Polyacetylene in Diamond Films Evidenced by Surface Enhanced Raman Scattering

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Trans-polyacetylene is evidenced by surface enhanced Raman scattering (SERS) in diamond films prepared by hot filament assisted chemical vapor deposition from CH_4 and H_2. The analysis of the Raman spectra for different excitation energies shows that the deposited trans-polyacetylene is composed of chains exhibiting short conjugation lengths. Together with polyacetylene, diamond crystals of nanometric dimension are evidenced by both SERS and high resolution transmission electron microscopy. [S0031-9007(96)00493-0]

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Though lately noticeable technical progress in the chemical vapor deposition (CVD) of diamond films has been accomplished, the basic phenomena leading to the formation of diamond are still to be comprehended [1]. Since most of the surface-sensitive techniques are incompatible with the CVD environments, the chemical reactions and the nature of the intermediate species involved in the low pressure diamond growth process are still poorly known. Opposite to most surface-sensitive techniques, surface enhanced Raman scattering (SERS) [2] has been reported to be compatible with the CVD environments [3]. In this paper, this technique is shown to give new insight into the nature of CVD diamond codeposited species.

Here, we report *in situ* SERS measurements which prove that trans-polyacetylene [trans-$(CH)_n$] [4] is formed together with nm-sized diamond crystals. Deposited trans-$(CH)_n$ is found to be composed exclusively of short distance conjugation chains and to be surprisingly stable at fairly high temperature.

Using a Kr^+ laser and a U1000 Jobin-Yvon spectrometer, Raman scattering by diamond films is measured *in situ* in a hot filament assisted CVD reactor. This reactor is a UHV compatible chamber which is equipped with a silver source used to generate SERS. A rhenium filament which can be heated up to 1900 °C is set 0.5 cm from the sample. During the deposition, the sample is kept at the constant temperature of 700 °C. Si(111) wafers which were previously scratched in an ultrasound bath containing 1 μm diamond powder were used as substrates. Prior to diamond deposition and in order to remove the silicon native oxide, the substrates were heated up to 900 °C for about 10 min in a vacuum in the 10^{-7} torr range. CH_4 and H_2 were sequentially introduced into the reactor in order to obtain a gaseous mixture with a relative mass concentration $c = [CH_4]/[H_2]$ of a few percent. The diamond film depositions were performed under the static pressure of 20 torr. While recording the Raman spectra, the rhenium filament was switched off and the sample was kept near room temperature. To generate SERS, a few nm-thick silver films were deposited on the samples in vacuum. During the evaporation of silver, in order to stop the deposition when the Raman enhancement is maximum, we monitored the inelastic background of SERS. The deposited silver films consist of particles of several tenths of a nanometer.

Some of our samples have also been investigated by transmission electron microscopy (TEM) using a Philips CM300 microscope operated at 300 kV. Self-supported thin diamond films were prepared by dissolving the Si substrate in HF/HNO_3 acid and were picked up on a carbon-coated copper grid for TEM plane-view observations. Figure 1 shows two micrographs, both corresponding to the same sample which was deposited during 60 min ($c = 3.2\%$). Figure 1 (top) shows that the

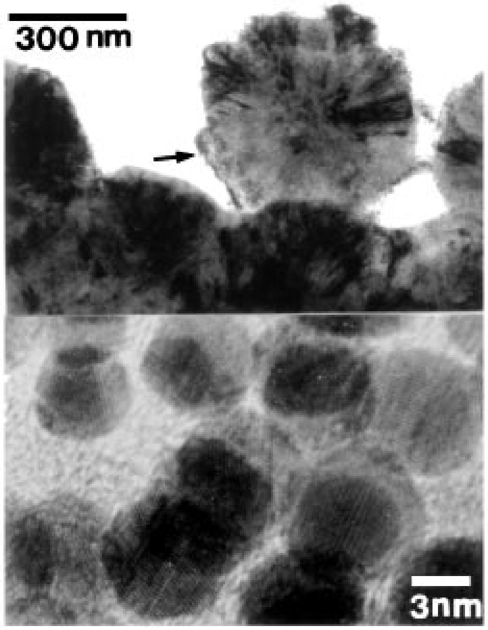

FIG. 1. Transmission electron micrographs of a diamond film deposited during 60 min ($c = [CH_4]/[H_2] = 3.2\%$). The bottom picture corresponds to the region indicated by an arrow in the top picture.

film is continuous and mainly consists of several hundred nm large diamond crystals. However, in agreement with Ref. [5], crystals of much smaller dimensions which are embedded in an amorphous tissue are observed in cracks and holes in the film. The distribution of nanocrystal sizes is 6 nm ± 30%.

