Cent. Eur. J. Phys.
DOI: 10.2478/s11534-012-0138-4

VERSITA

Central European Journal of **Physics**

Raman studies of Pd-C nanocomposites

Research Article

Radoslaw Belka[1],* Malgorzata Suchanska[1], Elzbieta Czerwosz[2], Justyna Keczkowska[1]

1 *Kielce University of Technology,*
Al. Tysiaclecia P.P.7, 25-314 Kielce, Poland,

2 *Tele & Radio Research Institute,*
Ratuszowa 11, 03-450 Warsaw, Poland,

Received 15 March 2012; accepted 21 September 2012

Abstract: The results of studying palladium-carbon (Pd-C) nanocomposites using Raman spectroscopy are presented. This method has been used for studying samples having various palladium content, prepared by a one-step Physical Vapour Deposition (PVD) process and a Chemical Vapour Deposition (two-step PVD/CVD) process using different process parameters. For samples obtained by PVD, the vibration bands characteristic of C_{60} fullerene molecules were observed in the spectra, whereas for layers obtained by PVD/CVD, the Raman spectra displayed mainly D and G bands characteristic solely of the prescence of graphite-like layers' vibrations. The analysis of the obtained Raman spectra reveals that its shape is affected by many parameters including type of substrate, temperature, and the percentage content of Pd in the studied layer. The quantitative analysis of spectra for layers obtained using the PVD/CVD process shows a difference in the relative intensity of bands D and G, reflecting the different degrees of amorphisation in the investigated nanocomposites.

PACS (2008): 78.30.Na, 81.05.Tp

Keywords: Pd-C nanostructures • fullerene • Raman spectroscopy • PVD/CVD

1. Introduction

The necessity to guarantee safety of the systems using hydrogen fuel leads to the increased interest in the detectors of hydrogen in its gaseous form. The research is aimed at developing efficient, fast, safe, and relatively cheap sensors which would be able to detect small changes in the intensity of hydrogen and associated compounds. One of the best known hydrogen sensor (H-sensors) groups are based on palladium sorption properties [1, 2]. Such sensors have an active component in the form of a thin palladium film with optical and electrical properties that depend on the amount of hydrogen molecules adsorbed. Another group of materials characterised with hydrogen sorption abilities are the carbonaceous structures such as nanofoams or nanoporous structures [3]. The carbonaceous nanomaterials can be characterised with variable molecular systems which in certain circumstances may lead to creating nanopores which are able to store hydrogen. The properties of such material types are discussed in literature with respect to hydrogen storage rather than to sensors [4, 5].

In recent years research on palladium-carbon (Pd-C)

---

*E-mail: r.belka@tu.kielce.pl

nanocomposites has also been carried out; where palladium nanocrystallites are placed in the carbonaceous matrix [6–9]. Such structures enable to use new design concepts of H-sensors based on the resistance change of the nanocomposites as a result of a hydrogen gas presence. A successful Pd-C sensor is presented in [10] where it is shown that the electrical conductivity of the carbonaceous - Pd film increases in contact with hydrogen as a result of creating conductive paths between single palladium nanoparticles. Hydrogen detection takes place owing to the change of the electrical conductivity in the film. The study of the Pd-C nanocomposite properties for use in H-sensors is important for both the scientific and practical point of view.

One of the basic research methods applied for carbonaceous structures is Raman spectroscopy. It allows the analysis of structural changes in carbon via observation of G and D bands behaviour, which are the main features in the Raman spectra of disordered graphite and amorphous carbons [11–13]. However, the research of carbonaceous structures with palladium inclusions are still an open issue. At present there is no unequivocal answer to the question of how the presence of palladium nanocrystals can influence the shape of Raman spectra.

This article presents the Raman spectroscopy results of Pd-C nanostructure obtained using physical vapour deposition (PVD) and chemical vapour deposition (CVD) methods. The primary aim of this investigation is to characterise the carbonaceous structure in the presence of palladium. This paper presents the work performed to assess the influence of palladium content and different parameters of deposition process (e.g. temperature, type of substrate) on the carbonaceous molecular structure in such types of nanocomposites.

