

Investigation and modification of carbon nanotubes by ion beam and scanning probe methods

Summary of the PhD thesis

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Literature review

Carbon nanotubes were discovered by Sumio Iijima in 1991 [1]. They can be defined as hollow cylindrical objects made from graphene layers with diameters varying between 1 and 50 nm, and lengths which might exceed 10 μm . Carbon nanotubes were intensely studied in the past fifteen years due to their unique mechanical [ii] and electronic [iii] properties which open numerous potential applications. They can be used as building elements in the future nanoelectronics [iv, v], as reinforcement elements in composite materials [vi], in flat panel displays [vii], or in field emitting lamps [viii].

There are several methods for carbon nanotube production. The as-grown nanotube samples usually contain also catalyst particles (and the catalyst bearer), graphitic nanoparticles and amorphous carbon. Hence, the purification methods had to be developed soon after the production methods. These involve wet oxidation procedures [ix] using different acids, which can dissolve catalyst particles and oxidize amorphous carbon (amorphous carbon is oxidizing faster than carbon nanotubes) [x].

In the past decade, several interesting phenomena had been observed during the study of carbon nanotubes. For example, during the TEM investigation of a single-wall carbon nanotube, researchers observed that the diameter of the nanotube shrank due to electron irradiation [xi]. Another experiment shows that crossing single-wall carbon nanotubes can be joined by focused electron beam welding to form molecular X-type junctions [xii]. The shrinkage of nanotube diameter and the welding of two nanotubes could also be observed using focused Ga^+ ions of 30 keV [xiii]. These structural changes in the nanotube walls can be explained by the large number of simple or multiple vacancies induced by irradiation which can transform into other defect types (e.g. non-hexagonal rings) by dangling bond saturation [xi, xii]. Molecular dynamics simulations show that when a bundle of single-wall nanotubes is irradiated with Ar^+ ions of 0,1 – 1 keV, covalent bonds can form between adjacent nanotubes [xiv]. The bonds created between the nanotubes improve the mechanical [xv] and transport properties [xvi] of the bundle. Similar covalent bonds can also form between the adjacent walls of multi-walled carbon nanotubes [xvii]. Krashennnikov and co-workers calculated the STM images of nanotube defects (vacancies) induced by ion irradiation [xviii, xix]. The vacancies appear as hillock-like protrusions on the simulated images due to the locally changed density of states. Experimental STM investigations dealing with irradiation-induced carbon nanotube defects lack from the literature.

Objectives

At an early stage, I had to acquire the skills necessary for doing scanning tunneling microscopy (STM) and atomic force microscopy (AFM). I started the work in the frame of the EU FP5 NANOCOMP Research Training Network and my main task was the STM characterization of carbon nanotubes produced by different methods.

One of my objectives was to study by STM the effect of a two-step chemical purification procedure, and to determine the catalyst content remained in the carbon nanotube samples after each purification step, using ion beam techniques.

The second objective was to create point defects in the nanotube walls by ion irradiation, and to investigate the nanotube defects by atomic resolution STM and scanning tunneling spectroscopy (STS). I studied carbon nanotubes irradiated with different ion doses, and also investigated the nanotube defects after annealing the samples at 450 °C. The perspective of this research is the examination of gas sensing properties of irradiated nanotubes, and the exploitation of the possibility of attaching functional groups to the created defects.

Experimental methods

In the first part of the thesis I investigated the catalyst content (Co) of CVD grown carbon nanotube samples after each purification step. The catalyst content was determined by Rutherford Backscattering Spectrometry (RBS), Particle Induced X-ray Emission analysis (PIXE), and X-ray Fluorescence analysis (XRF).

In case of RBS and PIXE methods the samples are probed with energetic ions (in our case $^4\text{He}^+$). In RBS, the energies of the ions backscattered from the sample give information about the type of elements present in the sample. The yield of backscattered ions in a given channel of the detector is directly proportional to the concentration of a given chemical element in a certain depth. In case of PIXE the X-ray emission induced by the ions is detected, which is characteristic for the emitting element. PIXE is an important complementary method of RBS, particularly if neighbouring atoms with larger atomic masses are to be distinguished.

