Inclusion of carbon nanotubes in a TiO$_2$ sol–gel matrix

P. Vincent *, A. Brioude, C. Journet, S. Rabaste, S.T. Purcell, J. Le Brusq,
J.C. Plenet

*Département de Physique des Matériaux, Université Claude Bernard Lyon-1 CNRS UMR 5586,
43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne cedex, France*

Received 20 August 2001; received in revised form 15 March 2002

Abstract

We report here the successful inclusion of carbon nanotubes (CNs) into a TiO$_2$ matrix prepared by a sol–gel method. The presence of CNs in the sol–gel matrix and the structure of the film were analyzed principally by transmission electron microscopy. Complementary information about the behavior of embedded carbon nanotubes versus heat treatment and ion irradiation were obtained by X-ray photoelectron spectroscopy. The elaboration of an inorganic matrix containing embedded carbon nanotubes leads to a new nanocomposite. The possible applications of this nanocomposite are discussed.
© 2002 Elsevier Science B.V. All rights reserved.

PACS: 61.46; 81.20.F; 68.37.L; 79.60

1. Introduction

Since their discovery by Iijima in 1991 [1], carbon nanotubes (CNs) have been the subject of numerous studies concerning mainly their production and structural characterization with an emphasis on the CNs as independent nanoobjects. The CNs are characterized by a high Young's modulus [2] and varied electronic properties [3,4]. Due to their anisotropic shape and their structure, they can be used as support for grafting [5] and their hollow core can be filled by gas, metals and organic solvents [6,7]. An interesting question is whether some of the novel properties of CNs can be transferred to macroscopic solids by impregnating them in a matrix to form new nanocomposites. Recent first examples are the inclusion of CNs in polymer organic films for the enhancement of electrical conductivity [8] or the use of nanotube films for photovoltaic devices [9]. However, to our knowledge, no examples exist in the literature where inorganic films were used. In this work we study the inclusion by the sol–gel (SG) technique of CNs into inorganic films of TiO$_2$.

The SG technique is a well-known method [10] for fabricating optical quality films. It is currently used for surface coating of glass and for forming planar optical wave guides. One of our principal

* Corresponding author. Tel.: +33-4 72 44 85 18; fax: +33-4 72 43 26 48.

E-mail address: pvincent@dpm.univ-lyon1.fr (P. Vincent).

interests in this method is that it permits the easy realization of doping profiles of nanoparticles homogeneous over molecular scales. Furthermore, the possibility to make homogeneous films over wide thickness ranges of a few nanometers to several micrometers allows the elaboration of new nanocomposite materials and makes their characterization easier.

An essential part of the SG preparation process is a thermal treatment that is necessary to form optical quality and pure TiO_2 films. During this treatment carbon residues introduced for the preparation of the SG solution are removed by interaction with O_2. However, this annealing procedure may pose problems for the stability of CNs included in the SG since they are also formed of carbon. Therefore the main experimental challenge is to obtain good quality SG films with no carbon residues that still include well graphitized CNs.

In this article we first describe sample preparation which consist of (1) obtention of CNs of good quality, (2) elaboration of the SG solution, (3) the mixture of the two components and (4) thermal treatment of the mixture. Next, transmission electron microscopy (TEM) observations and X-ray photoelectron spectroscopy (XPS) studies of CNs in the SG matrix are presented and analyzed which show clearly that we have developed a method for inclusion of the CNs in a SG matrix. Finally, we briefly discuss potential applications.

2. Sample preparation

2.1. Nanotubes preparation

The carbon multiwall nanotubes were produced by chemical vapor deposition (CVD) by catalytic decomposition of acetylene. Cobalt supported on a NaY zeolite prepared by porous impregnation [11] was used as a catalyst. It was introduced into a quartz tube inserted in a furnace heated at 580 °C under nitrogen flow. After 10 min, the reactive gas mixture (composed of 10 ml/min of acetylene and 100 ml/min of nitrogen) was allowed to pass through the tube during 1 h. After reaction, the final product was cooled down to room temperature. The carbon nanotubes obtained are multiwall

nanotubes covered with a thin layer of amorphous carbon. The average inner and outer diameters are respectively 5 and 15 nm [11] for lengths of up to 1 μm. The CNs can be used directly for the SG elaboration or chemically purified.

