

Resonant Raman scattering from polyacetylene and poly(*p*-phenylene vinylene) chains included into hydrogenated amorphous carbon

M. Rybachuk^{1,3*}, A. Hu², J.M. Bell³

¹ *Federal Institute for Materials Research and Testing (BAM), Division VI.4 Surface Technology, Unter den Eichen 87, 12205 Berlin, Germany*

² *Department of Physics, University of Waterloo, 200 Univ. Ave. West, Waterloo, ON, N2L 3G1, Canada*

³ *Faculty of Built Environment and Engineering, Queensland University of Technology, 2 George St, Brisbane, Qld 4001, Australia*

ABSTRACT

The resonant Raman scattering in N-IR – UV range from amorphous hydrogenated carbon (*a*-C:H) reveal inclusions of trans-polyacetylene (*trans*-(CH)_x) chains with approximate length of up to 120 C=C units and inclusions of poly(*p*-phenylene vinylene) (PPV) polymer chains. The PPV is evidenced by a strong dispersive mode at *ca.* 1175 cm⁻¹. It was found that the Raman response from core *A_g* *trans*-(CH)_x modes incorporated into *a*-C:H to changing excitation energy is identical to of free-standing chains thus facilitating identification of *trans*-(CH)_x in complex carbonaceous materials spectra.

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MAIN TEXT

It is known that diamond-like carbon (DLC) can host a basic polymer, the *trans* isomer of polyacetylene (*trans*-(CH)_x) initially reported for CVD grown diamond¹ and later found in low temperature grown hydrogenated amorphous carbon (*a*-C:H) films². Excellent conductivity of *trans*-(CH)_x due to strong electron-phonon (*e*-ph) and electron-electron coupling originating from delocalised π electrons and an effective lattice nonlinearity^{3,4} and the large third-order nonlinear optical susceptibility that allows the chain to withstand high peak pump powers without damage to the sample, ensure considerable interest in this polymer as a non-linear optical material⁵. Achieving controlled inclusion of *trans*-(CH)_x into host DLC has been difficult and only short (≤ 20 of *C=C* units) *trans*-(CH)_x segments have been found to date^{1,6}. Recently, Hu *et al.*^{7,8} demonstrated that variably bonded carbon atoms, including *trans*-(CH)_x, can be incorporated on a carbon surface using ultra-short laser pulses. Apart from *trans*-(CH)_x segments DLC can also contain nanoparticles like carbon onions⁹ or spherical nanocrystallites as reported by Chen *et al.*¹⁰. These greatly reduce internal stress and thus are favourable for tribological applications.

We present here a resonant Raman scattering (RRS) investigation of *a*-C:H films synthesised in a low temperature inductively coupled plasma (ICP) reactor¹¹. Although films are indeed of low stress and host *trans*-(CH)_x chains of significant length (≤ 120 of *C=C* units), they also contain poly(*p*-phenylene vinylene) (PPV)

inclusions that have not been reported previously. The RRS technique probes atomic configurations in materials via the vibrational density of states^{3,6,12} and in this work laser excitation energies, $\hbar\omega_L$ ranging from 1.58 eV (N-IR) to 5.08 eV (UV) are used, ensuring bonding and structural disorder in the great majority of sp^3 , sp^2 and sp carbon mixtures are studied. We also demonstrate that the response of $trans-(CH)_x$ segments in $a-C:H$ to changing excitation energy is identical to that of free-standing isolated $trans-(CH)_x$ chains, both empirically and theoretically, using either the bimodal distribution model proposed by Brivio *et al.*¹³ or the amplitude mode theory proposed by Ehrenfreund *et al.*³. Our findings exemplify an approach which facilitates the extraction of $trans-(CH)_x$ contributions from the core $a-C:H$, DLC or carbonaceous materials spectra thus precluding overfitting as in case of Piazza *et al.*².

