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Diamond & Related Materials 15 (2006) 1085 – 1089

DIAMOND AND RELATED MATERIALS

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Low temperature electron spin resonance investigation on SWNTs after hydrogen treatment

S. Musso [a,*,1], S. Porro [a,1], M. Rovere [a], A. Tagliaferro [a], E. Laurenti [b], M. Mann [c], K.B.K. Teo [c], W.I. Milne [c]

[a] *Department of Physics and LAQ Intese, Politecnico di Torino, Torino, Italy*
[b] *Department of Inorganic, Physical and Material Chemistry, Università di Torino, Torino, Italy*
[c] *Department of Engineering, University of Cambridge, Cambrdige, UK*

Abstract

We report a study of hydrogen adsorption experiment on SWNT samples deposited by chemical vapor deposition (CVD) and investigated with Electron Spin Resonance spectroscopy (ESR) before and after hydrogen treatment. The ESR investigation was performed at room and low temperature (4–30 K). We found that ESR technique is very useful to investigate paramagnetic centers and their interaction with hydrogen.

The morphology and structure of the samples were characterized by Micro-Raman spectroscopy. Subsequently the thermal stability was investigated by thermogravimetric analysis (TGA) testing. Brunauer Emmett Teller (BET) analysis was used to calculate the specific surface area and porosity of the as grown samples. All characterizations showed a small presence of residual Fe impurity (3.3 wt.%).

Keywords: Carbon nanotubes; Chemical vapor deposition; Hydrogen storage; ESR

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1. Introduction

The world is becoming more and more conscious about its consumption of fossil fuels and about consequent environmental problems. As a result, interest towards possible alternative sources of energy is rapidly increasing. Hydrogen is expected to be the best candidate [1] as a renewable and clean energy carrier. The current ways of storing hydrogen are gas bombs, refrigerated (at 77 K) tanks and adsorbed in solids such as metal hydrides.

Recently, tremendous interest has been aroused by the discovery of the hydrogen adsorption capacity in carbon materials [2], such as nanoporous carbon or nanofiber and, in particular, carbon nanotubes (CNTs) [3]. CNTs show unique physical/chemical properties for many potential applications [4] and their low density and high porosity makes them a potentially useful and safe solid hydrogen storage system [5]. However the reported amounts of hydrogen uptake in CNTs varies significantly depending on the research groups, and the mechanism lying behind the gas interaction with the carbon layer is not yet fully understood [6].

In this study, we used electron spin resonance as a toll to investigate the effect of hydrogen adsorption in SWNTs grown by chemical vapor deposition (CVD) on the various properties of the ESR signal, such as spin density and relaxation time.

2. Experimental

The single wall carbon nanotubes (SWNTs) investigated in this report (average diameter <2 nm; length of a few microns) were provided by Thomas Swan and Co. They have been deposited by CVD and have a 70–90% purity level in weight. No attempt to perform further purification or catalyst extraction was made in order to prevent large-scale modification of the material [7].

As-grown samples were characterized by electron microscopy (not reported in this work) and Raman spectroscopy (MicroRaman Renishaw Ramascope, 514.5 nm excitation) in order to check the amount of SWNTs.

The thermal degradation of the samples was investigated by means of a thermogravimetric analysis (TGA) 2050 balance

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* Corresponding author. Dip. Fisica, Politecnico Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy. Tel.: +39 011 5647381; fax: +39 011 5647399.
E-mail address: simone.musso@polito.it (S. Musso).

[1] These authors contributed equally to this work.

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doi:10.1016/j.diamond.2005.11.018

(TA inc.). About 10 mg of the samples were placed in an alumina sample pan, and the TGA experiments were performed with a 60 cm^3/min nitrogen flow (99.999% purity) and with a 20 °C/min heating ramp. The purity of the SWNTs was checked and the iron content determined by the same apparatus, using a similar temperature ramp and a 60 cm^3/min air flow, in order to achieve thermo-oxidation.

