



<b>Title</b>	Transpolyacetylene chains in hydrogenated amorphous carbon films free of nanocrystalline diamond
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<b>Publication date</b>	2003
<b>Original citation</b>	Piazza, F., Golanski, A., Schulze, S. and Relihan, G. (2003) 'Transpolyacetylene chains in hydrogenated amorphous carbon films free of nanocrystalline diamond', Applied Physics Letters, 82(3), pp. 358-360. doi: 10.1063/1.1538349
<b>Type of publication</b>	Article (peer-reviewed)
<b>Link to publisher's version</b>	<a href="http://aip.scitation.org/doi/abs/10.1063/1.1538349">http://aip.scitation.org/doi/abs/10.1063/1.1538349</a> <a href="http://dx.doi.org/10.1063/1.1538349">http://dx.doi.org/10.1063/1.1538349</a> Access to the full text of the published version may require a subscription.
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Citation: *Appl. Phys. Lett.* **82**, 358 (2003); doi: 10.1063/1.1538349

View online: <http://dx.doi.org/10.1063/1.1538349>

View Table of Contents: <http://aip.scitation.org/toc/apl/82/3>

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# Transpolyacetylene chains in hydrogenated amorphous carbon films free of nanocrystalline diamond

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(Received 1 October 2002; accepted 25 November 2002)

The microstructure of distributed electron cyclotron resonance plasma-deposited hydrogenated amorphous carbon films (*a*-C:H) was investigated using electron diffraction, Raman spectroscopy, and Fourier transform infrared spectroscopy. Experimental evidence of the existence of transpolyacetylene (TPA) chains in *a*-C:H films free of nanocrystalline diamond is presented. The values of the mean bond angles and lengths and first neighbor numbers are consistent with the TPA data. The Raman spectra were fitted using the G and D bands and the bands centered at 1140, 1233, and 1475  $\text{cm}^{-1}$  assigned to TPA chains modes. The relative intensity of the latter decreases while hydrogen content decreases. A significant  $sp^2$ -CH olefinic mode contribution to the infrared stretching band is observed for the low-density films ( $\sim 1.2 \text{ g/cm}^3$ ). TPA chains growth is enhanced when ion current density and energy decrease. © 2003 American Institute of Physics.

[DOI: 10.1063/1.1538349]

In the plasma deposited hydrogenated amorphous carbon films (*a*-C:H), the  $sp^2$ -carbon is known to form variable size olefinic chains and/or aromatic clusters, more or less distorted, depending on the process parameters.<sup>1</sup> However, they have never been observed in transmission electron microscopy but their presence is consistent with the experimental results such as the photoluminescence or the D band in the visible Raman spectra.

The knowledge of the composition and hybridization ratio is not sufficient to understand the optical and electrical properties. The assessment of the  $sp^2$ -carbon structure is paramount since the  $\pi$  states determine the band gap. Transpolyacetylene (TPA) chains have been extensively studied.<sup>2</sup> Three features present in chemical vapor deposition (CVD) nanocrystalline diamond Raman spectra have been shown to correspond to TPA modes.<sup>3</sup> However, the existence of the TPA chains in *a*-C:H films free of nanocrystalline diamond has not been reported so far. In this work we report on presence of the TPA chains in *a*-C:H films grown using distributed electron cyclotron resonance (DECR) plasma.

*a*-C:H films were grown on  $\langle 100 \rangle$  silicon substrates using a DECR plasma reactor.<sup>4</sup> A microwave power of 800 W at a frequency of 2.45 GHz was used.  $\text{C}_2\text{H}_2$  was used as precursor. The plasma pressure was varied from 0.1 to 0.9 mTorr. The negative bias  $V_0$  applied to the substrate holder was regulated within the range between 25 and 600 V using a power supply operating at 13.56 MHz. It was kept constant during deposition by an automatic modulation of the power. The substrate holder was water cooled enabling deposition in the vicinity of room temperature. The hydrogen content and thickness were determined, respectively, from nuclear reac-

tion analysis (NRA)<sup>5</sup> and spectroscopic ellipsometry (SE).<sup>4,5</sup> The density was deduced from the SE and NRA data. The bond length  $r_1$  and angle  $\alpha$ , first neighbor number  $n_1$  and  $sp^3$ -carbon fraction were deduced from electron diffraction.<sup>4</sup> A Renishaw Raman microscope system 2000 was used to get the Raman spectra using the 514 nm line of an argon laser. A laser beam spot 50  $\mu\text{m}$  in diameter was used and the power was kept  $\sim \leq 1$  mW. Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Bio-Rad FTS-40 APC spectrometer in the transmission mode to assess the carbon-hydrogen bonding. Whatever the conditions used, the hydrogen content  $N_H \geq 20$  at. %,  $sp^2$ -carbon content  $C_2 > 47$  at. % and  $sp^3$ -carbon content  $6 \leq C_3 \leq 30$  at. %. The density  $\rho$  varies between 1.2 and 2.3  $\text{g cm}^{-3}$ .