2. Experimental setup

The investigated Pd-C nanocomposites were prepared at Tele & Radioresearch Institute (Warsaw, Poland) using a two-step PVD/CVD method [6–9]. Figure 1 illustrates the PVD/CVD experimental setup. In the PVD process, films were evaporated from two separate sources – the first containing fullerene (C_{60}), and the second containing palladium acetate ($Pd(CH_3COO)_2$). Depending on the fabrication process parameters (i.e. temperature of the source, distance between the source and substrate, and substrate temperature) it is possible to obtain films with various Pd content (from 1 up to 22 wt. %). Nanocomposite films built of Pd nanocrystals embedded in a carbonaceous matrix were obtained. These films were modified using a CVD process with xylene pyrolysis (temperature - 650°C, duration time - 30 min, xylene flow - 0.1 ml/min). The PVD and PVD/CVD samples, 300 - 400 nm in thickness, were prepared on four different substrates: fused silica, silicon, molybdenum and alumina.

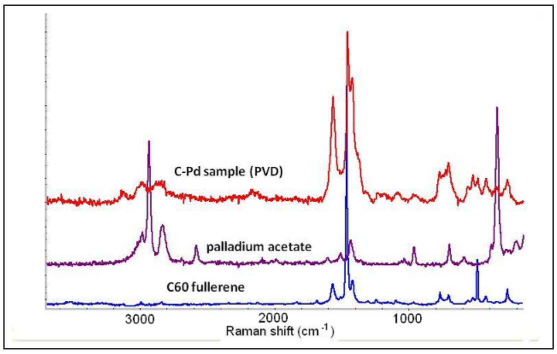

Figure 1. PVD (left) and CVD experimental setup.

The samples were studied using Raman spectroscopy using a Almega XR (Nicolet - Thermofisher) spectrometer. The measurements were made in 'micro mode', with an excitation of 532 nm (provided from an Nd:YAG laser source) at a power of 0.25 mW. The obtained spectra were analysed by decomposition using the Voigt-profiled bands (Nicolet Omnic 8 software).

3. Results

3.1. PVD samples

The Raman spectrum of the Pd-C nanocomposite obtained in the single-step PVD process (PVD samples), as well as spectra of C_{60} fullerene and palladium acetate are presented in Figure 2. The PVD sample was obtained at temperature of 58°C, with a deposition rate 0.5 nm/s. The spectra were recorded under identical measurement conditions (wavelength, laser power, lens type and acquisition time).

In the spectrum of the Pd-C nanocomposite, the characteristic bands of C_{60} fullerene are clearly predominant. No bands deriving from palladium acetate were observed. Palladium atoms created during palladium acetate decay probably become embedded into the carbon matrix, creating nanocrystallites, which were identified by the studies using SEM and TEM [6, 9]. The absence of intense bands characteristic of the carbon-hydrogen bonding in the range of 2900 - 3000 cm^{-1} indicates the absence of hydrocarbon groups being the acetate disintegration products.

In the spectra of PVD samples, all 10 modes characteristic of C_{60} fullerene were extracted, though there were no

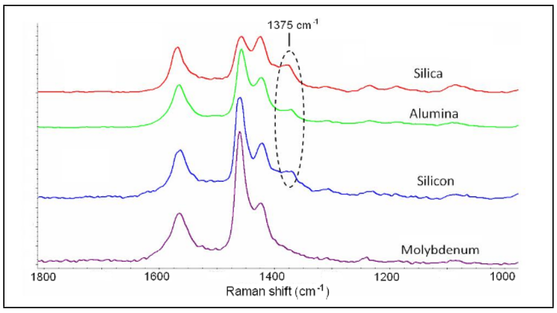

Figure 2. Raman spectra of the palladium-carbon nanocomposite obtained in the PVD process, and of its precursors (C_{60} fullerene and palladium acetate).

bands deriving from graphite-like phases. The C_{60} bands identification (e.g. Hg(8), Ag(2)) refers to irreducible representations of the icosahedral symmetry group (I_h) [16]. The intense band detected in 1570 cm^{-1} range should be identified with Hg(8) fullerene mode rather than with G band of graphite. However, the intensity and shape of particular bands differ from the fullerene bandwidth shape. This refers in particular to the so-called 'fully symmetrical' modes, the intensity of which is significantly decreased when compared to Hg modes. The decrease in the Ag(2) mode intensity was detected when compared to the Hg(8) mode located at 1570 cm^{-1}. Moreover, in the range of 1375 cm^{-1} a clear additional band appears which is not found in spectrum of pristine fullerene.

The spectra of PVD samples grown on various substrate types are presented in Figure 3. All of the samples where prepared using the same technological parameters (temperature of substrate - 58^{o}C, deposition rate - 0.5nm/s). The newly-appeared band at 1375 cm^{-1} is labelled. It can be seen that there are clear differences in spectrum shapes, primarily in the variable intensity and location of the Ag(2) mode in the region of 1460-70 cm^{-1}.