$a-C:H$ films were deposited on *Si* at the rate of ~ 30 nm/hour using CH_4/Ar plasma in Helmholtz type ICP reactor¹¹ at temperatures of ≤ 400 K as described elsewhere¹⁴. The deposition pressure was $\sim 6 \times 10^{-2}$ Pa and the substrate was negatively DC biased at 250-300 V. The fabricated films were of low stress ≤ 1 GPa, with hardness of ≤ 20 GPa and a friction coefficient of 0.07 at 70 % humidity as measured by nano-mechanical testing (UMIS). Electrical resistivity was $\geq 8 \times 10^8 \Omega \text{ cm}$. Films were ~ 140 nm thick with a maximum refractive index of 2.2 in the UV-blue region measured by IR-UV spectroscopic ellipsometry (J.A. Woollam Co.) The hydrogen content was found to be $27.5 (\pm 2.5)$ at. % for all films as determined from Fourier Transform infrared (FT-IR) spectroscopy (Nicolet Nexus). Analysis of C_{1s} and valence bands of X-ray photoelectron spectra (Kratos Axis Ultra) determined the sp , sp^2 and sp^3 contents to be 2, 68 and 30 % respectively with the uncertainty of 1.25 %. The sp -hybridised content was verified using Raman and FT-IR, and the sp^3 content using 244 nm Raman results¹². Unpolarised Raman spectra (5.08 - 1.58 eV) were

obtained *ex situ* at 293 K using 244, 532, 633 and 785 nm Renishaw instruments and 325 nm and 442 nm Kimmon Raman instruments. All excitation wavelengths excluding 785 nm were pulsed; the 785 nm was a continuous wavelength laser source. The frequency-doubled *Ar* ion laser was used for 244 nm, *He/Cd* for 325 nm and 442 nm, the frequency-doubled YAG laser was used for 532 nm, *He/Ne* gas laser was used for 633 nm and a diode laser source was used for 785 nm excitations. All measurements were taken in dynamic mode where a specimen is moved linearly at speeds of $\leq 30 \mu\text{m/s}$ and laser power was kept $< 1 \text{ mW}$ minimizing thermal damage.

Fig. 1 shows RRS spectra of an *a*-C:H film. After a linear background subtraction the spectra were all fitted with Gaussian line-shapes using a nonlinear least squares fitting¹⁵. Fitted bands are the common DLC *D* and *G* modes (N-IR and visible) and *T* mode (UV)¹² and the two A_g zone center vibrational modes of *trans*-(CH)_x^{3,4,13}: the C-C ω_1 at $\sim 1060 \text{ cm}^{-1}$, and the C=C backbone stretching ω_3 mode at $\sim 1450 \text{ cm}^{-1}$. The weak ω_2 mode at $\sim 1280 \text{ cm}^{-1}$ was not detectable though its contributions may be obscured by the *D* and ω_1 bands. The absorption for bulk *trans*-(CH)_x occurs at 1.5 - 1.7 eV^{4,13} and corresponds to positions of the A_g zone centres at 1060, 1280 and 1450 cm^{-1} . This applies for N-IR excitation. As $\hbar\omega_L$ increases moving away from resonance, shoulders appear at the high frequency side of the ω_1 and ω_3 modes, eventually developing into secondary peaks^{3,13,16} at excitation energies well above the band gap of 2.71 eV⁴. The RRS spectra disperse⁶ and these peaks change in intensity (*I*) and widths (*Γ*). The complexity of separating intercalated *trans*-(CH)_x from the host DLC modes lead us to analyse a single symmetric band distribution. This proved to be sufficient³ to account for a double peak Raman structure.