Figure 1 shows the evolution of  $r_1$  and  $\alpha$  as a function of the  $sp^3$ -carbon fraction for the films deposited at 0.9 mTorr using a variable substrate bias ( $1.5 \leq \rho \leq 2.1 \text{ g/cm}^3$ ). The re-

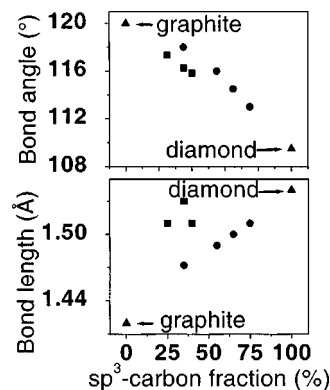


FIG. 1. Bond angle and length as a function of the  $sp^3$  fraction for the films deposited at 0.9 mTorr (square) including data from Ref. 6 (circles), graphite, and diamond (triangles).

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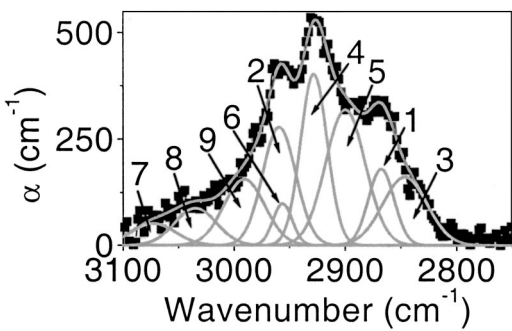


FIG. 2. Decomposition of the infrared C-H stretching band ( $P = 0.1$  mTorr,  $V_0 = -400$  V). The modes are labeled: (1)  $C(sp^3)$ -H<sub>2</sub> symmetrical, (2)  $C(sp^3)$ -H<sub>2</sub> asymmetrical, (3)  $C(sp^3)$ -H<sub>3</sub> symmetrical, (4)  $C(sp^3)$ -H<sub>3</sub> asymmetrical, (5)  $C(sp^3)$ -H, (6)  $C(sp^2)$ -H<sub>2</sub> symmetrical olefinic, (7)  $C(sp^2)$ -H<sub>2</sub> asymmetrical olefinic, (8)  $C(sp^2)$ -H aromatic, (9)  $C(sp^2)$ -H olefinic.

sults published previously<sup>6</sup> and the points corresponding to graphite and diamond are shown for comparison. While the bond angle ( $\alpha > 115^\circ$ ) is close to the value in graphite, the  $r_1$  values are closer to those for diamond than for graphite. In addition, for  $V_0 = -75$  V  $n_1 \approx 2.3$ . In order to explain these apparently inconsistent results it is proposed that the microstructure of the  $sp^2$ -carbon is dominated by the presence of hydrogenated  $sp^2$ -carbon chains such as TPA chains. Indeed, for unconstrained TPA chains  $\alpha = 120^\circ$  and  $r_1$  depends on the conjugated chain length. An increase of the conjugated length of such chains could explain the high value of the bond length. Also  $n_1$  is close to the TPA chains value (2).

The infrared C-H stretching band was investigated for the low-density films ( $\sim 1.2$  g/cm<sup>3</sup>) deposited at 0.1 mTorr. Figure 2 shows the C-H stretching band corresponding to a film deposited with  $V_0 = -400$  V after a baseline correction. The decomposition of the stretching band proposed previously<sup>7</sup> was used to qualitatively assess the bonding between carbon and hydrogen. In Fig. 2 the contribution of the  $C(sp^2)$ -H olefinic mode is visible although the infrared absorption cross-section  $\Gamma$  for this mode is expected to be significantly lower than the  $\Gamma$  values for the other modes, as in free molecules.<sup>8</sup> The relative intensity of the distinct vibration modes has been estimated. In order to take into account the difference in  $\Gamma$  between the modes it was assumed that the corresponding cross sections are those of free molecules.<sup>8</sup> The  $C(sp^2)$ -H olefinic mode contribution is of  $\sim 12\%$ . It reaches  $\sim 23\%$  for a film deposited using  $V_0 = -150$  V. The  $\Gamma$  values may vary with  $V_0$  because of the bias-related changes in the microstructure. However, since the density of the films deposited at 0.1 mTorr is relatively low and remains constant within the bias range considered, we consider that the bias-related variation in  $\Gamma$  is negligible. In conclusion, a significant fraction of hydrogen is bonded to  $sp^2$ -carbon. This is consistent with the presence of TPA chains where each  $sp^2$ -carbon is bonded to hydrogen.