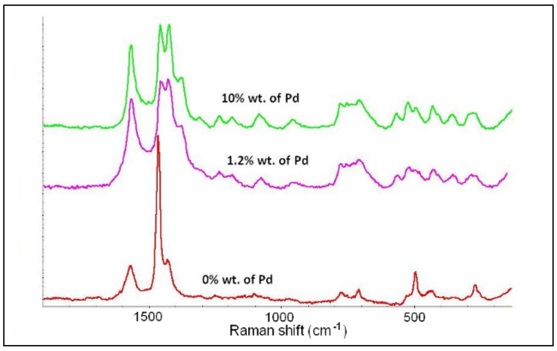

Figure 3. Spectra of PVD samples grown on different substrates.

It can be seen that the spectra distortion degree is connected with the coefficient of thermal conductivity of the substrates. The samples grown on the molybdenum and silicon (substrates characterised with high thermal conductivity) have the spectra more resembling the pure fullerene spectrum than in the case of layers created on silica substrates (low thermal conductivity). The influence of the substrate on morphology and structure of the Pd-C samples was reported in [11]. The suspected cause of this effect is the presence of diversified thermodynamic conditions on the layer-substrate boundary during the deposition process. As a result, this may influence the arrangement of molecules deposited and the degree of metal-fullerene intercalaction.

Although palladium presence is of crucial importance on the Raman spectrum shape, the percentage weight content (wt. %) of Pd, measured using the atomic absorption spectroscopy (AAS) method is of lesser importance. Figure 4 presents the spectra of PVD samples deposited on a silica substrate for which the weight content of palladium was known. A sample created using the PVD method without palladium acetate shows similarities to the fullerene spectrum, although the silica substrate has been used. An influence of % wt. of Pd on the shape of Raman spectra is not observed. This result can be seen as Pd is mostly clustered in the nanocrystallite form and has only a weak influence on the structure of fullerene.

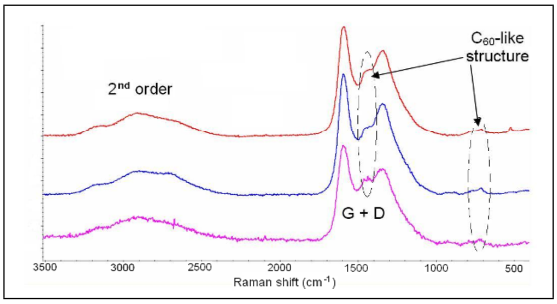

Figure 4. Influence of Pd content on Raman spectra of PVD samples grown on silica substrates.

3.2. CVD samples

Pd-C nanocomposites modified using a PVD/CVD process are characterised with a different structure which is typical of graphite-like carbon (Fig. 5). This is related to the high temperature of CVD process (typically 650°C) which leads to disintegration (graphitisation) of any fullerenes in the samples.

The location, shape, and intensity of the G and D bands in the Raman spectrum of CVD nanocomposites are characteristic for the graphite-like amorphous carbon (charcoal) [13, 14]. Nevertheless, presence of clear and ir-

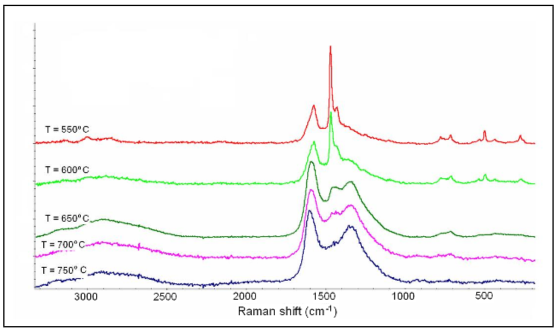

Figure 5. Raman spectra of Pd-C nanocomposites prepared in two-step PVD/CVD method on various substrates

regular bands with a peak around 1450 - 1455 cm^{-1} and 719 cm^{-1} is a feature not observed in spectra of typical carbon. Those bands according to their position correspond to C_{60} characteristic vibrations which may indicate the remains of the fullerene-like phase (product of degradation of C_{60} molecules) in the samples. In the range of 2500 - 3500 cm^{-1} 3 overlaid bands can be observed which are identified as having 2^{nd}-order modes (2G band around 3180 cm^{-1} and 2D at about 2700 cm^{-1}) and the band related to the presence of C-H bonds typical of amorphous graphite. In the case of CVD samples no correlation between the spectrum shape and the substrate type was detected, which is in contrary to PVD samples.

