the G peak shifts upwards from 1575 to 1598 cm^{-1} for visible excitation and from 1595 to 1630 cm^{-1} for UV excitation. With increase of sp^3 content the I(D)/I(G) ratio shifts to low values and for high sp^3 content tends to zero. The dispersion of the G peak is a crucial parameter to distinguish between different structures of amorphous carbon. It was confirmed that the bigger dispersion of G peak observed for ta-C films with high sp^3 content indicates the larger disorder in these films.

References

1. J. Robertson, *Mater. Sci. Eng. R* 37 (2002) 129
2. A.C. Ferrari, J. Robertson, *Phys. Rev. B* 64 (2001) 075414
3. A.C. Ferrari, J. Robertson, *Phys. Rev. B* 61 (2000) 14095
4. S. Praver, K.W. Nugent, Y. Lifshitz, G.D. Lempert, E. Grossman, J. Kulik, I. Avigal, R. Kalish, *Diamond Relat. Mater.* 5 (1996) 433
5. J. W. Ager, S. Anders, A. Andres, I. G. Brown, *Appl. Phys. Lett.* 66 (1995) 3444
6. A.C. Ferrari, B. Kleinsorge, N. A. Morrison, A. Hart, V. Stolojan, J. Roberston, *J. Appl. Phys.* 85 (1999) 7191
7. G. G. Stoney, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* (1905-1934) 82, 172-175 (1909)
8. D.W.M. Lau, J.G. Partridge, M.B. Taylor, D.G. McCulloch, J. Wasyluk, T.S. Perova, D.R. McKenzie, *J. Appl. Phys.* 105 (2009), 084302
9. K. W. R. Gilkes, H. S. Sands, D. N. Batchelder, J. Robertson, and W. I. Milne, *Appl. Phys. Lett.* 70 (1997) 1980
10. G. Irmer, A. Dorner-Reisel, *Advance Engineering Materials* 7 (2005) 8
11. Casiraghi, A. C. Ferrari, J. Robertson, R. Ohr, M.V. Gradowski D. Schneider, *Diamond Relat. Mater.* 13 (2004) 1480
12. K. W. R. Glikes, S. Praver, K. W. Nuget, J. Robertson, H. S. Sands, Y. Lifshitz, X. Shi, *J. Appl. Phys.* 87 (2000) 7283
13. G. Adamopoulos, K. W. R. Gilkes, J. Robertson, N. M. J. Conway, B. Y. Kleinsorge, A. Buckley, D. N. Batchelder, *Diamond and Related Materials* 8 (1999) 541

Figure captions:

Fig. 1. (a) Visible Raman spectra (457 nm) and (b) UV Raman spectra of the a-C films with different sp^3 content.

Fig. 2. (a) The G peak position as a function of sp^3 content measured by 457 nm and (b) 325 nm of excitation wavelength.

Fig. 3. (a) The full width at half maximum (FWHM) of the G peak as a function of sp^2 content measured by excitation with 457 nm and 325 nm. (b) Dispersion of G peak position vs. excitation wavelength for selected ta-C and a-C samples (note, that the connecting lines are used as guide to the eye).

Fig. 4. (a) The intensity ratio of the D to G peak as a function of the sp^3 content for visible (457 nm) excitation. (b) Raman peak intensity of the T band as a function of the sp^3 content.

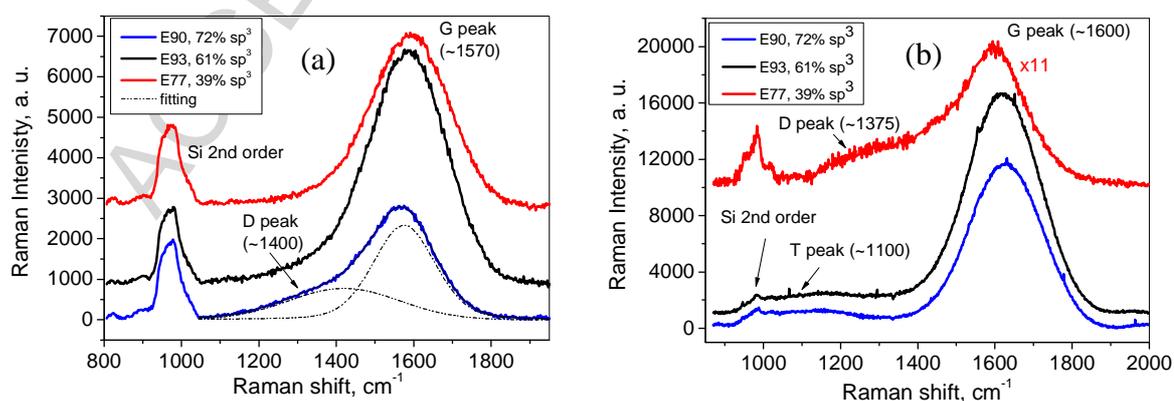


Fig. 1 (J. Wasyluk)