After a linear background subtraction, the Raman spectra were fitted assuming that they represent a linear combination of five Gaussian distributions. Those features correspond to the D and G bands, and bands centered at  $\sim 1140$ ,  $1233$ , and  $1475$  cm<sup>-1</sup>. The three latter have been foreseen by theoretical studies,<sup>9</sup> observed in CVD nanocrystalline diamond and in  $a$ -C:H containing nanocrystalline diamond,<sup>10,11</sup> and as-

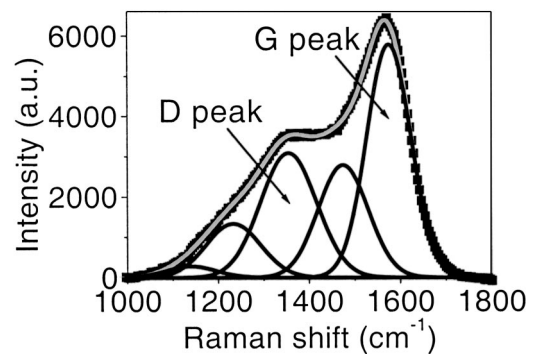


FIG. 3. Decomposition of the Raman spectra ( $P = 0.1$  mTorr,  $V_0 = -400$  V).

signed to the TPA chain modes.<sup>3</sup> Figure 3 shows the decomposition corresponding to a film deposited with  $V_0 = -400$  V at 0.1 mTorr. All the fitted spectra exhibit a large skew toward the lowest wave numbers. If it is related to TPA modes, it is likely that the band centered at  $\sim 1475$  cm<sup>-1</sup> also contributes to the spectra but is partly hidden by the G band. Indeed, the bands centered at  $1150$  and  $1475$  cm<sup>-1</sup> are often associated to one another.<sup>3</sup> The TPA bands position and full width at half-maximum remain constant for all the spectra. Figure 4 shows the evolution of the hydrogen content and of relative intensity of the  $1475$  cm<sup>-1</sup> band  $I_4$  as a function of  $V_0$  for the films deposited at 0.9 mTorr. The evolution of the  $1233$  cm<sup>-1</sup> band  $I_2$  (not shown) is similar. A decrease of  $I_4$  is associated with decreasing hydrogen incorporation. This observation strengthens the interpretation of the bands centered at  $1233$  and  $1475$  cm<sup>-1</sup> since hydrogen content decrease leads to a decrease in the TPA chains formation probability. The analysis of the  $I_4$  and  $I_2$  evolution as a function of  $V_0$  for several pressures (plot not shown) shows that,  $I_4$  and  $I_2$  are twice as high at 0.1 mTorr than at 0.5 mTorr for  $|V_0| \leq 500$  V or at 0.9 mTorr for  $200 \leq |V_0| \leq 600$  V. At 0.9 mTorr for  $|V_0| < 200$  V, and at 0.1 mTorr for  $|V_0| \leq 500$  V,  $I_4$  and  $I_2$  values are similar. Clearly, TPA chains growth is enhanced when ion current density and energy decrease.<sup>5</sup> This is consistent with the evolution of the hydrogen content that increases in these conditions.<sup>5</sup>

In conclusion, experimental evidence of the presence of transpolyacetylene chains in  $a$ -C:H films free of nanocrystalline diamond is presented. In the presence of the chains the average bond length is close to that of diamond, while the average bond angle is close of that for graphite. TPA chain growth is enhanced when ion current density and energy decrease.

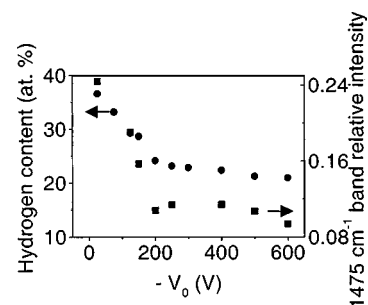


FIG. 4. Relative intensity of the  $1475$  cm<sup>-1</sup> band and hydrogen content as a function of the substrate bias for films deposited at 0.9 mTorr.

This work was supported by the European Community (Contract No. BRPR-CT98-0749).

- <sup>1</sup>J. Robertson and E. P. O'Reilly, *Phys. Rev. B* **35**, 2946 (1987).
- <sup>2</sup>A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, *Rev. Mod. Phys.* **60**, 781 (1988).
- <sup>3</sup>A. C. Ferrari and J. Robertson, *Phys. Rev.* **63**, 121405 (2001).
- <sup>4</sup>A. Golanski, F. Piazza, J. Werckmann, G. Relihan, and S. Schulze, *J. Appl. Phys.* **92**, 3662 (2002).
- <sup>5</sup>F. Piazza, D. Grambole, F. Herrmann, G. Relihan, M. F. Barthe, P. Desgardin, and A. Golanski, *Mater. Res. Soc. Symp. Proc.* **675**, W10.3.1 (2000).
- <sup>6</sup>M. Weiler, S. Sattel, T. Giessen, K. Jung, H. Ehrhardt, V. S. Veerasamy, and J. Robertson, *Phys. Rev. B* **53**, 1594 (1996).
- <sup>7</sup>J. Ristein, R. T. Stief, and L. Ley, *J. Appl. Phys.* **84**, 3836 (1998).
- <sup>8</sup>J. Fox and A. Martin, *Proc. R. Soc. London, Ser. A* **175**, 208 (1940).
- <sup>9</sup>D. Beeman, J. Silverman, R. Lynds, and M. R. Anderson, *Phys. Rev. B* **30**, 870 (1984).
- <sup>10</sup>T. Lopez-Rios, E. Sandré, S. Leclercq, and E. Sauvin, *Phys. Rev. Lett.* **76**, 4935 (1996).
- <sup>11</sup>M. Zarrabian, Thèse de Doctorat, Université de Nantes, France, 1998.