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

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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=O 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.
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 diamond$^1$ and later found in low temperature grown hydrogenated amorphous carbon ($a$-C:H) films$^2$. Excellent conductivity of *trans*-(CH)$_x$ due to strong electron-phonon (e-ph) and electron-electron coupling originating from delocalised $\pi$ 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 material$^5$. Achieving controlled inclusion of *trans*-(CH)$_x$ into host DLC has been difficult and only short ($\leq 20$ 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 onions$^9$ 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) reactor$^{11}$. Although films are indeed of low stress and host *trans*-(CH)$_x$ chains of significant length ($\leq 120$ 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\textsuperscript{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)$_n$ segments in a-C:H to changing excitation energy is identical to that of free-standing isolated trans-(CH)$_n$ chains, both empirically and theoretically, using either the bi-modal distribution model proposed by Brivio \textit{et al.}\textsuperscript{13} or the amplitude mode theory proposed by Ehrenfreund \textit{et al.}\textsuperscript{3}. Our findings exemplify an approach which facilitates the extraction of trans-(CH)$_n$ contributions from the core a-C:H, DLC or carbonaceous materials spectra thus precluding overfitting as in case of Piazza \textit{et al.}\textsuperscript{2}.

\textit{a}-C:H films were deposited on \textit{Si} at the rate of \textasciitilde 30 nm/hour using $CH_4$/Ar plasma in Helmholtz type ICP reactor\textsuperscript{11} at temperatures of $\leq$ 400 K as described elsewhere\textsuperscript{14}. The deposition pressure was $\sim$6\times10$^{-2}$ Pa and the substrate was negatively DC biased at 250-300 V. The fabricated films were of low stress $\leq$ 1 GPa, with hardness of $\leq$ 20 GPa and a friction coefficient of 0.07 at 70 % humidity as measured by nano-mechanical testing (UMIS). Electrical resistivity was $\geq$ 8\times10$^8$ $\Omega$ cm. Films were $\sim$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 (\textpm 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 results\textsuperscript{12}. Unpolarised Raman spectra (5.08 - 1.58 eV) were
obtained \textit{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 \textit{Ar} ion laser was used for 244 nm, \textit{He/Cd} for 325 nm and 442 nm, the frequency-doubled YAG laser was used for 532 nm, \textit{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 \textit{a-C:H} film. After a linear background subtraction the spectra were all fitted with Gaussian line-shapes using a nonlinear least squares fitting\textsuperscript{15}. Fitted bands are the common DLC \textit{D} and \textit{G} modes (N-IR and visible) and \textit{T} mode (UV)\textsuperscript{12} and the two \textit{A} \textit{g} zone center vibrational modes of \textit{trans-} \((\text{CH})_x\)^\textsuperscript{3,4,13}: the \textit{C}-\textit{C} \( \omega_1 \) at \( \sim 1060 \text{ cm}^{-1} \), and the \textit{C}=-\textit{C} backbone stretching \( \omega_3 \) mode at \( \sim 1450 \text{ cm}^{-1} \). The weak \( \omega_2 \) mode at \( \sim 1280 \text{ cm}^{-1} \) was not detectable though its contributions may be obscured by the \textit{D} and \( \omega_1 \) bands. The absorption for bulk \textit{trans-}(\text{CH})\textsubscript{x} occurs at 1.5 - 1.7 eV\textsuperscript{4,13} and corresponds to positions of the \textit{A} \textit{g} zone centres at 1060, 1280 and 1450 cm\textsuperscript{-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 \( \omega_1 \) and \( \omega_3 \) modes, eventually developing into secondary peaks\textsuperscript{3,13,16} at excitation energies well above the band gap of 2.71 eV\textsuperscript{4}. The RRS spectra disperse\textsuperscript{6} and these peaks change in intensity \((I)\) and widths \((\Gamma)\). The complexity of separating intercalated \textit{trans-} \((\text{CH})_x\) from the host DLC modes lead us to analyse a single symmetric band distribution. This proved to be sufficient\textsuperscript{3} to account for a double peak Raman structure.
FIG. 1. The RRS spectra of examined α-C:H films showing contributions from trans-(CH)_x (ω_1 and ω_2 modes), PPV (1175 cm\(^{-1}\) mode) and DLC (D, G and T modes).

An asymmetric peak visible at N-IR – visible (green) hω_L at ~950 cm\(^{-1}\) is the second order Si.
A peak positioned at 1175 cm\(^{-1}\) at N-IR \(h\omega_L\) 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 \(\pi\) 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 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 vinylene\(^{20}\) is at 1145 cm\(^{-1}\).

As \(h\omega_L\) energy increases all peaks shift to a higher frequency; DLC modes are obeying phonon confinement rules\(^{12}\), 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 \(\Gamma\) for all fitted peaks. The steady \(I(D)/I(G)\) ratio decrease from \(~0.9\) to 0.2, pronounced reduction in \(\Gamma_D\) and \(\Gamma_G\) and the G peak saturation\(^{12}\) 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 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, \(\Gamma_{1175}\) 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)\(_x\), \(\omega_1\) and \(\omega_3\) peaks that become transformed when the \(h\omega_L\) exceeds the band gap (~1.5 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, $\Gamma$ 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 $\lambda$, $p(\lambda)$ of the amplitude mode (AM) theory proposed by Ehrenfreund et al. $^3$ gives $\lambda \sim 0.17$ for N-IR and $\sim 0.24$ for UV; in good agreement with the AM model. $\lambda$ 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 $\pi$-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 bi-modal distribution model proposed by Brivio et al. $^{13}$ and was found to be $\sim 120$ 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 formalism$^3$.

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 model$^{13}$. All trans-(CH)$_x$ chains are highly disordered as evidenced by wide $\omega_1$ and $\omega_3$ 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.\textsuperscript{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 $\text{trans-}(\text{CH})_x$ chains with up to 120 $\text{C}=\text{C}$ bond length units and also poly($p$-phenylene vinylene) as evidenced by the 1175 cm\textsuperscript{-1} Raman mode. We have postulated the origin of this PPV mode and provided a theoretical basis for arguing the response of $\text{trans-}(\text{CH})_x$ 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 $\text{trans-}(\text{CH})_x$ modes will facilitate identification of $\text{trans-}(\text{CH})_x$ modes in other complex carbonaceous materials spectra.

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