As previously demonstrated by experiments in air [6], silver particles deposited on diamond films amplify the Raman scattering. Figure 2 shows four Raman spectra recorded using an exitation wavelength of 530.9 nm considering one sample which was grown during 40 min ($c = 3\%$). Figure 2(a) corresponds to the bare deposit. Figure 2(b) shows the enhanced Raman spectrum measured after silver was deposited. Opposite to spectrum 2(a), the first order Raman scattering of diamond at 1330 cm^{-1} in spectrum 2(b) exhibits a tail towards lower wave numbers. This asymmetric diamond peak is always observed in our SERS spectra. Quite often, a small structure at 1240 cm^{-1} which corresponds to the maximum in the density of states of phonons in diamond can be distinguished. The asymmetry in the shape of the peak at 1332 cm^{-1} and the structure at 1240 cm^{-1} can be ascribed to nonconserved momentum phonon excitations which take place in nm-sized crystals [7], such as the ones seen in Fig. 1.

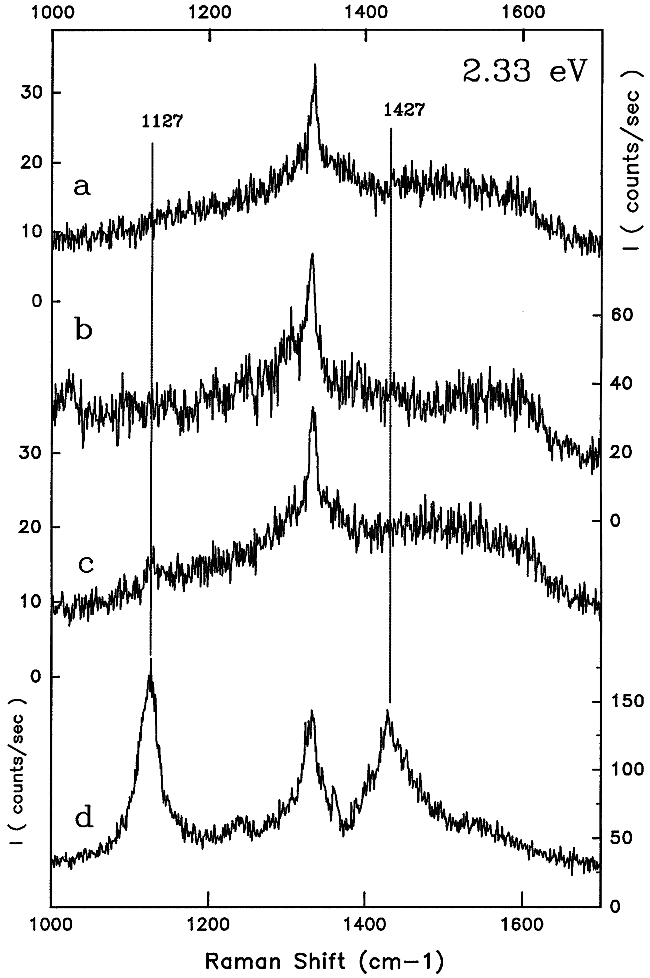

FIG. 2. Raman spectra (excitation laser energy = 2.33 eV) of a film deposited during 40 min ($c = [CH_4]/[H_2] = 3\%$): (a) bare film (no silver); (b) after silver deposition; (c) after heating the film up to 850 °C during 10 min (no silver); (d) subsequent silver deposition after thermal treatment. A SERS background can be seen in (b) and (d).

While the samples were kept at 850 °C for several minutes, we observed that the previously deposited silver particles evaporate. Figures 2(c) and 2(d), respectively, correspond to nonenhanced and enhanced Raman spectra which were measured after thermal treatment. Since Figs. 2(a) and 2(c) exhibit the same main features, it results that the film is not chemically modified by the silver deposition followed by the 850 °C thermal treatment. The only relevant difference takes place at 1127 cm^{-1} where the shoulder in Fig. 2(a) is transformed into the small peak in Fig. 2(c). This peak which is often weakly observed in diamond film Raman spectra is generally attributed to amorphous or microcrystalline diamond. However, this assignment is still a matter of debate [8–13].