An important factor influencing the Raman spectra shape is, however, the CVD process temperature. Figure 6 shows the Raman spectra of samples deposited at a temperature range of between 550 - 750^{o}C on alumina substrates.

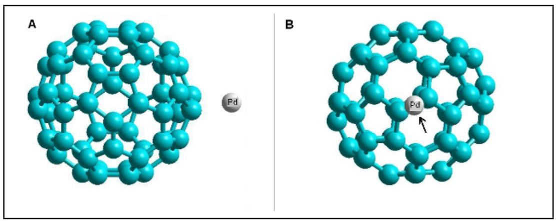

Figure 6. Raman spectra of CVD samples deposited at different process temperatures.

In the Raman spectra of CVD samples prepared at lower temperatures (550 - 600°C) the characteristic bands of C_{60} fullerene is observed. When the temperature increases, the intensive growth of D and G bands is also visible. This observation could be connected with the presence of different forms of carbon in the matrix. As the process temperature is further increased, it is accompanied with the dominance of the graphite-like structure in the layer and the band in the 1450 cm^{-1} range begins to disappear. Simultaneously, the C_{60} bands observed in the range below 1000 cm^{-1} begin also to disappear.

4. Discussion

In Raman spectrum of the fullerene the presence of 10 characteristic bands is observed. There are 2 fully symmetrical vibrational Ag modes and 8 Hg modes, corresponding to molecular vibrations according to the selection rules for the I_h symmetry group [16]. The bands in the spectrum range below 1000 cm^{-1} (low-energy Hg(1-4) and Ag(1) modes) correspond to radial bending vibrations, while the bands in the range 1000 - 1800 cm^{-1} correspond to tangential stretching vibrations. The measured values of intensity and the locations of C_{60} fullerene bands correspond to those described in reference papers [15–17]. The spectrum is dominated by intense bands deriving from fully symmetrical Ag(1) modes (Breathing Mode - BM) and Ag(2) (Pentagonal Pinch Mode - PPM) located at 495 cm^{-1} and 1465 cm^{-1}, respectively. The intensity ratio of Ag(2)/Hg(8) mode was determined to be 12 while Ag(1)/Hg(8) - 2.35.

In PVD samples, palladium atoms can be found not only in nanocrystalline clusters but they can also be observed being embedded in the immediate surroundings of fullerene molecules. A review of literature data shows the possibility of the existence of direct Pd-C_{60} bonds in the fullerene framework [18, 19]. This is a result of the alkene character of the C_{60} molecule which makes it a potential ligand of olefin type in metal-ligand complexes. Metal atoms are usually coordinated in the C-C double bond (6 - 6 bond) located between two hexagons on the surface of the C_{60} molecule. Some of $[(PR_3)_2Pd\ (\eta_2\text{-}C_{60})]$ complexes (where R = H, ethylene or phenyl group) were synthesised and theoretically and experimentally analysed and presented in the literature [18–21]. In addition, organometal polymers with a transition element Pd_nC_{60}, by reaction of fullerene C_{60} with a dibenzylideneacetone (DBA) complex of Pd, were prepared as well [22, 23]. Metal - fullerene complexation leads to the deformation of the fullerene molecule (prolongation and weakening of the 6 - 6 bonds).

In such circumstances the existence of immediate Pd-C_{60} interactions and breaking the fullerene molecules symmetry cannot be excluded in PVD samples. Disintegration and graphitisation in the most extreme situation is also possible. The absence of characteristic carbon D and G bands in the Raman spectra of PVD samples provides evidence against the hypothesis concerning fullerene graphitisation catalysed with palladium. The increase of disordering resulting from metal atoms present provides a hypothesis which is still feasible given the results presented in this paper. As it has already been mentioned, in PVD samples spectra significant decrease in the Ag/Hg intensity ratio were observed. For samples deposited on molybdenum and silicon substrates, the value of this parameter is about 2.2 - 2.5, while for silica-based layers it is about 1 - 1.2. The decrease in the Ag/Hg ratio is accompanied by the growth of the 1375 cm^{-1} band intensity.

