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Project acronym: SPANG

Project title: Spark Ablation for Nanotube Growth

SPECIFIC TARGETED RESEARCH OR INNOVATION PROJECT

SIXTH FRAMEWORK PROGRAMME
PRIORITY 3 - NMP
FP6-2002-NMP-1

Publishable Final Activity Report

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SPANG

SPANG refers to "Spark Ablation for Nanotube Growth". The goal of the project is to develop low-price synthetic routes for high-quality single-walled carbon nanotubes. The benchmark method for producing high-quality carbon nanotubes is laser ablation: graphite is evaporated in a laser beam, and using the right catalyst and the right process conditions, the carbon plasma condenses to fairly long, nearly defect-free single-walled carbon nanotubes and a small amount of by-products (amorphous carbon and graphitic particles). In the spark ablation method the laser beam is replaced by an electron beam form a spark discharge, which in much less expensive. Alternatively, high-quality nanotubes can be produced by evaporating graphite in an electric arc. The Arc-Jet method injects a hydrocarbon gas into the arc and thus provides similar gas flow conditions as the laser ablation method. Furthermore it can be set up as a continuous process (as opposed to batch processes in conventional nanotube synthesis). In the SPANG project nanotubes are produced by three methods: Laser Ablation, Spark Ablation, and Arc-Jet.

To control the quality of nanotubes a procedure has been standardized involving the combination of electron microscopy, Raman spectroscopy, optical absorption, X-ray diffraction, thermal gravimetry and electrical measurements. Based on the nanotubes produced and characterized in the project, devices have been prepared and their use in printed circuit bards has been studied (leads, resistors, capacitors).

Project Partners

Max-Planck-Institut für Festkörperforschung, **Stuttgart**
ISMN Consiglio Nazionale delle Ricerche, **Bologna**
Sineurop Nanotech, **Stuttgart**
Organic Spintronics, **Bologna**
AT&S Austria Systemtechnik AG, **Leoben**
Shanghai Yangtze Nanomaterials Co., Ltd., **Shanghai**
Shanghai Nanotechnology Promotion Center, **Shanghai**
Danubia NanoTech, **Bratislava**

Project Execution

As examples of generators for nanotube production in this project we show photographs of the spark ablation device (Fig.1) and the Arc-Jet device (Fig.2). Both methods have been developed up to the stage of production, but the cost issues have not yet been evaluated due to the still small market demand of nanotubes, which makes large-scale production not very sensible at the time being.

Fig. 1 Generator for producing single-walled carbon nanotubes by the Channel Spark Ablation Method.

Fig. 2 Generator for producing single-walled carbon nanotubes by the Arc-Jet® method.

The key part of the standardized quality control procedure is optical absorption on nanotube suspensions prepared by following a detailed prescription. Fig.3 shows the overall absorption spectrum. There is more or less a continuous background with some wiggles. These wiggles are caused by Van Hove singularities in the electronic density of states of the nanotubes and are fingerprints of single-walled nanotubes. The nanotube concentration is determined by properly subtracting a baseline and integrating over the spectrum, as indicated in Fig.4.

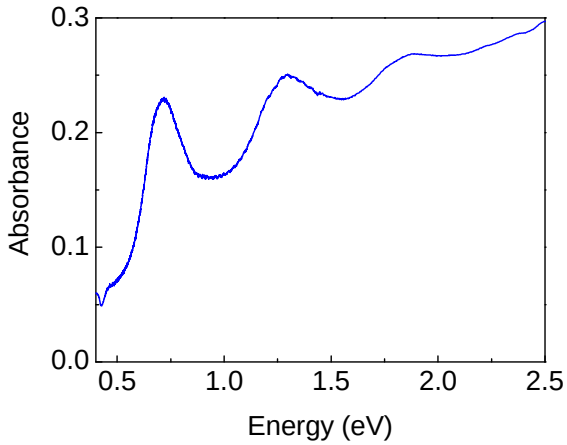

Fig. 3 Absorption spectrum of a carbon nanotube sample containing nanotubes and other carbonaceous components (amorphous carbon, graphitic particles). Wiggles are fingerprints of single-walled nanotube (coming from Van Hove singularities in the electronic density of states).