Surface area investigation was carried out by Brauner-Emmett-Teller method (BET MICROMETRICS ASAP 2010, N_2). The samples were at first heated at 200 °C in vacuum to perform degassing. Subsequently they were immerged in a liquid nitrogen bath. Nitrogen desorption at higher temperature was monitored and the information on the surface area per gram obtained.

In the hydrogenation experiment 1.840 g of SWNT were pressed into a pellet shape and loaded into the BUCHI system. The stainless-steel chamber was heated up to 190 °C in a nitrogen gas atmosphere for approximately 1-h in order to get rid of oxygen. Subsequently and at the same temperature the sample was exposed for 3.6×10^3 s to a high purity (99.99%) hydrogen gas at a pressure of 14 bar. The amount of hydrogen introduced in the chamber, with and without the sample, was monitored. The additional hydrogen introduced when the samples is in the chamber is adsorbed (i.e. stored) in it. Hence, by taking into account the volume occupied by the sample and the different amount of hydrogen introduced in the two measurements, the amount of hydrogen stored in the sample is determined.

Electron spin resonance measurements were performed using a X-band Bruker ESP300E Spectrometer in the temperature range 4–30 K. The signal lineshape was investigated in order to obtain information on the type of broadening (homogeneous or inhomogeneous). From the linewidth ΔH_{pp} of the recorded first derivative signal we obtained the spin–spin relaxation time t_2 [8]:

$$t_2 = 2\left[\Delta H_{pp} g \gamma K\right]^{-1} \tag{1}$$

where g is the g-factor (i.e. Landé factor) of the signal, γ ($=1.42 \times 10^7$ G^{-1} s^{-1}) is the giromagnetic ratio and K is a constant (=5.44 for a Lorentzian lineshape).

The saturation behaviour was investigated in order to determine the spin-lattice relaxation time t_1. This result is obtained by fitting the saturation curve with the following relationship [8]:

$$I(P) = A0 \frac{g\gamma P^{1/2} t_2^{1/2}}{\left[1 + (g\gamma)^2 P t_1 t_2\right]^{3/2}} \tag{2}$$

where P is the microwave power and A0 is a proportionality factor which has no relevance to the present analysis.

As we have not used a standard pitch during measurements in order to avoid possible spurious interaction, we compared the intensities before and after hydrogenation at a given temperature exploiting the noise to signal ratio with the following procedure. All measurements were performed at very similar frequencies, with the same number of scans. As a consequence at a given temperature the noise intensity varies only with the Q factor of the cavity. Before comparison with standards became of common use this fact was exploited in order to estimate the spin density in samples [8]. On our side we will exploit this fact in another way, by using noise amplitude as a scale to compare different samples. By indicating with $\Delta A^{\mathrm{N}}_{\mathrm{noH}}$ and $\Delta A^{\mathrm{S}}_{\mathrm{noH}}$ the amplitude of noise and signal respectively, we define the signal to noise ratio for the non hydrogenated case:

$$(S/N)_{\mathrm{noH}} = \Delta A^{S}_{\mathrm{noH}} / \Delta A^{N}_{\mathrm{noH}} \tag{3}$$

In a similar way we evaluate the signal to noise ratio after hydrogenation

$$(S/N)_{\mathrm{H}} = \Delta A^{S}_{\mathrm{H}} / \Delta A^{N}_{\mathrm{H}} \tag{4}$$

The assumption $\Delta A^{\mathrm{N}}_{\mathrm{noH}} = \Delta A^{\mathrm{N}}_{\mathrm{H}}$ allows us to get the ratio of the signals, recorded at the same temperature and microwave power, before and after hydrogenation

$$I_{\mathrm{noH}}/I_{\mathrm{H}} = (S/N)_{\mathrm{noH}} / (S/N)_{\mathrm{H}} \tag{5}$$