We will now discuss spectrum 2(d). Other SERS spectra which are very similar to spectrum 2(d) were obtained each time the sample was previously heated up to 850 °C. For any given sample, the shape of the SERS spectrum remains unchanged upon repeated heating and subsequent deposition of silver. The peaks at 1429 and 1127 cm^{-1} are very similar to the ones which are reported for trans-$(\text{CH})_n$ [4,14–16]. These peaks (hereafter, respectively, named ν_1 and ν_3 [14]) mainly involve the stretching of the double (ν_1) and the single (ν_3) carbon-carbon bonds. The observation of three other less pronounced peaks at 2245, 2573, and 2810 cm^{-1} confirm such assignment [4]. Actually, we do not know the mechanism which leads to the preferential enhancement of trans-polyacetylene after the thermal treatment. Because silver dissolves in the acid which is used to prepare the TEM sample, the Ag particles could not be observed by TEM. Nevertheless, scanning electron microscopy observations clearly prove that the thermal treatment induces a widening of the grain boundaries which should favor the migration of silver particles inside the film.

As seen in Fig. 2(d) the SERS spectra which show both the ν_1 and ν_3 peaks systematically exhibit a pronounced asymmetry in the peak at 1332 cm^{-1} and also a small structure at 1240 cm^{-1} [7]. Consequently, it appears that the deposition of silver on preheated samples leads to the preferential enhancement of the Raman scattering by both polyacetylene and nm-sized diamond crystals. Since SERS enhancement only concerns the chemical entities which are located near the silver particles [2], it may be that either silver migrates to two different regions where either nanocrystals or trans-$(\text{CH})_n$ are located or to a region where both nanocrystals and trans-$(CH)_n$ are located. Considering the later hypothesis, since the nanocrystals and the amorphous phase detected by TEM are intimately mixed (Fig. 1), we suggest that this amorphous phase could be trans-$(CH)_n$. In the following lines, we will now concentrate on better characterizing the structure of the deposited polyacetylene.

From one sample to the other, some changes in the shape of the strong fundamental band ν_1 at 1429 cm^{-1} are observed [4]. Since both ν_1 and ν_3 bands are characteristic of the motion of conjugate polymer skeletons with a substantial contribution from the stretching vibrations of the double carbon-carbon bonds, transitions between π (bonding) and π^* (antibonding) electronic states are induced by photons from the laser and a strong Raman resonance is observed [4,14–16]. Figure 3 gathers SERS spectra recorded for three different lines of the Kr^+ laser (520.8, 530.9, and 568.2 nm). The measured film was grown during 30 min ($c = 3\%$) and was kept at 850 °C during 5 min before Ag was deposited. As expected, the peak at 1332 cm^{-1} which is attributed to diamond does not exhibit any frequency shift. On the contrary, a downshift of the trans-$(CH)_n$ peak frequencies with decreasing laser excitation energies and an inversion between their relative intensity is observed.