2.2. Sol–gel preparation

As already stated, CNs have strong anisotropic shapes with outer diameters around 15 nm which is in the range of layer thicknesses obtained by the SG technique. As a consequence, a precise control of SG film thicknesses is required. Among available SG materials such as TiO_2, SiO_2, ZrO_2, HfO_2, we chose TiO_2 which we have the most studied. It allows the fabrication of good films with thicknesses varying from a few to several hundred nanometers [12,13] and allows easy TEM observations.

Very thin films of TiO_2 were prepared by SG route following a procedure already described [14] and were deposited by a dip-coating method onto pre-cleaned substrates. The precursor solution was obtained by mixing titanium isopropoxide $[Ti[OCH(CH_3)_2]_4$, Aldrich] and propan-2-ol $[(CH_3)_2CHOH$, Merk]. Acetic acid (AcOH) was then added with an AcOH to Ti molar ratio of 6. Once the hydrolysis and condensation reactions have been performed, methanol is added to the solution. Methanol is just used to dilute the solution and consequently control the thickness obtained without changing the chemical reactions. Produced films are continuous and crack-free as proven by micro-optical observations.

The next step in the procedure is the introduction of the CNs in the SG solution. The concentration of CNs introduced in the SG solution can be varied accordingly to the properties desired for the final materials. It also depends on the type and purification of CNs used. In this first study, we work on the basis of 40 mg of CN for a solution of 25 cm^3 which assured a sufficient concentration for TEM observations and XPS measurements. The introduction of CNs into the SG solution can be realized by two main methods. In the first method, after complete preparation of the SG solution, CN powder is added as in standard SG doping. In the

second method, a preliminary solution of CNs diluted in methanol is added to the SG solution during its preparation. The second method has been chosen here because it produces a better mixing of CNs in the SG solution. Actually, we observed that CN dispersion in the solution increases with time. For both methods, several weeks after preparation, the same mixtures appear more homogeneous and more stable when exposed to sonification. We attribute this phenomenon to a partial oxidation of CNs in the solution which acts as a superficial functionalization. It has been already shown [15,16] that purification and functionalization improve the dilution of CNs in solution. The good dispersion of CNs is important so as to prevent precipitation in the SG solution and hence to allow the obtention of homogeneous films of optical quality. We observed that the second method in which CNs are introduced before complete reaction of the TiO_2 precursor gave better dispersion. Once the solution is made, deposition of the films on the substrate from the solution is performed with a home-made dip-coating apparatus as already reported [12].

The next two steps in the process are the dip-coating on a substrate and a subsequent heat treatment. These steps are varied depending on which analysis technique is employed. Samples realized for TEM study were deposited on glassy substrate and first dried at a temperature of 80 °C. The samples were then annealed under infra red (IR) lamp during 15 min in air atmosphere. Annealing treatment under IR lamp allowed the densification of the film and eliminated carbon residues. The two samples presented in the microscopy study were annealed using an IR lamp at 750 and 350 °C during 15 min. For such temperatures, pure TiO_2 films are still amorphous. Samples were then peeled off the glass by an acidic treatment [12] and deposited on a 3 mm copper grid for direct observation.

Samples realized for the XPS study have been prepared by first dip-coating a film onto a pre-cleaned Si substrate. The sample was then split into eight parts, each annealed at different temperatures in a tubular furnace. One sample was simply dried at 80 °C without an annealing treatment and 6 samples were annealed during 15 min

at 100, 200, 300, 400, 500 and 1000 °C respectively under O_2 flow rate of few ml/s. Another sample has also been treated at 500 °C but during 4 h in order to show the influence of the heat treatment duration. A final reference sample of a film of pure CNs was prepared. Annealing in tubular furnace was generally used to achieve crystallisation. The porosity of such prepared films are in the order of 20% [12] for both methods.