3. Results and discussion

The Raman spectra of the CNTs is reported in Fig. 1. We can observe that the signature for SWNTs is present in this spectra. Both the G peak (1594 cm^{-1}, assigned to the Raman-allowed E_{2g} mode) and the D peak (1340 cm^{-1}, assigned to the disorder-induced A_{1g} phonon mode) are present and sharp. Moreover, the G peak is much more intense than the D one and the radial breathing modes (RBM) can be observed in the region between 200 and 300 cm^{-1}. These are distinctive features for SWNTs [9]. The lack of a broad peak in the region of the D and G ones indicates that a very low amount, if any, of amorphous carbon is present.

These findings are supported by the results of TGA analysis, reported in Fig. 2a and b. In Fig. 2a the TGA performed in nitrogen atmosphere is reported. Up to 900 °C only 5% in weight of the material is lost and the weight loss up to 200 °C is negligible. This confirms that the degassing treatment

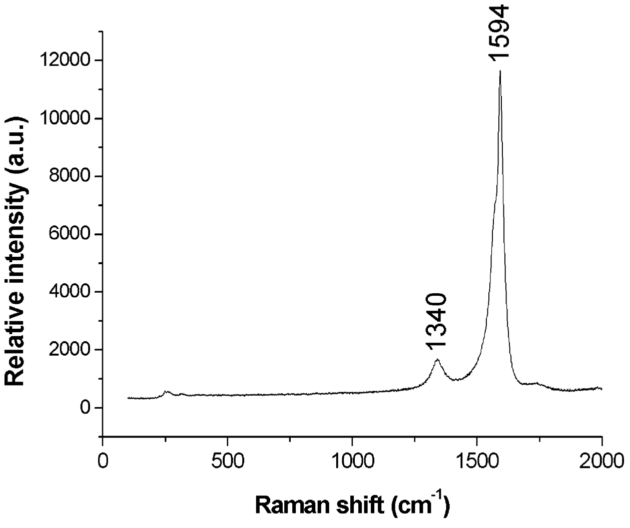

Fig. 1. Raman spectra of the CNT sample analysed in this work.

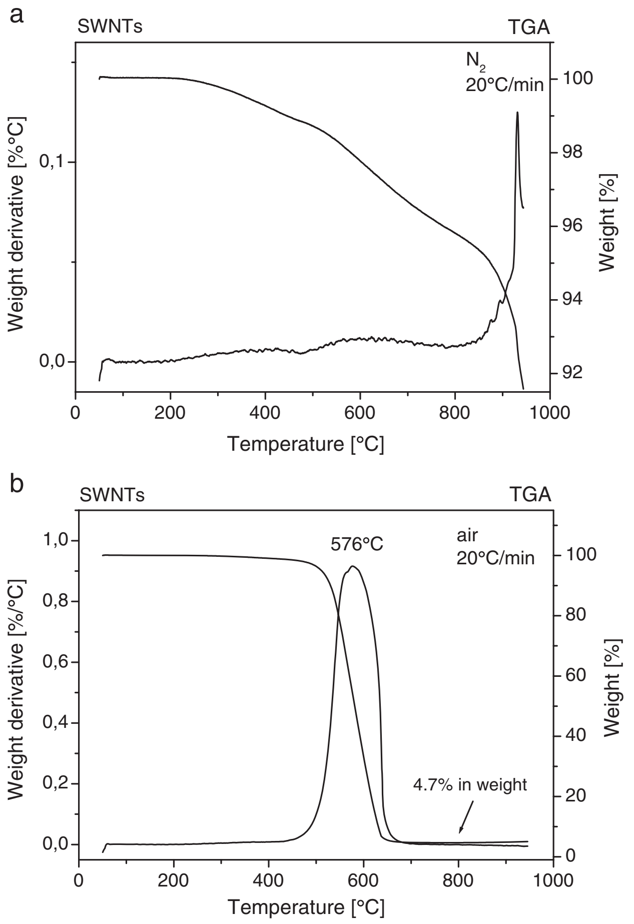

Fig. 2. TGA curves of SWNTs (a) in nitrogen atmosphere and (b) in air.