In the XRF method one uses the primary emission of an X-ray tube or a radioactive element to excite the atoms of the sample. The elemental composition can be determined from the energy analysis of the secondary (fluorescent) X-ray emission, and the intensity of the fluorescent emission emitted by an element is proportional to the concentration of the given element in the sample.

In the second part of the thesis I investigated nanotube point defects produced by irradiation with Ar^+ ions of 30 keV. The irradiation was done in one of the ion implanters of our institute. I used scanning tunneling microscopy (STM) for the investigation of the irradiated nanotubes.

STM is a modern method which is able to investigate metallic and semiconducting surfaces with atomic resolution. It was also very effective in detecting atomic-scale carbon nanotube defects. In STM a very sharp tip is placed at nanometric distance and scanned over the sample surface. The tip – sample bias voltage (~ 1 V) gives rise to a tunneling current (~ 1 nA) which is held constant by a feedback loop during the scanning process (constant current mode). The feedback loop controls the vertical movement of the STM tip which gives the surface topography. The magnitude of the tunneling current depends on the local density of states of the sample, thus the measured surface contains both topographic and electronic information. The electronic information can be better explored by scanning tunneling spectroscopy (STS), which is another operating mode of the STM. In this mode one measures a current-voltage characteristic of the sample while the STM tip is staying in the same place.

In order to estimate the percentage of irradiation-induced defects appearing as hillocks due to geometrical change and not due to electronic effects, I used atomic force microscopy (AFM) as a complementary tool. In AFM, a pyramid-like silicon-nitride tip is fixed to a cantilever which is moved above the investigated surface. When the tip comes in contact with the surface, the cantilever slightly deflects from the equilibrium (contact mode). The deflection of the cantilever is kept constant by a feedback loop during scanning, which is achieved by controlling the vertical position of the AFM tip. The constant cantilever deflection ensures that the tip – sample force is also constant, and thus the measured vertical tip positions give the topography of the sample.

The research presented in the thesis was done in broad national and international cooperation. The nanotube samples were supplied by European research partners. The STM and AFM investigations were done in our institute (MFA) using a *Veeco* Nanoscope E instrument.

Results

The most important results are summarized in the following statements:

- 1) I used the RBS, PIXE, and XRF techniques to measure the cobalt catalyst content in CVD grown carbon nanotube samples after each purification step. The residual cobalt content was 1 (wt) % after the whole purification procedure, which showed a decrease by a factor of 2.5 relative to the initial material. Based on TEM images I showed that the residual cobalt found in the nanotube sample resides inside of carbon nanotubes and other graphitic structures. I demonstrated by STM that the applied purification procedure modifies the surface of the nanotubes and generates craters of 1 – 3 nanometers [1, 2].
- 2) I detected by STM carbon nanotube point defects produced by low dose ($5 \cdot 10^{11}$ ions/cm²) Ar⁺ ion irradiation of 30 keV. These defects appear as hillock-like protrusions of several angstroms in the STM images. I demonstrated by STS measurements that the local density of states at the defect sites differs from the density of states measured at the undamaged nanotube portions [3, 4, 6].
Using STM and AFM on the graphite (HOPG) substrate, I demonstrated that the major part (90 %) of the hillock-like protrusions induced by irradiation was due to the local change in the density of states, and only a small part (10 %) can be attributed to clusters and deformations topographically emerging from the HOPG surface (to be published).
- 3) I observed by STM the partial healing of irradiation induced nanotube defects after annealing the sample at 450 °C. After annealing, I observed additional electronic states at the defect sites at about 0.35 eV above the Fermi energy by STS, while before annealing similar states were present at about 0.1 eV. From these observations I concluded that the type of the defects had changed during the annealing [4, 5, 6].