3. Microscopy study

TEM studies of the TiO_2 SG films have been performed using a TOPCON EM-002B working at 200 kV to obtain general images on changes in the crystalline phases of the TiO_2 matrix, to check for the presence of CNs and to control the evolution of CN structure with thermal treatment. We present results obtained on the samples annealed at 750 and 350 °C mentioned above.

TEM images of the 750 °C sample are presented in Fig. 1(a) and (b) which show that the primary goal of CN inclusion has been achieved. Fig. 1(a) shows a CN of about 10 nm in diameter encapsulated in an amorphous matrix. The nanotube is straight and the hollow structure is visible.

The image of the encapsulated CN in the Fig. 1(b) corresponds to a different zone of the sample than that of Fig. 1(a) and shows a somewhat different morphology. The CN is surrounded with nanocrystals of TiO_2. Nanocrystals of TiO_2 are well-dispersed around the CN clearly showing the start of crystallization of the matrix though the dominant phase remains amorphous. Therefore, the CN appears to act as a preferential site of crystallization and allows crystallization of the SG matrix which usually requires higher temperature and an annealing procedure in a tubular furnace [13].

To illustrate the typical case of one nanocrystal of TiO_2 and determine its crystalline phase, a high resolution TEM (HRTEM) study of the area shown in Fig. 1(b) has been conducted. The results are presented in Fig. 2. A precise measurement of atomic planes and angles between them allows us to determine that the TiO_2 phase of the nanocrystals surrounding the CN is Rutile (space
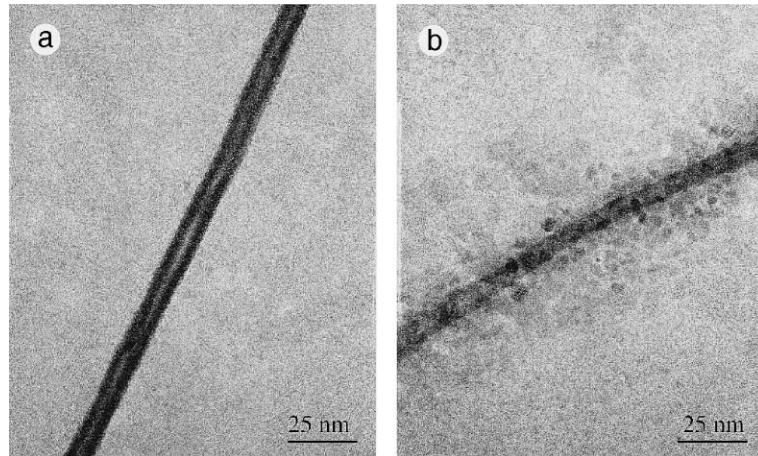
Fig. 1. Conventional TEM images of the sample annealed at 750 °C showing CNs in a TiO_2 matrix film formed by the SG method. (a) A CN with a visible hollow core embedded in an amorphous TiO_2 matrix. (b) Another embedded CN at another zone within the same layer. The CN acts as a catalyst for crystallization of the surrounding TiO_2.

group: $P4_2/mnm$). We have already observed this crystalline phase for thinner films [12] , but mixed with the Brookite phase (space group: $Pbca$). In the present case, no other phases have been found.
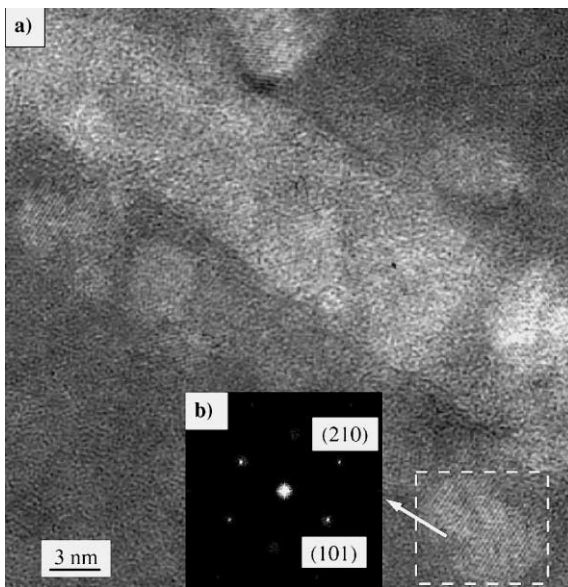