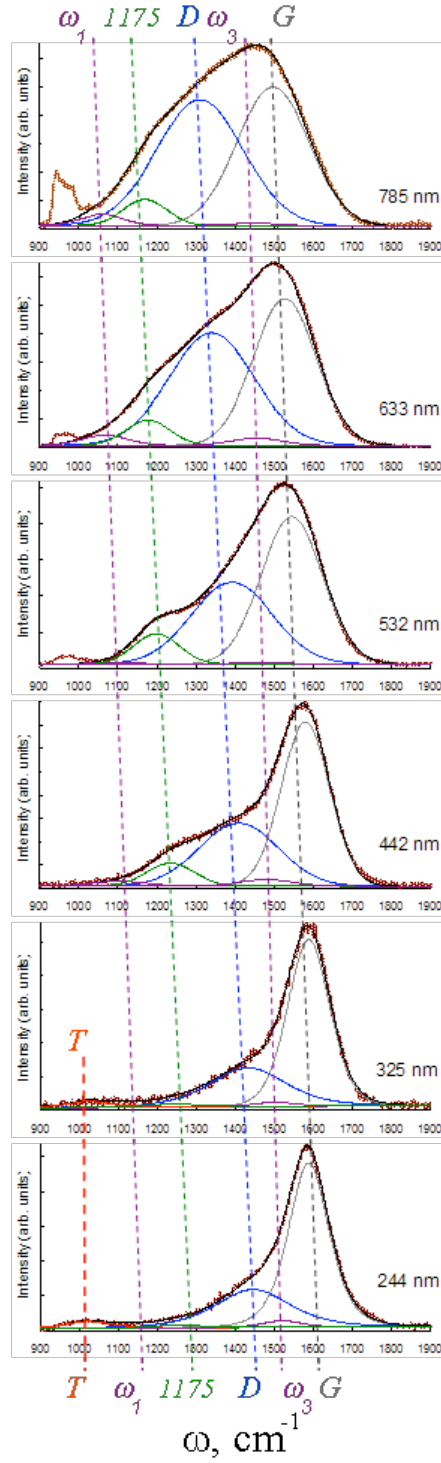


FIG. 1. The RRS spectra of examined $a\text{-C:H}$ films showing contributions from $trans\text{-}(\text{CH})_x$ (ω_1 and ω_3 modes), PPV (1175 cm^{-1} mode) and DLC (D , G and T modes). An asymmetric peak visible at N-IR – visible (green) $\hbar\omega_L$ at $\sim 950 \text{ cm}^{-1}$ is the second order Si .

A peak positioned at 1175 cm^{-1} at N-IR $\hbar\omega_L$ we assign to a $CC-H$ bending mode of the ring in neutral poly(*p*-phenylene vinylene)¹⁷⁻¹⁹. The origin of this mode could be due to introduction of heteroatoms (defects) in sp^2 rings since in single crystals these lead to a relaxation of wave vector $k=0$ selection rule^{6,12} thus providing a mechanism for phonons from outside the centre of the Brillouin zone to contribute to the Raman scattering. Introduction of heteroatoms allows delocalisation of π electrons confined to the sp^2 rings and thus dispersion^{12,17}.

Other PPV zone centre vibrational modes should be positioned at higher frequencies in the ranges^{18,19} $1200 - 1330$ and $1540 - 1625 \text{ cm}^{-1}$, but these are certainly obscured by the host D and the G modes. The large width of the 1175 cm^{-1} mode suggests a combination of a vinylene and a $CC-H$ ring bend modes since the zone mode frequency for vinylene²⁰ is at 1145 cm^{-1} .

As $\hbar\omega_L$ energy increases all peaks shift to a higher frequency; DLC modes are obeying phonon confinement rules¹², Fig. 2 (a) shows peak dispersion, $\Delta\omega$, the shift in peak position relative to the N-IR excitation peak position. Fig. 2 (b) summarizes changes in Γ for all fitted peaks. The steady $I(D)/I(G)$ ratio decrease from ~ 0.9 to 0.2 , pronounced reduction in Γ_D and Γ_G and the G peak saturation¹² at ~ 1590 for 244 nm excitation are indicative of a highly ordered and symmetric sp^2 phase^{12,14}. The band gap for PPV is $2.2 - 2.3 \text{ eV}$ ¹⁸ and that is selectively probed by a resonance frequency of green 532 nm laser; Fig. 1 shows the elevated intensity, I_{1175} and Fig. 2 (b) the broadening peak width, Γ_{1175} for the PPV peak. This peak is almost certainly of sp^2 origin since its contributions disappear in UV excitation. There is an increase in $I(\omega_3)/I(\omega_1)$ intensity ratio (Fig. 1) and in peak widths (Fig. 2 (b)) for *trans*-(CH)_x ω_1 and ω_3 peaks that become transformed when the $\hbar\omega_L$ exceeds the band gap ($\sim 1.5 \text{ eV}$ ^{4,13}) indicative of resonant probing of an inhomogeneous chain. Our results show

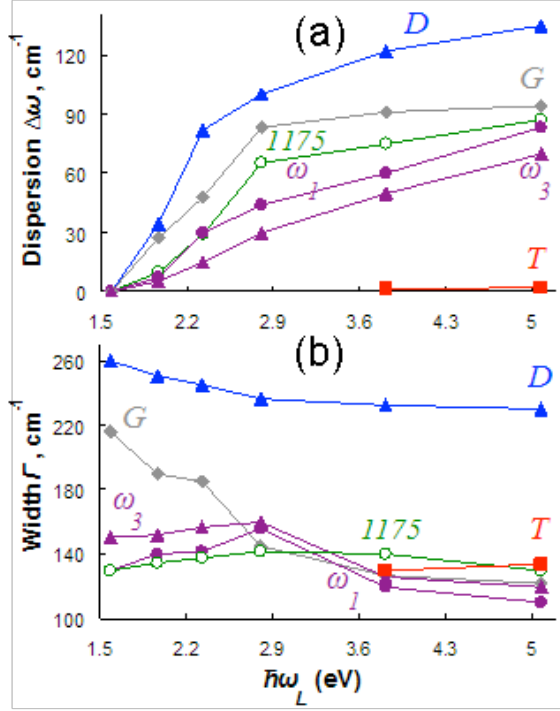


FIG. 2. (a) Peak dispersion, $\Delta\omega$ and (b) peak widths, Γ for all constituent peaks as a function of the laser excitation energy $\hbar\omega_L$.