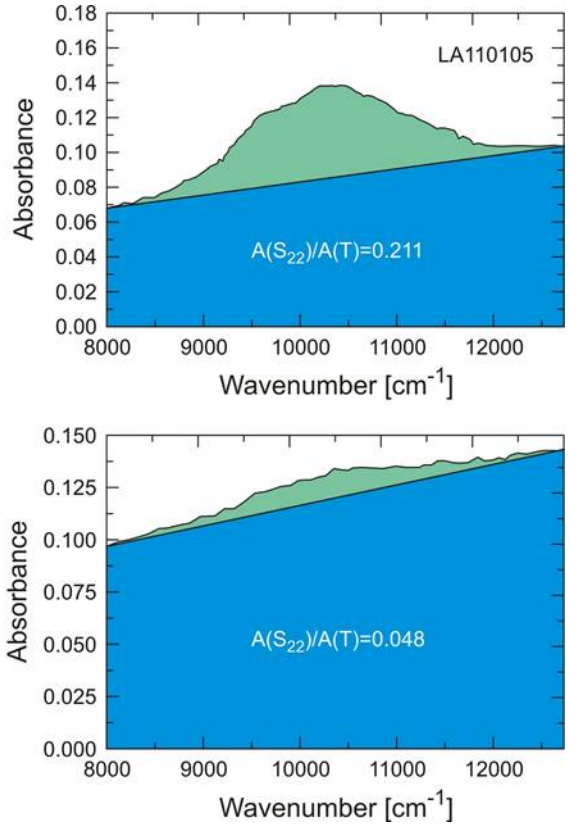

Fig. 4 Evaluating nanotube concentration from absorption spectra. Large green peak indicated a high concentration.

If nanotubes are used on a large scale, this will very likely be in the form of a composite. During the project intensive studies on polymers loaded with nanotubes to various concentrations have been carried out (electrical, mechanical, and thermal properties). The electrical surface conductivity is shown in Fig. 5.

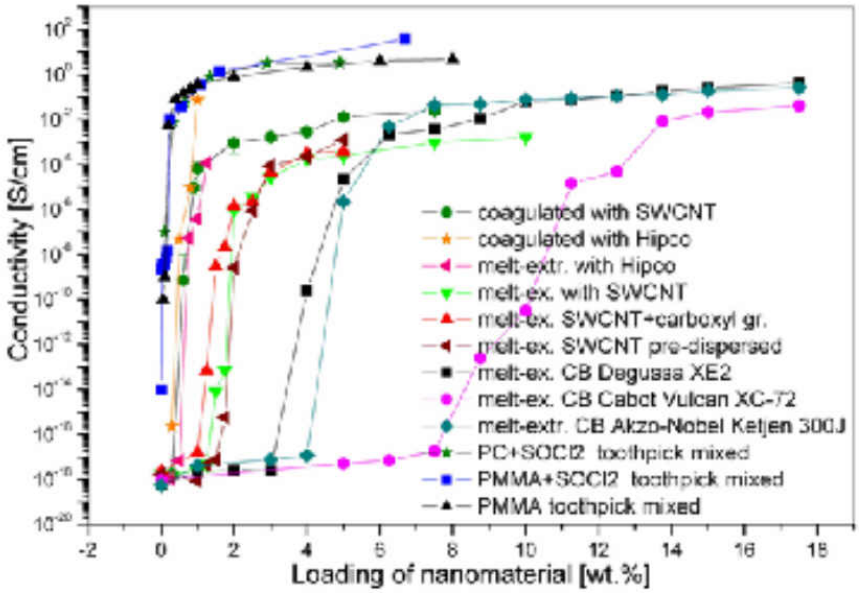

Fig. 5 Change of electrical conductivity of various polymers (polycarbonate, Plexiglas) upon loading with carbon nanotubes. The abrupt change is at the percolation threshold. Low thresholds and high end conductivities are desired. The threshold is low for long and thin filler particles.