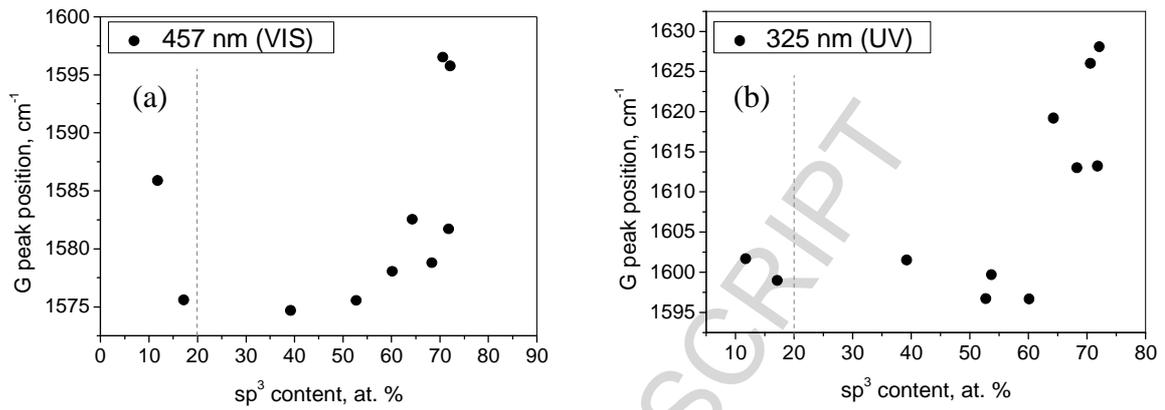


Fig. 2 (J. Wasyluk)

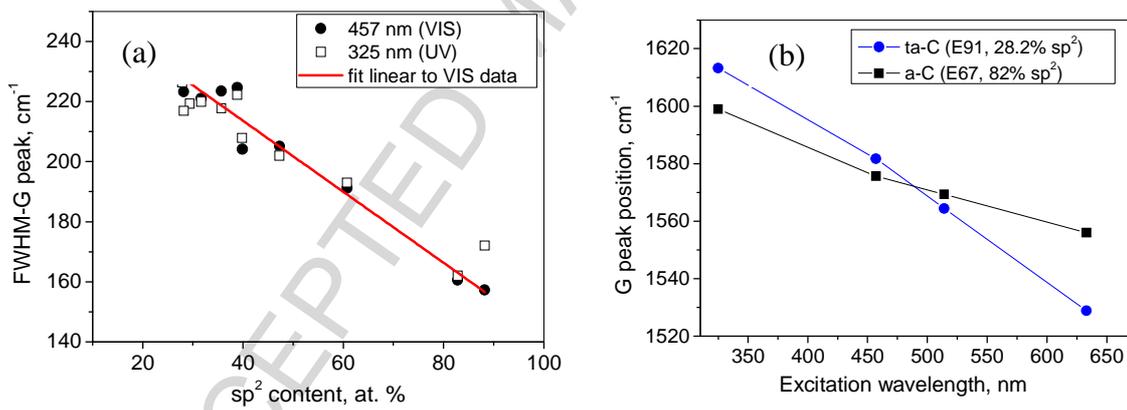


Fig. 3. (J. Wasyluk)

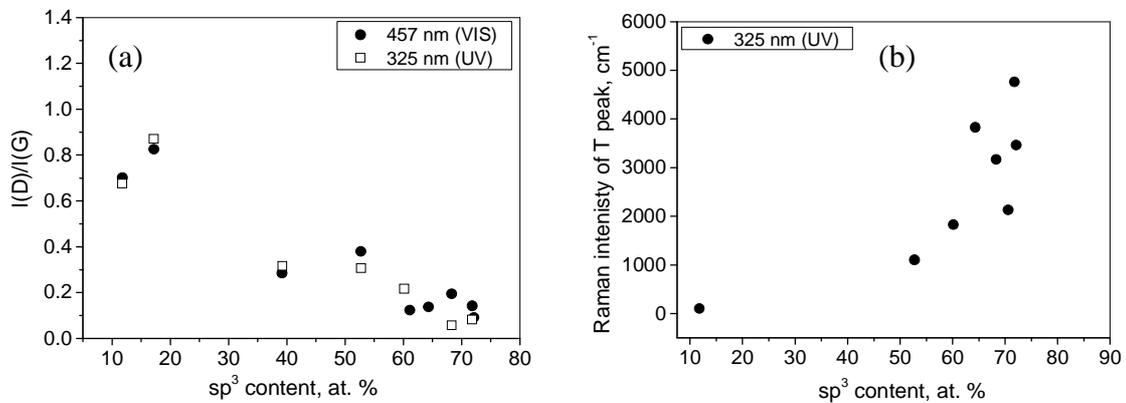


Fig. 4. (J. Wasyluk)