The analysis carried out using computational methods of quantum chemistry reveals that the Pd-C$_{60}$ intercalaction can be responsible for spectrum shape modification in PVD samples. The calculations were carried out using the 'Hyperchem' software (Hypercube Inc.) using the semi-empirical computing method PM3 (Parametric Model 3 [24]). In the process of optimising the arrangement geometry the palladium atom takes the central position above the double fullerene bonding. The fullerene molecule is slightly deformed in this process which takes the form of clear elongation of this double C=C bond from 138 pm to about 150 pm and the resulting weakening, which was also observed in Pd-fullerene complexes presented in [18, 19]. The symmetry break can lead to a decrease in the full symmetrical mode intensity. Simultaneously, the weakening of C=C bonds, as mentioned before, can be responsible for the appearance of the 1375 cm^{-1} band in the PVD sample spectrum; resulting from the stretching vibration of Pd-coordinated C - C double bonds, since it is known that complexation between the transition metal and the alkene decreases the vibration frequency of the bonds [18, 19] .

The presented model shows that the differences in the Raman spectra of PVD samples are related to the presence of Pd atoms in the immediate vicinity of fullerene molecules. From the measurements presented in this paper, it can be seen that the Pd atoms in the nanocrystallites have no significant impact on the fullerene structure and its spectrum shapes. It is concluded that the metal content in the nanocomposite is less important than dispersion and agglomeration of Pd nanoparticles.

Both the temperature and duration of technological processes described in this paper have an influence on the structure of the CVD samples. Measurements of the samples prepared in a temperature below 600°C show a presence of fullerene with a small amount of carbon in the graphite-like phase. In higher temperatures (about 650°C) fullerene disintegrates and we observed so-called fullerene-like structures, which is indicative of carbon clusters with hybridisation typical for C$_{60}$ molecules. This is confirmed by the presence of bands in the range of 1450 cm^{-1} and 710 cm^{-1}. In the case of samples produced in temperatures >700°C these bands disappear. It has also been observed that the intensity of those bands decreases, corresponding to the increase in the process duration.

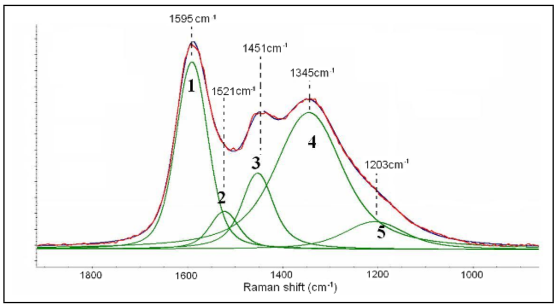

Figure 7. Decomposition of Raman spectrum of CVD sample in range of 800 - 2000 cm^{-1}.

Decomposed Raman spectra in the D and G band regions using the Voigt profile are presented in Figure 7. Bands 1 and 4 are defined as bands G and D respectively. These plots are both characteristic of amorphous carbon and defective graphite structures (sp^2 bonds). G band observed in the range 1588 - 1595 cm^{-1} was active primarily in monocrystal graphite which is occurs from the spatial chain configuration of carbon bonds with sp^2 hybridisation. This results from the appearance of a ring spatial configuration of carbon bonds with sp^2 hybridisation [13] where the bonds also with sp^1 and sp^3 are formed. The increased intensity of D peak in relation to G peak indicates the growth of the existing aromatic rings, or formation of new ones, where the presence of graphite clusters with sp^2 bonds is closely related to the amount of sp^3 carbon. Other bands (2 and 5) with peaks at 1520 cm^{-1} and 1200 cm^{-1} also appear during decomposition of the typical spectrum of graphite-like amorphous carbon which indicates that they are not a characteristic feature for CVD samples. The band 3 spectra at 1450 cm^{-1} confirms the presence of a fullerene-like phase. The intensity of this band decreases with an increase of the CVD process temperature.

The degree of amorphisation of the graphite-like carbon structure is determined by value of the D/G intensity ratio according to the Tuinstra-Koening relationship [12]. The spectrum shape of the studied CVD samples indicates a relatively high level of disorder and consequently it is more appropriate to use the relationship presented in [13].

$$I_D/I_G = C(\lambda) * L_a^2, \qquad (1)$$

where C(λ) is a coefficient depending on the excitation wavelength, evaluated in [13] to be about 0.55 for λ = 514 nm, while L$_a$ is the average size of a carbon nanocluster (in nm).