Fig. 2. HRTEM of the sample annealed at 750 °C in the same zone as Fig. 1(b). (a) Graphitic layers of the CN are not discernible. Rutile nanocrystals are present all around the CN. (b) The diffraction pattern of the nanocrystal enclosed in the dashed square is presented.

The second aspect in the image in Fig. 2 is the lack of any evidence of the atomic planes of the CN. Usually HRTEM images of free CNs allow the measurement of the distance between graphitic layers. The graphitic structure of CN has probably been destroyed by the annealing process, transforming the carbon graphitic structure into an amorphous one.

In order to better understand the evolution of the CNs under thermal treatment, the second sample was annealed at 350 °C under otherwise strictly equivalent conditions. An HRTEM image of this sample is represented in Fig. 3. It shows clearly the intact graphitic layers parallel to the
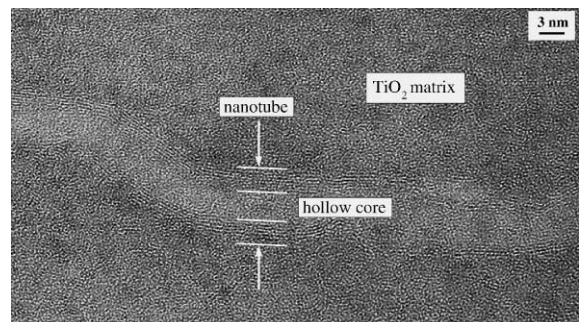

Fig. 3. HRTEM image of a CN embedded in a TiO_2 matrix taken from sample annealed at 350 °C. Intact graphitic layers parallel to the hollow core of the CN are visible.

hollow core of the CN in the SG amorphous matrix. Therefore the graphitic structure of CNs encapsulated in a SG matrix can be destroyed by the relatively high temperature annealing. This observation was confirmed with an XPS study presented next.

4. XPS study

An XPS study has been performed in a NANOSCAN 100 (Cameca-RIBER) apparatus using AlK_α X-ray line (1486.6 eV, power 240 W) to further investigate the transformation of graphitic layers of CNs into an amorphous structure as a function of heat treatment or ion irradiation. XPS provides a surface analysis of the chemical composition of the samples to a depth of a few nanometers.

4.1. XPS spectra of the pure CN film and a CN TiO_2 sample

In Fig. 4, an XPS spectrum of the sample annealed at 200 °C is compared with the reference XPS spectrum of the pure CN film. The spectrum of the pure CN film is similar to those obtained [17] for CNs prepared by nearly the same process,

that is by CVD synthesis and using the same catalyst. The binding energy of the C 1s is 285.85 eV. This position of the C 1s peak has been fixed without taking into account any possible charging effects caused by the SG oxide matrix. The following discussion concerns peak position measurements relative to this fixed one. The C 1s shake-up spectrum exhibits a large shoulder between 4 and 6.4 eV which is due to the superposition of a shoulder at 4 eV attributed to a electronic transition in the nanotube and a peak at 6.4 eV attributed to π bulk plasmons [17]. The peak at 9.89 eV is characteristic of a transition between different valence states in amorphous carbon. The peak at nearly 30 eV, due to the contamination and the presence of amorphous carbon does not allow us to distinguish $\sigma + \pi$ plasmons of CNs.