performed in the hydrogenation chamber does not alter the sample. Fig. 2b shows that the onset of massive weight loss in air is at about 500 °C. The derivative of the weight loss curve shows that mainly one type of structure are present in the sample (i.e. SWNTs). The residual weight, related to the catalyst, is of about 3.8%. As the iron particles have been in contact with oxygen in a highly reactive environment, they have been oxidised as Fe_3O_4. Hence, the amount of metal present in the sample was of about 2.8%. This iron is most probably located near the tip of the SWNTs.

The results of BET show that the surface area of SWNTs is in the range of 800 m^2 g^{-1}, while the average pore diameter was estimated to be about 5–6 nm. Some doubt can be cast on the reliability of this last figure, because its evaluation is based on the details of the kinetic of degassing and the usual hypothesis valid for catalysts might not apply “tout court” to SWNTs systems. On the other hand, the surface area is a more reliable number. A simple calculation based on the average diameter and length of SWNTs performed assuming that nitrogen can reach both the internal surface too lead to a value twice larger than that found. This might indicate that the internal part of SWNTs, in our sample at least, is out of reach for nitrogen [10]. This is probably due to the presence of the caps and to the fact that nitrogen molecules are too large to diffuse through aromatic rings.

The experiment of hydrogen storage show that our sample has a capacity of storing (at 14 bars and 190 °C) approximately 1.3 wt.% of hydrogen. This figure is not as high as required by DoE (6.5 wt.%), but is in the range of usual values. Hence our experiment, although performed on CVD grown SWNTs, might give information on a more general basis. We notice that 1.3 wt.% amounts to say that one hydrogen molecule is stored for every 13 carbon atoms or so (i.e. every 3 fused aromatic rings). Hence, assuming that such molecules are more or less uniformly distributed, any carbon atom has a hydrogen molecule close to it. Moreover the density of hydrogen is so high that it can affect the local properties of the network and, especially, of the spin defects, that are very sensitive to the environment [11]. We have also performed the same experiment at room temperature and found that 0.2 wt.% of hydrogen was stored in our system. This indicates that although we have not performed hydrogenation in-situ during ESR measurements the modification of ESR signal is mainly related to the hydrogen treatment performed.

ESR measurements were performed before and after hydrogen treatment. In all cases the broad signal due to the metal particles [7] was present. However, as we are focusing our analysis on the carbon-related peaks, we will disregard such contributions in both discussion and figures. The results obtained at 8 K for a microwave power of 25 mW are reported in Fig. 3, with and without noise. The lineshape are neither fully symmetric nor dysonian. So, we analysed the signal as a superposition of symmetric components. The best fit was always obtained by using two Lorentzian components having *g*-values close to 2.00. We remind that Lorentzian components are usually associated [8] with interacting spins systems and homogenous broadening behaviour. Hence the use of Eqs. (1) and (2) is appropriate.

The values of the ratios defined by Eq. (5) at the various temperatures and at a microwave power of 1 mW (high enough to have a good signal to noise ratio but low enough to avoid saturation) are 3.7 (4 K), 1.6 (8 K), 1.2 (15 K) and 0.9 (30 K). The ratio steadily decreases as temperature increases. Although the error bar of the values is such that a conclusive word cannot be said without further measurements, it can be observed that the temperature dependence of the intensities is quite close to 1/T. The lack of a standard in reference in the measurements does not allow to say if the intensity of nonhydrogenated sample follows a Curie law (1/T law). If this was the case, hydrogenated samples will follow Pauli paramagnetism. Nevertheless, it remains that hydrogenation decreases the low temperature spin density, in agreement with the report of [12], and varies the temperature dependence of the magnetisation.