- 4) I performed atomic resolution STM study of multi-wall carbon nanotubes with point defects. I observed “ $\sqrt{3} \times \sqrt{3} R$ ”-type superstructures in the close vicinity of the hillock-like protrusions corresponding to the defects. These superstructures appear due to the interference between normal and backscattered electron waves. I demonstrated that the superstructures observed on a nanotube with a given chirality had the same orientation [4, 5, 6, 7].
- 5) Using STM I showed that the surface of multi-wall carbon nanotubes became ragged after high dose (10^{15} ions/cm²) Ar⁺ ion irradiation of 800 eV. I attributed the ragged nanotube surfaces to the high number of point defects (vacancies, interstitials, etc.) created by the Ar⁺ ions, and also to the links appearing between adjacent nanotube walls, which offer alternative tunneling paths for the electrons [3].
- 6) During the STM investigation of multi-wall carbon nanotubes irradiated with high dose (10^{15} ion/cm²) Ar⁺ ions of 800 eV, I removed carbon atoms from the outer nanotube walls by varying the tunneling parameters and fast scanning (1 – 10 Hz) with the STM tip. Using line-cut analysis I determined that the STM tip removed carbon atoms from the outer 2 – 3 atomic layers. Since I did not observe similar modification in case of non-irradiated nanotubes, I concluded that the high-dose Ar⁺ irradiation significantly modified the graphitic structure of the external nanotube walls. I observed that the shape of the STM tip used in the investigation changed during the interaction with the nanotube [8].

Utilization of the results

The results presented in the thesis contributed to the success of the following projects:

EU FP5 NANOCOMP: „*Large scale synthesis of carbon nanotubes and their composite materials*”

OTKA projects No. T030435, T043685, and T043704.

Publications

Contributions related to the statements of the thesis:

- [1] L. P. Biró, N. Q. Khanh, Z. E. Horváth, Z. Vértesy, A. Kocsonya, Z. Kónya, **Z. Osváth**, A. Koós, J. Gyulai, X. B. Zhang, G. Van Tendeloo, A. Fonseca, J. B. Nagy, *Catalyst traces after chemical purification in CVD grown carbon nanotubes*, Electronic Properties of Molecular Nanostructures, AIP Conference Proceedings Vol. **591** (2001) 183

- [2] L. P. Biró, N. Q. Khanh, Z. Vértesy, Z. E. Horváth, **Z. Osváth**, A. Koós, J. Gyulai, A. Kocsonya, Z. Kónya, X. B. Zhang, G. Van Tendeloo, A. Fonseca, J. B. Nagy, *Catalyst traces and other impurities in chemically purified carbon nanotubes grown by CVD*, Materials Science and Engineering C **19** (2002) 9
- [3] **Z. Osváth**, G. Vértesy, G. Pető, I. Szabó, J. Gyulai, W. Maser and L. P. Biró, *STM investigation of irradiated carbon nanotubes*, Electronic Properties of Synthetic Nanostructures: XVIII International Winterschool on Electronic Properties of Novel Materials, AIP Conference Proceedings Vol. **723** (2004) 149
- [4] **Z. Osváth**, G. Vértesy, L. Tapasztó, F. Wéber, Z. E. Horváth, J. Gyulai and L. P. Biró, *Atomically resolved STM images of carbon nanotube defects produced by Ar⁺ irradiation*, Physical Review B **72** (2005) 045429
- [5] **Z. Osváth**, G. Vértesy, L. Tapasztó, F. Wéber, Z. E. Horváth, J. Gyulai and L. P. Biró, *Atomically resolved STM images of carbon nanotube defects produced by Ar⁺ irradiation*, Virtual Journal of Nanoscale Science & Technology **12** (2005) Issue 4 (selected paper, published online on 25 July 2005 - <http://www.vjnano.org>)
- [6] **Z. Osváth**, G. Vértesy, L. Tapasztó, F. Wéber, Z. E. Horváth, J. Gyulai and L. P. Biró, *Scanning tunneling microscopy investigation of atomic-scale carbon nanotube defects produced by Ar⁺ ion irradiation*, Materials Science and Engineering C (2006), *in press*
- [7] **Z. Osváth**, G. Vértesy, L. Tapasztó, F. Wéber, Z. E. Horváth, J. Gyulai, and L. P. Biró, *STM images of atomic-scale carbon nanotube defects produced by Ar⁺ irradiation*, Electronic Properties of Novel Nanostructures: XIX International Winterschool on Electronic Properties of Novel Materials, AIP Conference Proceedings Vol. **786** (2005) 154
- [8] **Z. Osváth**, W. Maser, I. Szabó, G. Pető, A. A. Koós, J. Gyulai, L. P. Biró, *STM study on multi-wall carbon nanotubes irradiated with Ar⁺ ions*, EUROMAT 2003, 8th European Congress and Exhibition on Advanced Materials and Processes, 1-5 September 2003, Lausanne, Switzerland – *poster*