The I_D/I_G ratio for CVD samples calculated from the presented work is equal to 0.7 - 0.82, depeding on the process parameters used during fabrication. A decrease of this value indicates an increase in the degree of amorphisation in the layer [13]. The average size of carbon nanoclusters is estimated in this work to be between 1.2 - 1.25 nm. The layers where the fullerene-like bands exist are characterised with a lower I_D/I_G ratio (between 0.7 - 0.72) and also by the lower intensity of the 2D band. The absence of the fullerene-like phase can be connected with a higher value of the I_D/I_G ratio (about 0.8). In this case the 2D band is more intense and has a more definite shape. This leads to the conclusion that there is a higher level of amorphisation for structures containing degradation product of C_{60} molecules. The SEM studies of such sample types, performed in [6, 9], reveal the existence of nanoporous structure in CVD layers. From this work there is the indication of a relationship between the presence of fullerene-like structures and porous nature of the CVD Pd-C nanocomposites.

5. Conclusion

The Raman spectroscopy method has been used first to determine the structure of the Pd-C nanocomposites. The Raman spectra analysis reveals that Pd-C structures prepared using PVD method show presence of C_{60} fullerene. Some interesting information concerning the nature of direct Pd-C_{60} interaction was obtained. A clear influence of the substrate type (its thermal properties) on the structure of Pd-C nanocomposites prepared by PVD method was observed. This conclusion complies with results published in [11] where an influence of the substrate type on structure of Pd-C films was studied using AFM (atomic force microscopy), SEM (scanning electron microscopy) and AAS (atomic absorption spectroscopy) methods. The proposed model of Pd-C_{60} interactions incorporates the understanding of the influence of the metal content on the modifications of the carbonaceous nanostructure.

The CVD process leads to the amorphisation of the carbonaceous structure which is evidenced both in the increased I_D/I_G ratio, decreased carbon nanocluster size, and in the appearance of a band in the range 2300 - 3500 cm^{-1} . Additionally, the presence of bands in the range 1450 cm^{-1} and 710 cm^{-1} facilitates the conclusion that the nanoporous carbon obtained in PVD/CVD method consists of the mixed form of a-C:H (hydrogenated amorphous carbons) and fullerene-like structure.

Acknowledgments

This research was co-founded by the European Regional Development Fund within the Innovative Economy Operational Programme 2007-2013 (No UDA-POIG.01.03.01-14-071/08-06).

This research was performed using equipment founded by the European Regional Development Fund within the Innovative Economy Operational Programme 2007-2013 (No POIG 02.02.00-26-023/08-00).

References

[1] W. Grochala, P. P. Edwards, Chem. Rev. 104, 1283 (2004)
[2] R. Pitts et al., Proc. of the 2001 DOE Hydrogen Program Review (2001)
[3] E. A. Evard et al., Mater Sci+ 36, 499 (2000)
[4] B. Panella, M. I. Hirscher, S. Roth, Carbon 43, 2209 (2005)
[5] M. I, Hischer et al., J. Alloy. Compd. 356-357, 433 (2003)
[6] E. Czerwosz et al. Nato Science Peace S, 227 (2009)
[7] E. Czerwosz et al., Vacuum 82, 372 (2007)
[8] E. Czerwosz et al., Proc. of SPIE 7502, 50223 (2009)
[9] E. Czerwosz et al., Mater. Sci+ 26, 119 (2008)
[10] I. Pavlovsky et al., Sensors & Transducers Journal 73, 793 (2006)
[11] E. Kowalska et al., Elektronika 7, 61 (2011)
[12] F. Tuinstra, J. L. Koenig, J. Chem. Phys. 53, 1126 (1970)
[13] A. C. Ferrari, J. Robertson, Phys. Rev. B 61, 14096 (2000)
[14] D. D. L. Chung, J. Mater. Sci. 37, 1475 (2002)
[15] H. Kuzmany et al., Phil. Trans. R. Soc. Lond. A 362, 2375 (2004)
[16] M. S. Dresselhaus et al., J. Raman Spectrosc. 27, 351 (1996)
[17] K. L. Lo, M. C. Lee, Chinese J. Phys. 31, 653 (1993)
[18] V. N. Ivanova, J. Struct. Chem. 41, 135 (2000)
[19] A. L. Balch, M. M. Olmstead, Chem. Rev. 98, 2123 (1998)
[20] P. J. Fagan, J. C. Calabrese, B. Malone, Science 252, 1160 (1991)
[21] C. Bo, M. Costas, J. M. Poblet, J. Phys. Chem. 99, 5914 (1995)
[22] H. Nagashima et al., J. Chem. Soc. Chem. Comm. 142, 377 (1992)
[23] K. Winkler et al., J. Solid State Electr. 10, 761 (2006)
[24] E. G. Lewars, Computational Chemistry (Springer. 1st ed., 2003)