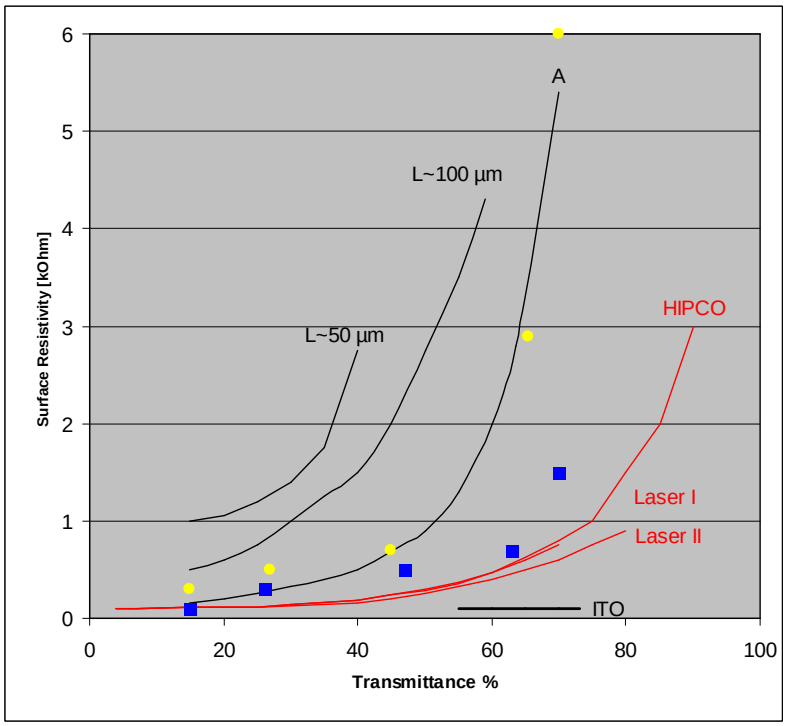

Fig. 6 Surface resistance of thin nanotube films plotted as a function of optical transparency.

A special outcome of these investigations are thin transparent conducting films, such as needed for cover layers of solar cells and light emitting devices. Relevant data are summarized in Fig. 6. The benchmark material of today is indium-tin-oxide (ITO). We do not yet beat this material but films based on laser ablation single-walled carbon nanotubes come already pretty close.

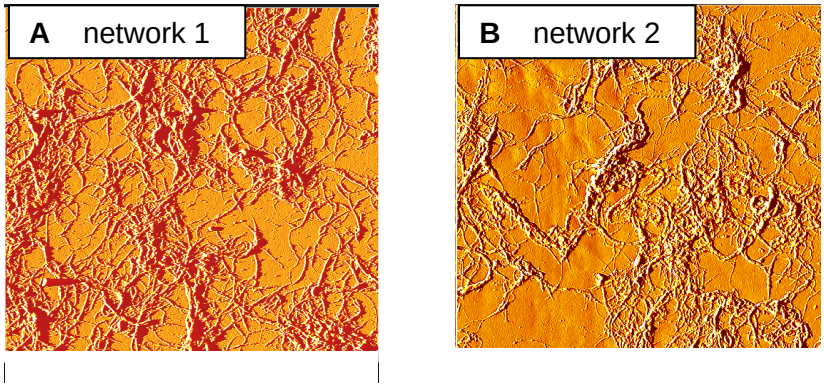

Fig. 7 AFM Images of nanotube networks to be used as resistors on printed circuit board.