Other publications:

- [9] **Z. Osváth**, L. Nagy, *Double-differential cross sections for the ionization-excitation of the helium by fast proton and antiproton impact*, Physics Letters A **271** (2000) 385
- [10] G. I. Márk, L. P. Biró, A. Koós, **Z. Osváth**, J. Gyulai, A. M. Benito, P. A. Thiry, Ph. Lambin, *Charge spreading effects during 3D tunneling through a supported carbon nanotube*, Electronic Properties of Molecular Nanostructures, AIP Conference Proceedings Vol. **591** (2001) 364

- [11] **Z. Osváth**, A. A. Koós, Z. E. Horváth, J. Gyulai, A. M. Benito, M. T. Martínez, W. K. Maser and L. P. Biró, *Arc-grown Y-branched carbon nanotubes observed by scanning tunneling microscopy (STM)*, Chemical Physics Letters **365** (2002) 338
- [12] G. I. Márk, A. A. Koós, **Z. Osváth**, L. P. Biró, J. Gyulai, A.M. Benito, W.K. Maser, P.A. Thiry, Ph. Lambin, *Calculation of the charge spreading along the carbon nanotube as seen in STM*, Diamond and Related Materials **11** (2002) 961
- [13] L. P. Biró, R. Ehlich, **Z. Osváth**, A. A. Koós, Z. E. Horváth, J. Gyulai, J. B.Nagy, *Room temperature growth of single-wall coiled carbon nanotubes and Y-branches*, Materials Science and Engineering C **19** (2002) 3
- [14] L. P. Biró, R. Ehlich, **Z. Osváth**, A. A. Koós, Z. E. Horváth, J. Gyulai, B. J. Nagy, *From straight carbon nanotubes to Y-branched and coiled carbon nanotubes*, Diamond and Related Materials **11** (2002) 1081
- [15] Z. Kónya, I. Vesselényi, K. Niesz, A. Kukovecz, A. Demortier, A. Fonseca, J. Delhalle, Z. Mekhalif, J. B.Nagy, A.A. Koós, **Z. Osváth**, A. Kocsonya, L.P. Biró and I. Kiricsi, *Large scale production of short functionalized carbon nanotubes*, Chemical Physics Letters **360** (2002) 429
- [16] **Z. Osváth**, A. A. Koós, Z. E. Horváth, J. Gyulai, A.M. Benito, M.T. Martínez, W. Maser, and L. P. Biró, *STM observation of asymmetrical Y-branched carbon nanotubes and nano-knees produced by the arc discharge method*, Materials Science and Engineering C **23** (2003) 561
- [17] **Z. Osváth**, L. Fulcheri, G. I. Márk, L. Tapasztó, J. Gyulai, and L. P. Biró, *STM and STS investigation of few wall carbon nanotubes containing non-hexagonal carbon rings*, Nanotechnology, Proceedings of SPIE – The International Society for Optical Engineering Vol. **5118** (2003) 587
- [18] W. K. Maser, A. M. Benito, M. A. Callejas, T. Seeger, M. T. Martínez, J. Schreiber, J. Muszinski, O. Chauvet, **Z. Osváth**, A. A. Koós and L. P. Biró, *Synthesis and characterization of new polyaniline/nanotube composites*, Materials Science and Engineering C **23** (2003) 87
- [19] A. A. Koós, R. Ehlich, Z. E. Horváth, **Z. Osváth**, J. Gyulai, J. B.Nagy, L. P. Biró, *STM and AFM investigation of coiled carbon nanotubes produced by laser evaporation of fullerene*, Materials Science and Engineering C **23** (2003) 275
- [20] A. A. Koós, Z. E. Horváth, **Z. Osváth**, L. Tapasztó, K. Niesz, Z. Kónya, I. Kiricsi, N. Grobert, M. Rühle, and L. P. Biró, *STM investigation of carbon nanotubes completely covered with functional groups*, Nanotechnology, Proceedings of SPIE – The International Society for Optical Engineering Vol. **5118** (2003) 565

