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F. Piazza and A. GolanskiS. SchulzeG. Relihan

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Transpolyacetylene chains in hydrogenated amorphous carbon films free of nanocrystalline diamond

F. Piazza^{a)} and A. Golanski

Centre National de la Recherche Scientifique, Laboratoire PHASE, 67037 Strasbourg, France

S. Schulze

Chemnitz University of Technology, Institut für Physik, 09107 Chemnitz, Germany

G. Relihan

National Microelectronics Research Centre, Prospect Row, Cork, Ireland

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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 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 (~1.2 g/cm³). TPA chains growth is enhanced when ion current density and energy decrease. © 2003 American Institute of Physics.

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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.¹ 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 π states determine the band gap. Transpolyacetylene (TPA) chains have been extensively studied.² Three features present in chemical vapor deposition (CVD) nanocrystalline diamond Raman spectra have been shown to correspond to TPA modes.³ 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 <100> silicon substrates using a DECR plasma reactor.⁴ A microwave power of 800 W at a frequency of 2.45 GHz was used. C₂H₂ 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)⁵ and spectroscopic ellipsometry (SE).^{4,5} The density was deduced from the SE and NRA data. The bond length r_1 and angle α , first neighbor number n_1 and *sp*³-carbon fraction were deduced from electron diffraction.⁴ 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 μ 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 ρ varies between 1.2 and 2.3 g cm⁻³.

Figure 1 shows the evolution of r_1 and α as a function of the *sp*³-carbon fraction for the films deposited at 0.9 mTorr using a variable substrate bias ($1.5 \leq \rho \leq 2.1$ g/cm³). The re-

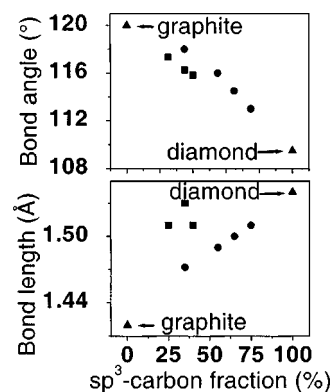


FIG. 1. Bond angle and length as a function of the *sp*³ fraction for the films deposited at 0.9 mTorr (square) including data from Ref. 6 (circles), graphite, and diamond (triangles).

^{a)}Electronic mail: fp221@eng.cam.ac.uk

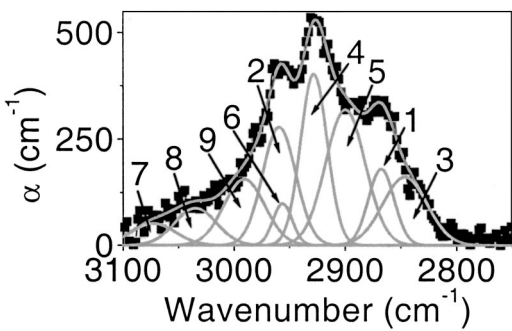


FIG. 2. Decomposition of the infrared C-H stretching band ($P = 0.1$ mTorr, $V_0 = -400$ V). The modes are labeled: (1) $C(sp^3)$ -H₂ symmetrical, (2) $C(sp^3)$ -H₂ asymmetrical, (3) $C(sp^3)$ -H₃ symmetrical, (4) $C(sp^3)$ -H₃ asymmetrical, (5) $C(sp^3)$ -H, (6) $C(sp^2)$ -H₂ symmetrical olefinic, (7) $C(sp^2)$ -H₂ asymmetrical olefinic, (8) $C(sp^2)$ -H aromatic, (9) $C(sp^2)$ -H olefinic.

sults published previously⁶ 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 (~ 1.2 g/cm³) 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 previously⁷ 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 Γ for this mode is expected to be significantly lower than the Γ values for the other modes, as in free molecules.⁸ The relative intensity of the distinct vibration modes has been estimated. In order to take into account the difference in Γ between the modes it was assumed that the corresponding cross sections are those of free molecules.⁸ 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 Γ 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 Γ 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 ~ 1140 , 1233 , and 1475 cm⁻¹. The three latter have been foreseen by theoretical studies,⁹ observed in CVD nanocrystalline diamond and in a -C:H containing nanocrystalline diamond,^{10,11} and as-

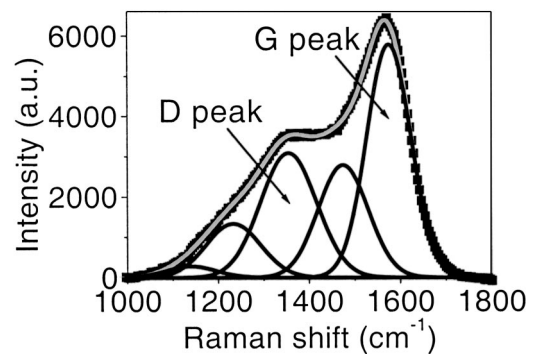


FIG. 3. Decomposition of the Raman spectra ($P = 0.1$ mTorr, $V_0 = -400$ V).

signed to the TPA chain modes.³ 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 ~ 1475 cm⁻¹ also contributes to the spectra but is partly hidden by the G band. Indeed, the bands centered at 1150 and 1475 cm⁻¹ are often associated to one another.³ 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⁻¹ band I_4 as a function of V_0 for the films deposited at 0.9 mTorr. The evolution of the 1233 cm⁻¹ 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⁻¹ 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.⁵ This is consistent with the evolution of the hydrogen content that increases in these conditions.⁵

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.

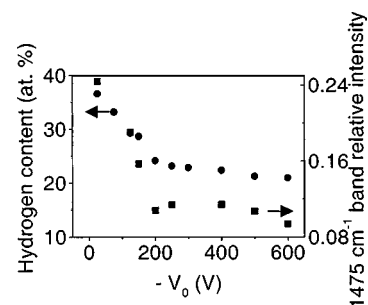


FIG. 4. Relative intensity of the 1475 cm⁻¹ band and hydrogen content as a function of the substrate bias for films deposited at 0.9 mTorr.

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