The C 1s spectrum of the prepared CN sol–gel film presents important differences with the reference spectrum. The main feature is clearly the strong peak at 4 eV. This peak is not present for a pure SG TiO_2 film and is therefore a characteristic signature of the presence of well graphitized CNs in the SG films. Although the exact understanding of this peak from a theoretical point of view is not yet available, certain analysis can be extracted. First, CNs present in the SG films are diluted and electronic collective effects between CNs are limited in comparison with pure CN films. Second, the CNs are embedded in a solid film which can modify the intrinsic electronic transitions of CNs or create transitions between the matrix and CNs. The apparition of the peak at 4 eV is probably due to one of these aspects.

4.2. Evolution of elaborated samples versus heat treatment

In order to follow the thermal behavior of CNs in a SG matrix, we have realized XPS spectra on each sample during the same measurement time of 30 min. We have then observed the evolution of the peak at 4 eV, characteristic of the presence of CNs (Fig. 5). Until 300 °C no change in the intensity and no shift have been noticed. A noticeable decrease in the intensity of the peak appears for the 400 °C sample and the peak has almost
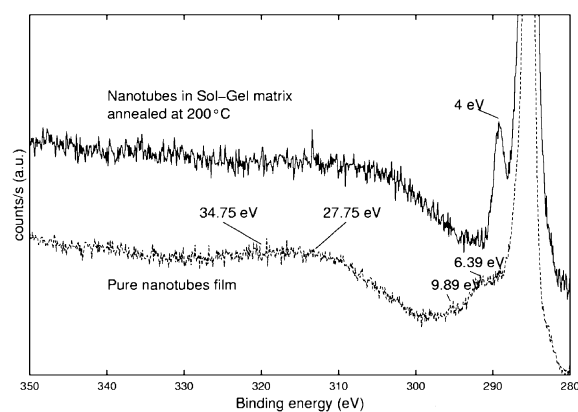

Fig. 4. Comparison of the XPS spectra corresponding to CNs embedded in SG matrix (sample annealed at 200 °C) and the pure carbon nanotube film deposited on a Si substrate. Peak positions are given from the shift of the peak versus the C 1s peak.
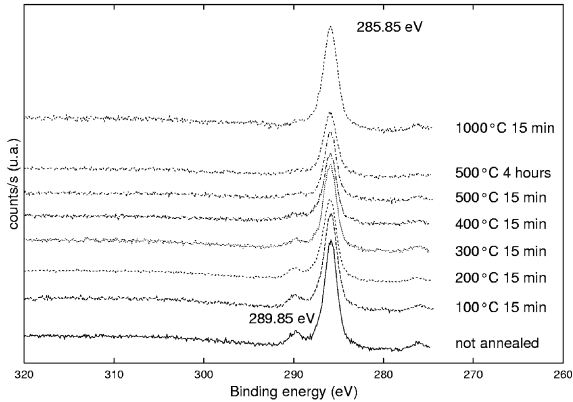
Fig. 5. XPS spectra showing the thermal behavior of CNs in a SG matrix versus heat treatment. The peak at 4 eV, characteristic of the CN presence, disappears for heat treatments between 400–500 °C.

disappeared at the higher temperature of 500 °C. At 1000 °C, the peak at 4 eV has totally disappeared and the spectrum seems identical to those of pure TiO_2 SG films where only the C 1s peak is observed corresponding to the surface contamination of the sample.