- [21] L. P. Biró, Z. E. Horváth, A. A. Koós, **Z. Osváth**, Z. Vértesy, Al. Darabont, K. Kertész, C. Neamțu, Zs. Sárközi, L. Tapasztó, *Direct synthesis of multi-walled and single-walled carbon nanotubes by spray-pyrolysis*, Journal of Optoelectronics and Advanced Materials **5** (2003) 661
- [22] A. A. Koós, Z. E. Horváth, **Z. Osváth**, L. Tapasztó, K. Niesz, Z. Kónya, I. Kiricsi, N. Grobert, M. Rühle, L. P. Biró, *STM investigation of carbon nanotubes connected by functional groups*, Materials Science and Engineering C **23** (2003) 1007
- [23] L. P. Biró, Z. E. Horváth, G. I. Márk, **Z. Osváth**, A. A. Koós, A. M. Benito, W. Maser, Ph. Lambin, *Carbon nanotube Y junctions: growth and properties*, Diamond and Related Materials **13** (2004) 241
- [24] L. Tapasztó, K. Kertész, Z. Vértesy, Z. E. Horváth, A. A. Koós, **Z. Osváth**, Zs. Sárközi, Al. Darabont, L. P. Biró, *Diameter and morphology dependence on experimental conditions of carbon nanotube arrays grown by spray pyrolysis*, Carbon **43** (2005) 970
- [25] A. Darabont, P. Nemes-Incze, K. Kertész, L. Tapasztó, A. A. Koós, **Z. Osváth**, Z. Sárközi, Z. Vértesy, Z. E. Horváth, L. P. Biró, *Synthesis of carbon nanotubes by spray pyrolysis and their investigation by electron microscopy*, Journal of Optoelectronics and Advanced Materials **7** (2005) 631
- [26] Darabont Sándor, Kertész Krisztián, Sárközi Zsuzsa, Tapasztó Levente, Biró László Péter, Horváth Zsolt Endre, Koós Antal, **Osváth Zoltán**, *A porlasztásos pirólízis módszer és a növesztési paraméterek vizsgálata a szén nanoszerkezetek előállításában*, Korszerű kísérleti és elméleti fizikatanulmányok, Sapientia Könyvek **20.**, Scientia Kiadó, Kolozsvár 2003, pp. 10 – 126
- [27] A. A. Koós, Z. E. Horváth, K. Kertész, Z. Vértesy, L. Tapasztó, **Z. Osváth**, Z. Sárközi, P. Nemes Incze, Al. Darabont, L. P. Biró, *Optimization of the synthesis of carbon nanotubes in a semi-continuous injection chemical vapor deposition method*, Proceedings of the First International Workshop on Semiconductor Nanocrystals, Semiconductor Nanocrystals, Vol. **1** (2005), page 51-54
- [28] L. Dózsa, G. Molnár, A.L. Tóth, E. Horváth, **Z. Osváth**, C.A. Dimitriadis, L. Papadimitriou, N. Vouroutzis, E. Paraskevopoulos, *Properties of β -FeSi₂ quantum structures grown on silicon*, NATO Science Series, Mathematics, Physics and Chemistry Vol. **204**, Nanostructured and Advanced Materials, pp. 331 – 334, 2005 Springer, Netherlands
- [29] Al. Darabont, N. Daróczi, P. Nemes-Incze, K. Kertész, Zs. Sárközi, A. A. Koós, Z. E. Horváth, **Z. Osváth**, Z. Vértesy, L. P. Biró, *Szén nanocsövek szintézise folyékony szénhidrogénekből katalizátor jelenlétében*, Erdélyi Magyar Műszaki Tudományos Társaság (EMT) Műszaki Szemle **31** (2005) 36