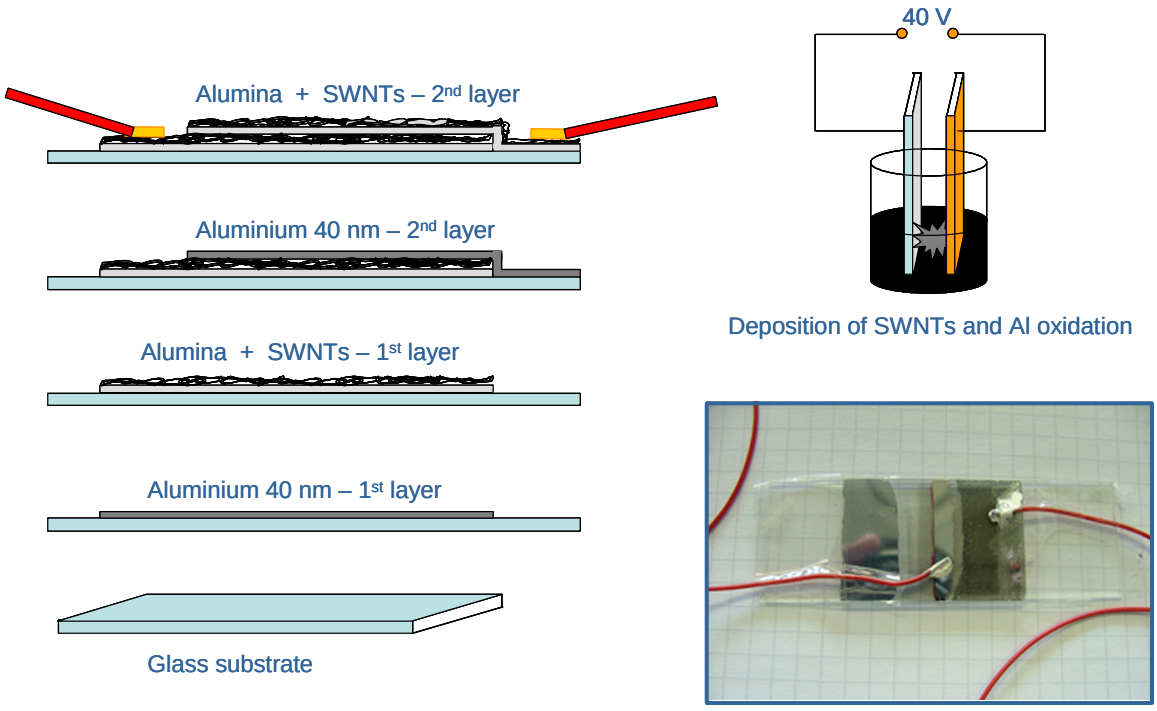

Fig. 8 Capacitors based on carbon nanotube networks.

For use in printed circuit boards resistors have been prepared from nanotube networks. AFM images of these networks are shown in Fig. 7. The resistance of nanotube networks has been carefully studied and a model for charge transport in nanotube networks has been developed. These investigations have lead to several publications.

A further use of nanotube in printed circuits would be nanotube-based capacitors. Fig. 8 shows schematically the first steps towards capacitor fabrication. So far a 1mm thick stack of nanotube nets (1cm² area) would lead to a capacitance of about 10nF.

Dissemination and Use

The new nanotube production methods (Spark Ablation and Arc-Jet) are ready for use and large-scale production can start, as soon as further development of nanotube application will have created a sufficient market volume. Then Spark Ablation will be marketed by the partner Organic Spintronics and Arc-Jet by Sineurop. Arc-Jet has also been protected by a patent. While waiting for that larger market, Laser Ablation nanotubes will be sold into niche markets. Our present estimate is that several hundred grams could be sold per year. The partners Danubia and Sineurop will closely cooperate in this respect and they have decided to build new laser ablation generators, both in Bratislava and in Stuttgart. These generators will be identical, so that spare parts can be shared and reliable nanotube supply is guaranteed.

The standardized nanotube control procedure has been presented at many conferences throughout the world (Europe, USA, China, Korea) and on request copies of the "Quality Control Protocol" are send to nanotube producers and users. For copies ask the partners Danubia, Sineurop, and Yangtze.

Commercialisation of nanotube applications on printed circuit boards still needs considerable development work. But on the way there, transparent conducting films and absorbers for electromagnetic radiation were developed. Some steps in respective material preparation have been patented. Negotiations with large companies to place these materials on the market are ongoing.

The following publications have been prepared in the course of the project:

1.) Skákalová, V., A. Kaiser, M. Kaempgen, and S. Roth: “Electron transport – from buckypaper to thin single wall nanotube networks”, In: *Electronic Properties of Novel Materials*, H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), American Institute of Physics, New York, USA, 2005.
AIP Conference Proceedings **786** (2005) 562-565.

2.) Skákalová, V., U. Dettlaff-Weglikowska, and S. Roth: “Electrical and mechanical properties of nanocomposites of single wall carbon nanotubes with PMMA”, *Synthetic Metals* **152** (2005) 349-352.