The preceding results suggest that the nanotubes present in the SG matrix are preserved during heat treatments for temperatures below or equal to 400 °C. Two important aspects can then be discussed. Firstly, it is well known that optical quality SG films can be obtained for annealing treatments equal to or above 350 °C. It is therefore possible to realize SG films for optical applications with well graphitized embedded CNs by heating in the 350–400 °C range. Secondly, the evolution of the CNs during heat treatment must be related to their specific oxidation behavior. The samples studied and obtained after dip-coating are a complex mixture including organic solvents, a metallic precursor and the CNs. This mixture is highly oxidative for carbon species during a heat treatment. Nevertheless, due to their stable graphitic structure, CNs are more resistive to oxidation than other carbon containing components of the SG media. Previous studies on weight losses of comparable CNs show that under air atmosphere, the CN structure is destroyed for temperatures between 400 and 500 °C [11]. This is in the same range as our results of 400–500 °C for CN struc-

ture alteration which means that the SG matrix has the same effect as an air atmosphere in the CN oxidation process. It is well known that CN stability under oxidation can be correlated to the number of defects. CNs elaborated by arc discharge, which present less defects than those made by the CVD process, start to be oxidized under air atmosphere at 700 °C [18]. Therefore, films coming from the mixture of SG with CNs produced by arc discharge should keep their initial properties without altering the perfect structure of nanotubes at higher annealing temperatures.

In summary, the XPS study confirms the conclusion made from the TEM observations that the structure of CNs can be altered with annealing temperatures higher than 400 °C.

4.3. Effect of Ar^+ ion beam irradiation on the CNs structure

Studies realized on our own CNs and by others [19] show that for pure CNs films, the graphitic structure of CNs are destroyed under ion beam irradiation. CNs are then transformed into amorphous carbon nanotubes similar in form to the original carbon nanotubes but without graphitic structure [19], as found in our oxidation studies. It was then interesting to study the evolution of CNs in SG matrix under ion irradiation because the SG media may shield CNs against ion amorphization. To verify this hypothesis we realized Ar^+ ion irradiation (ion gun CI 50-RIBER at 3 keV. The beam current was 5 μA/cm^2) during 20 min on CNs embedded in SG matrix. The result is shown in Fig. 6. In contrast to Ref. [19], we do not discuss the binding energy shift of the C 1s peak due to possible charging effects which make it difficult to determine the exact position of this peak. Nevertheless, the evolution of the shake-up peak at 4 eV, which is characteristic of carbon nanotube presence allows us to follow the structural evolution of CNs with Ar^+ irradiation. Fig. 6 shows clearly that this peak almost disappears after Ar^+ irradiation which means that there is a transformation of the graphitic structure of CNs into an amorphous one. The decrease of the C 1s peak indicates that carbon contamination is partially removed from the sample surface. It has also been
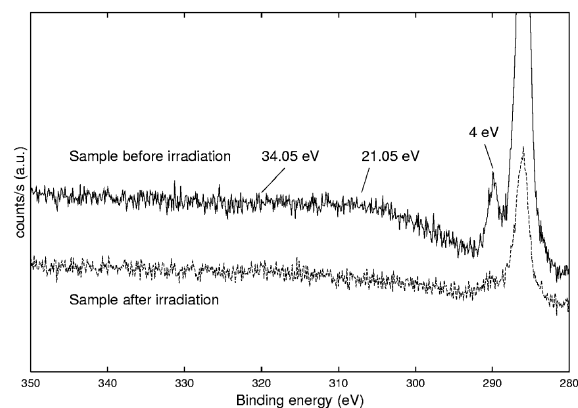
Fig. 6. XPS spectra showing the abrasion effect of Ar^+ ions on carbon nanotubes embedded in a SG matrix. The graphitic structure of the CNs is destroyed after irradiation.

noticed that the shoulder situated between 21 and 34 eV usually attributed to either surface contamination, amorphous carbon remaining in the SG matrix or to $\sigma + \pi$ plasmons of CNs, cannot be distinguished from the noise after Ar^+ irradiation. All these observations show the destructive effect of Ar^+ irradiation on CNs embedded in SG matrix. The energy of Ar^+ ions (3 keV) is sufficient to destroy the graphitic structure of CNs embedded in the SG matrix.