In comparison with [7] results, our narrower Lorentzian has a similar linewidth (about 20 G peak-to-peak) while the other is larger by a factor of 3–4. Further work would be required to highlight the origin of the two components, but such point is beyond the scope of this paper. Still we remind that our samples were not altered by chemical attack while those of [7] were.

The analysis of saturation behaviour (see Fig. 4a for an example) are quite interesting. First of all, let us note that the spin–spin relaxation time t_2 is always of the order of 10^{-9} s. This value is quite low but is consistent [7] with the presence of metallic particles that cause a rapid relaxation that increases the linewidth.

On the other hand, the spin relaxation time t_1, that is order of magnitudes larger than t_2, exceeds 10^{-4} s at 4 K. Fig. 4b shows that t_1 is at all temperatures larger for hydrogenated SWNTs. Since the spin-lattice relaxation time indicates the time needed to dissipative interaction to bring back the electron to its ground state, this indicates that hydrogen reduces the probability of such process to occur.

Fig. 4b shows that the probability of transition (proportional to t_1^{-1}) is almost linear with respect to temperature. This is usually associated with the so-called direct process of relaxation [12] that involves a single phonon of the frequency close to microwave photon frequency. This is consistent with the order of magnitude of t_1 as the phonon bottleneck effect comes into play [12] and with the fact that this is the usual behaviour of ordered systems at very low temperatures. Nevertheless the error bars are big enough not to completely rule out other possible mechanisms of spin lattice relaxation so that further analysis will be required to fully clarify this point.

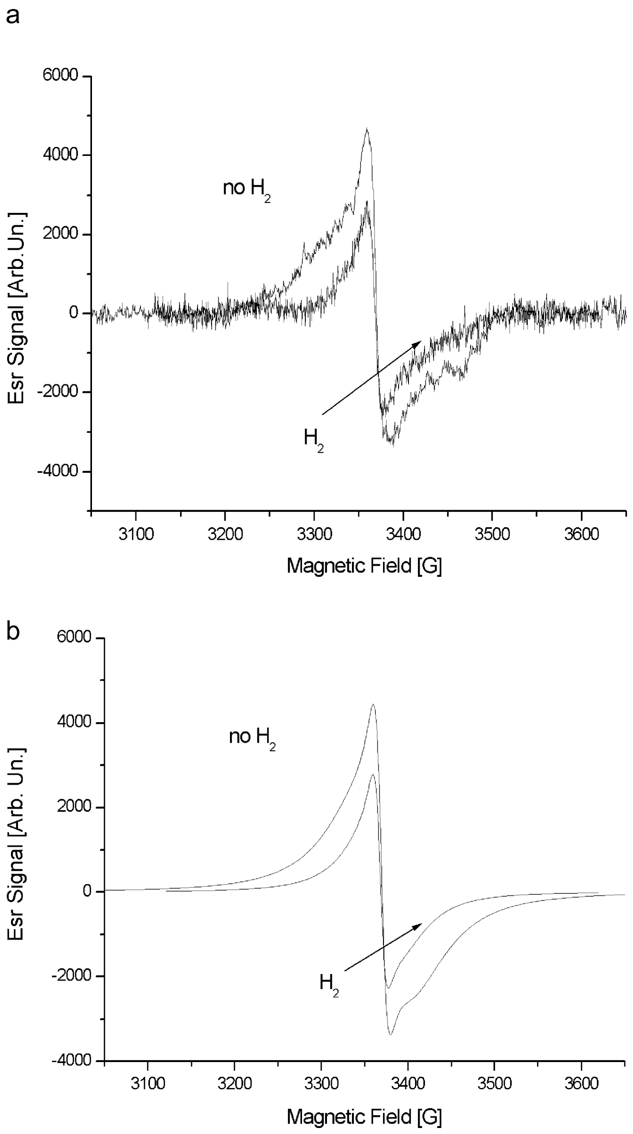

Fig. 3. ESR signals for SWNTs recorded at 25 mW and 8 K before (‘no H_2’ label) and after (‘H_2’ label) hydrogenation (a) with and (b) without noise.