- [30] Z. E. Horváth, K. Kertész, L. Pethő, A. A. Koós, L. Tapasztó, Z. Vértesy, **Z. Osváth**, A. Darabont, P. Nemes-Incze, Zs. Sárközi and L. P. Biró, *Inexpensive, Upscalable Methods For Nanotube Growth*, Current Applied Physics **6** (2006) 135
- [31] A. A. Koós, Z. E. Horváth, K. Kertész, Z. Vértesy, L. Tapasztó, **Z. Osváth**, Z. Sárközi, P. Nemes-Incze, Al. Darabont, L. P. Biró, *Influence of catalyst and carbon source on the synthesis of carbon nanotubes in a semi-continuous injection chemical vapor deposition method*, Carbon Nanotubes (Ed.: V. N. Popov, Ph. Lambin), NATO Science Series 222, 53 – 54, 2006 Springer, Netherlands
- [32] A. Tunyogi, F. Pászti, **Z. Osváth**, F. Tanczikó, M. Major, E. Szilágyi, *Asymmetric interfaces in Fe/Ag and Ag/Fe bilayers prepared by molecular beam evaporation*, Nuclear Instruments and Methods in Physics Research B (2006), *in press*

Citations

The above publications received 85 independent citations until 03 May 2006.

References

- ⁱ S. Iijima, Nature **354** (1991) 56
- ⁱⁱ M. M. Treacy, T. W. Ebbesen, and J. M. Gibson, Nature **381** (1996) 678
- ⁱⁱⁱ C. T. White, and T. N. Todorov, Nature **393** (1998) 240
- ^{iv} S. D. Li, Z. Yu, S. F. Yen, W. C. Tang, P. J. Burke, Nano Lett. **4** (2004) 753
- ^v L. Roschier, M. Sillanpaa, T. H. Wang, M. Ahlskog, S. Iijima, P. Hakonen, J. Low Temp. Phys. **136** (2004) 465
- ^{vi} E. Wong, P. Sheehan, C. Lieber, Science **277** (1997) 1971
- ^{vii} W. B. Choi, D. S. Chung, J. H. Kang, H. Y. Kim, Y. W. Yin, I. T. Han, Y. H. Lee, J. E. Jung, N. S. Lee, G. S. Park, J. M. Kim, Appl. Phys. Lett. **75** (1999) 3129
- ^{viii} Y. Saito, S. Uemura, K. Hamaguchi, Jpn. J. Appl. Phys. **37** (1998) L346
- ^{ix} I. W. Chiang, B. E. Brinson, R. E. Smalley, J. L. Margrave, R. H. Hauge, J. Phys. Chem. B **105** (2001) 1157
- ^x 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
- ^{xi} P. M. Ajayan, V. Ravikumar, J.-C. Charlier, Phys. Rev. Lett. **81** (1998) 1437
- ^{xii} M. Terrones, F. Banhart, N. Grobert, J.-C. Charlier, H. Terrones, and P. M. Ajayan, Phys. Rev. Lett. **89** (2002) 075505
- ^{xiii} M. S. Raghuvver, P. G. Ganesan, J. D'Arcy-Gall, and G. Ramanath, M. Marshall, and I. Petrov, Appl. Phys. Lett. **84** (2004) 4484
- ^{xiv} E. Salonen, A.V. Krasheninnikov, K. Nordlund, Nucl. Instrum. Meth. B **193** (2002) 603

-
- ^{xv} A. Kis, G. Csányi, J.-P. Salvetat, Thien-Nga Lee, E. Couteau, A. J. Kulik, W. Benoit, J. Brugger, and L. Forró, *Nature Mater.* **3** (2004) 153
- ^{xvi} H. Stahl, J. Appenzeller, R. Martel, Ph. Avouris, and B. Lengeler, *Phys. Rev. Lett.* **85** (2000) 5186
- ^{xvii} M. Huhtala, A. V. Krasheninnikov, J. Aittoniemi, S. J. Stuart, K. Nordlund, and K. Kaski, *Phys. Rev. B* **70** (2004) 045404
- ^{xviii} A. V. Krasheninnikov, K. Nordlund, M. Sirviö, E. Salonen, and J. Keinonen, *Phys. Rev. B* **63** (2001) 245405
- ^{xix} A. V. Krasheninnikov, K. Nordlund, *Phys. Solid State* **44** (2002) 470