that inhomogeneity of intercalated *trans*-(CH)_x chains measured using the distribution of the *e*-ph coupling constant λ , $p(\lambda)$ of the amplitude mode (AM) theory proposed by Ehrenfreund *et al.*³ gives $\lambda \sim 0.17$ for N-IR and ~ 0.24 for UV; in good agreement with the AM model. λ determines the Peierls relation for the energy gap and its distribution arises from finite localisation lengths and bond length disorder. The AM results indicate that *trans*-(CH)_x chains probed by high $\hbar\omega_L$ are of shorter π -conjugation lengths and of higher bond disorder. The approximate chain lengths for both single C-C and double C=C bonds of *trans*-(CH)_x segments were determined using the bimodal distribution model proposed by Brivio *et al.*¹³ and was found to be ~ 120 of bond lengths units (N-IR), at the estimation limit of the model, and with a population

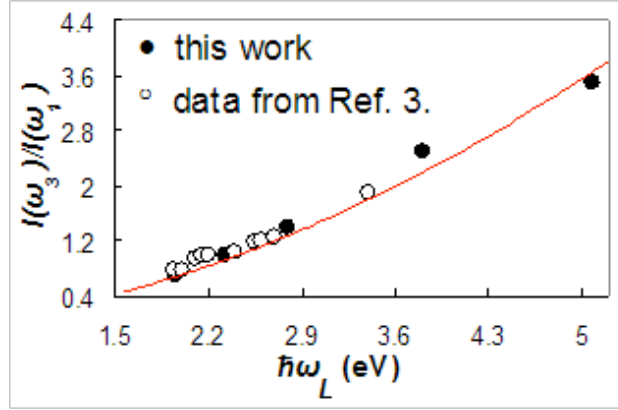


FIG. 3. The intensity ratio of $I(\omega_3)/I(\omega_1)$ vs. the laser excitation energy $\hbar\omega_L$ for *trans*-(CH)_x inclusions in *a*-C:H. Solid line is a theoretical calculation performed using the amplitude mode formalism³.

of short chain of approximately 8 (UV). Shorter chains are probed by higher $\hbar\omega_L$. The average chain population is $\sim 25 (\pm 5)$ bond length units owing to the uncertainties given by the Raman fitting and the bi-modal distribution model¹³. All *trans*-(CH)_x chains are highly disordered as evidenced by wide ω_1 and ω_3 Raman peaks reaching their maximum in the blue-green range.

We have extended the $I(\omega_3)/I(\omega_1)$ vs. $\hbar\omega_L$ theoretical AM distribution calculations (independent of chain length) of Ehrenfreund *et al.*³ for the visible range to include N-IR and UV $\hbar\omega_L$. Fig. 3 shows that our experimental results are in good agreement with the theoretical prediction and with Ehrenfreund's experimental data; clearly both the free-standing and incorporated *trans*-(CH)_x chains obey the same $I(\omega_3)/I(\omega_1)$ evolution formalism.

Long *trans*-(CH)_x chains and PPV inclusions are only possible in an ordered sp^2 *a*-C:H matrix that is achieved via deposition in ICP reactor analogous to used by Chen

*et al.*¹⁰ with high plasma density and low electron temperature compared to conventional DLC deposition systems.

In summary, the RRS investigation of ICP fabricated *a*-C:H films showed that films host long *trans*-(CH)_x chains with up to 120 C=C bond length units and also poly(*p*-phenylene vinylene) as evidenced by the 1175 cm⁻¹ Raman mode. We have postulated the origin of this PPV mode and provided a theoretical basis for arguing the response of *trans*-(CH)_x chains in the *a*-C:H matrix to changing Raman excitation energy is identical to of free-standing chains. The evolution of relative intensity ratio for core *trans*-(CH)_x modes will facilitate identification of *trans*-(CH)_x modes in other complex carbonaceous materials spectra.

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