5. Conclusion

In this paper we report the inclusion of CNs in an inorganic TiO_2 SG matrix. TEM and XPS studies have been conducted which showed successful inclusion of CNs in the matrix and which allowed to follow their behavior versus heat treatments and ion irradiation. In agreement with several previous works on non-encapsulated CNs, we have determined that for annealing temperatures between 400–500 °C, the graphitic structure of our CVD CNs is destroyed, showing that the TiO_2 matrix has a comparable oxidative effect as an air atmosphere during heat treatment. This offers the possibility to obtain for annealing treatments in the range of 350–400 °C, good quality TiO_2 films including intact CNs. Moreover, it should be noted that above 400 °C the wire-like form of the CNs is still preserved even if they tend to become amorphous.

The easy realization of SG matrix including CNs opens up the possibility of applications of such films. These applications may depend upon either the intrinsic mechanical or electrical properties or the geometrical form of the CNs. Possible applications are optical non-linear wave guides, unidimensional conductive films for aligned CNs structures and mechanically resistant films. They may even serve as skeletons for grafting or filling to obtain localized doping of the SG matrix.

Acknowledgements

References

[1] S. Iijima, Nature (London) 354 (1991) 56.
[2] J.P. Salvetat, A.J. Kulik, J.M. Bonard, G.A.D. Briggs, T. Stöckli, K. Méténier, S. Bonnamy, F. Béguin, N.A. Burnham, L. Forró, Adv. Mater. 11 (1999) 161.
[3] J.W.G. Wildöer, L.C. Venema, A.G. Rinzler, R.E. Smalley, C. Dekker, Nature (London) 391 (1998) 59.
[4] T.W. Odom, J.L. Huang, P. Kim, C.M. Lieber, Nature (London) 391 (1998) 62.
[5] Y. Chen, R.C. Haddon, S. Fang, A.M. Rao, P.C. Eklund, W.H. Lee, E.C. Dickey, E.A. Grulke, J.C. Pendergrass, A. Chavan, B.E. Haley, R.E. Smalley, J. Mater. Res. 13 (1998) 2423.
[6] S.C. Tsang, Y.K. Chen, P.J.F. Harris, M.L.H. Green, Nature (London) 372 (1994) 159.
[7] P.M. Ajayan, O. Stephan, P. Redlich, C. Colliex, Nature (London) 375 (1995) 564.
[8] I. Musa, M. Baxendale, G.A.J. Amaratunga, W. Eccleston, Synth. Met. 102 (1999) 1250.
[9] H. Ago, K. Petritsch, M.S.P. Shaffer, A.H. Windle, R.H. Friend, Adv. Mater. 11 (1999) 1281.
[10] L. Klein, Sol–gel Technology for Thin Films, Fibers Preforms, Electronics and Speciality Shapes, Noyes, NJ, 1988.
[11] J.F. Colomer, P. Piedigrosso, I. Willems, C. Journet, P. Bernier, G. Van Tendeloo, A. Fonseca, J.B. Nagy, J. Chem. Soc. Faraday Trans. 94 (1998) 3753.
[12] A. Brioude, F. Lequevre, J. Mugnier, J. Dumas, G. Guiraud, J.C. Plenet, J. Appl. Phys. 88 (2000) 6187.
[13] A. Bahtat, J. Mugnier, L. Lou, J. Serughetti, S.P.I.E. Sol–gel Opt. 173 (1992) 1758.

[14] A. Bahtat, M. Bonazaoui, M. Bahtat, C. Garapon, B. Jacquier, J. Mugnier, J. Non-Cryst. Solids 16 (1996) 202.

[15] K. Esumi, M. Ishigami, A. Nakajima, K. Sawada, H. Honda, Carbon 34 (1996) 279.

[16] M.S.P. Shaffer, X. Fan, A.H. Windle, Carbon 36 (1998) 1603.

[17] P. Simonis, master thesis, FUNDP, 1998.

[18] P.M. Ajayan, T.W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki, H. Hiura, Nature (London) 362 (1993) 522.

[19] Y. Zhu, T. Yi, B. Zheng, L. Cao, App. Surf. Sci. 137 (1999) 83.