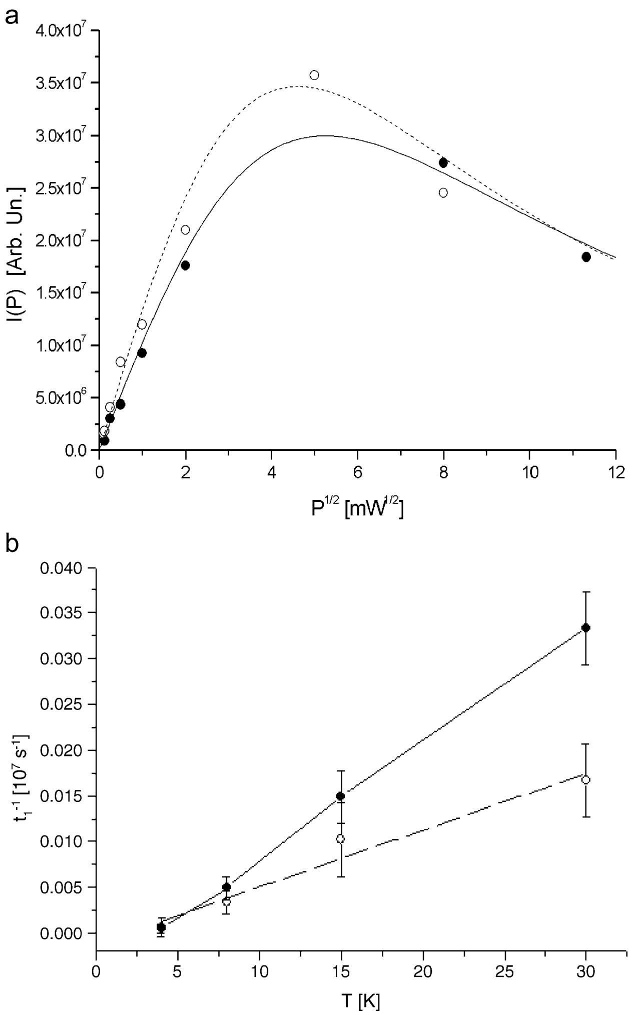

Fig. 4. (a) Saturation behaviour at 15 K and (b) spin-lattice relaxation times for non hydrogenated (solid line: interpolating curve; ● data) and hydrogenated (dashed line: interpolating curve; ○ data) SWNTs.

4. Conclusion

Raman spectroscopy and TGA showed a good quality SWNT, with mainly one type of structure present in analyzed samples, and a small presence of Fe impurity (3.3 wt.%). In the hydrogen experiment an adsorption of 1.3 wt.% of hydrogen was found (at 14 bars and 190 °C). This concentration of hydrogen was so high to affect the spin defects of the sample that are very sensitive to the environment. ESR technique revealed to be very useful to study the microstructure of paramagnetic centers and their interaction with the hydrogen. We found that the ratio of ESR signals before and after hydrogenation is larger than unity at 4 K and steadily decreases as the temperature is increased. Hence, hydrogenation decreases the low temperature spin density and varies the temperature dependence of the magnetization.

The spin-lattice relaxation time is increased by hydrogenation but its temperature dependence is consistent with a direct process in both cases.

Acknowledgments

The authors wish to thank Thomas Swan and Co. Carbon Nanomaterials for supplying samples, M. Zanetti and L. Costa of Turin University for TGA analysis, C. Galletti and V. Specchia of Polytechnic of Torino for BET measurements. This work was partly funded by the British Council-CRUI program. S. Musso acknowledges “Fondazione CRT-Progetto Lagrange” for financial support (PhD grant).

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