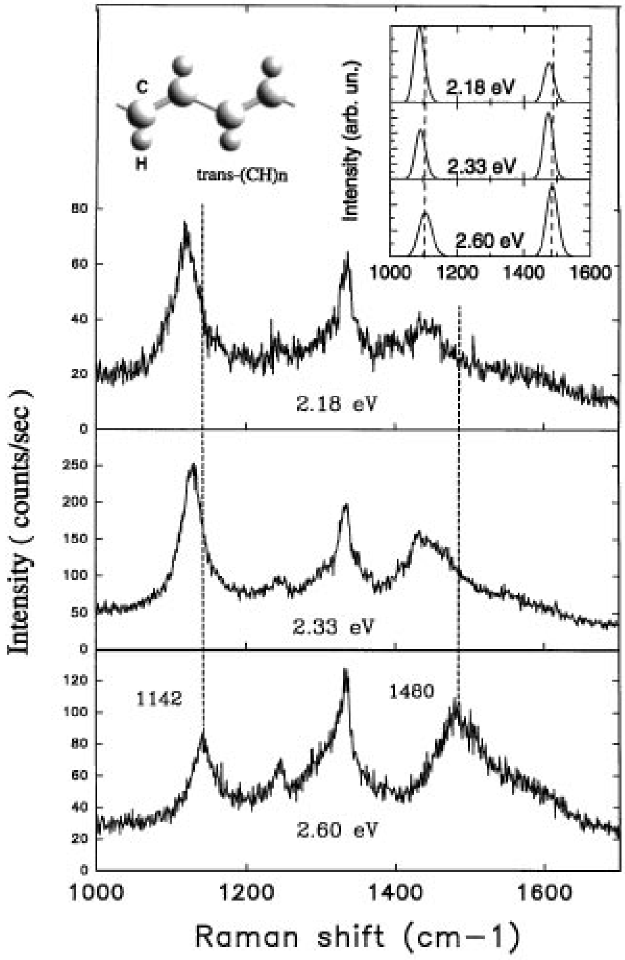

FIG. 3. SERS spectra recorded for the different excitation energies (indicated in the picture). The film is grown during 30 min ($c = [CH_4]/[H_2] = 3\%$). In the inset, computed Raman scattering of trans-polyacetylene chains with a conjugation length which equals 20 double carbon-carbon bonds is shown (formalism from Ref. [18]).

Many experiments and theories were devoted to understanding the Raman spectra of classically synthesized trans-polyacetylene [4]. It is now well admitted that the total Raman cross section is due to the separate contribution of both the short- and long-sized conjugated chains. The two peaks named ν_1 and ν_3 in the Raman spectra actually decompose into two subpeaks which are attributed to either long- or short-sized conjugated chains. Since the Raman peaks of trans-$(CH)_n$ in spectrum 2(d) do not exhibit any substructure, the CVD deposited trans-$(CH)_n$ is found to be only composed with one type of chain, namely, the short conjugated ones. Indeed, bromine doped or scratched trans-$(CH)_n$ are known to exhibit only the subpeaks which correspond to the short chains, and their Raman spectra are then very similar to the ones presented in this paper [17]. In order to model the experimental excitation spectra, Brivio and Mulazzi [18] chose two empirical relations of dependence upon the conjugation length (N) for the frequency of the ν_1 and ν_3 modes in shortly conjugated chains,

$$\omega_1(N) = (1450 + 500/N)\ \mathrm{cm}^{-1},$$

$$\omega_3(N) = (1060 + 600/N)\ \mathrm{cm}^{-1}.$$

The inset in Fig. 3 gathers three different simulated Raman spectra which have been computed using the formalism from [18], considering a mean conjugation length of 20 double carbon bonds and three different excitation wavelengths. Though some differences are seen in the spectral positions of both experimental and theoretical peaks, the resonant behavior is well reproduced by the calculation.

Differently from what is observed considering in-solution synthesized polyacetylene [19], CVD-tran-$(CH)_n$ is stable up to temperatures as high as 850 °C. This high temperature stability is certainly related to a different molecular structure which is reflected in the short conjugation length. Opposite to usual polyacetylene, CVD polyacetylene may be composed with interconnected chains which is consistent with the short conjugation length. Some efforts in order to better characterize the actual structure of CVD polyacetylene are necessary to understand the unusual physical properties observed here and which make this polyacetylene a promising material.

Finally, the possible role of such thermally stable polyacetylene in the diamond synthesis reaction is to be considered. Chemically, diamond results from the ordered dehydrogenation of trans-$(CH)_n$. From the crystallographic point of view, the very good lattice parameter agreement must be pointed out: the periodicity vector of trans-polyacetylene is 2.55 Å long; the unit-cell periodicities of the (100) and (111) surfaces are, respectively, 2.51 and 5.3 Å long. Diamond growth mechanisms involving sp^2 type growing agents have been proposed by different authors [20–22]. Since the chemical bond in trans-$(CH)_n$ strongly differs from the bond in usual covalent carbon species [23], we suggest that the reactivity of trans-$(CH)_n$ when opposed to diamond surfaces should be different from the reactivity of usual carbon containing compounds. In that sense, trans-$(CH)_n$ again appears to be an interesting compound to consider.

In conclusion, since it helped in showing that trans-polyacetylene is deposited together with diamond, SERS is a technique well suited to investigate this CVD reaction. A close analysis of the features of the deposited trans-polyacetylene SERS spectra helped us determine an estimated conjugation length of the chains which appears to be short compared to what is measured for in-solution synthesized polyacetylene. The high temperature stability of the CVD-synthesized polyacetylene suggests that the molecular structure strongly depends on the way the polymer is synthesized.

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