3.) Pötschke, P., B. Hornbostel, S. Roth, S. Dudkin, and I. Alig: “Purification an percolation – unexpected phenomena in nanotube polymer composites”, In: *Electronic Properties of Novel Materials*, H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), American Institute of Physics, New York, USA, 2005.
AIP Conference Proceedings **786** (2005) 596-601.

4.)Scalia, G., M. Haluska, U. Dettlaff-Weglikowska, F. Giesselmann, and S. Roth: “Polarized Raman spectroscopy study of SWCNT orientational order in an aligning liquid crystalline matrix”, In: *Electronic Properties of Novel Materials*, H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), American Institute of Physics, New York, USA, 2005.
AIP Conference Proceedings **786** (2005) 114-117.

5.) Dettlaff-Weglikowska U., J. Wang, J. Liang, B. Hornbostel, J. Cech, and S. Roth: “Purity Evaluation of Bulk Single Wall Carbon Nanotube Materials”, In: *Electronic Properties of*

Novel Materials, H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), American Institute of Physics, New York, USA, 2005.
AIP Conference Proceedings **786** (2005) 129-134.

6.) Haluska M., V. Skákalová, D. Carroll, and S. Roth: "The Influence of Sulfur Promoter on the Production of SWCNTs by the Arc-Discharge Process", In: *Electronic Properties of Novel Materials*, H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), American Institute of Physics, New York, USA, 2005.
AIP Conference Proceedings **786** (2005) 87-91.

7.) Hornbostel B., M. Haluska, J. Cech, U. Dettlaff, and S. Roth: "Arc Discharge and Laser Ablation Synthesis of single-walled Carbon Nanotubes", V.N. Popov, P. Lambin (Eds.), *Carbon Nanotubes (NATO Science Series II: Mathematics, Physics and Chemistry. Proceedings of the NATO Advanced Study Institute on Carbon Nanotubes: from Basic Research to Nanotechnology, held in Sozopol, Bulgaria, (May 2005) 21-31),* **222** (2006) 252. ISBN: 1-4020-4572-7

8.) Skakalova, V., A.B. Kaiser, Y.-S. Woo and S. Roth: "Electronic transport in carbon nanotubes: From individual nanotubes to thin and thick networks", *Physical Review B* **74** (2006) 085403

9.) Dettlaff-Weglikowska, U., M. Kaempgen, B. Hornborstel, V. Skakalova, J. Wang, J. Liang and S. Roth: „Conducting and transparent SWNT/polymer composites",*Physica Status Solidi* **B** (2006) 1-5

10.) Ferrer-Anglada, N., M. Kaempgen and S. Roth: "Transparent and flexible carbon nanotube/polypyrrole and carbon nanotube/polyanaline pH sensors", *Physica Status Solidi* **B** (2006) 1-5

11.) Lagerwall, J.P.F., G. Scalia, M.Haluska, U. Dettlaff-Weglikowska, F. Giesselmann, and S. Roth: "Simultaneous alignment and dispersion of carbon nanotubes with lyotropic liquid crystals", *Physica Status Solidi* **B** (2006) 3046–3049

12.) Ansaldo A., M. Haluška, J. Čech, D. Ricci, F. Gatti, E. Di Zitti, S. Cincotti, and S. Roth: "CVD synthesis of single wall carbon nanotubes devoted to ULSI electronic applications", *Physica Status Solidi* **B** 243 **13** (2006) 3077–3081

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14.) Cech, Jiri, S.A. Curran, D. Zhang, J.L. Dewald, A. Avadhanula, M. Kandadai and S. Roth: "Functionalization of multi-walled carbon nanotubes: Direct proof of sidewall thiolation", *Phys. Stat. Sol. (b)* **243** *13* 3221-3225 (2006)

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16.) Hornbostel, B., P. Pötschke, J. Kotz and S. Roth: "Single-walled carbon nanotubes/polycarbonate composites: basic electrical and mechanical properties", *Phys. Stat. Sol. (b)* **243** *13* 3445-3451 (2006)

17.) Scalia, G., J.P.F. Lagerwall, M. Haluska, U. Dettlaff-Wegliskowska, F. Giesselmann and S. Roth: "Effect of phenyl rings in liquid crystal molecules on SWNTs studies by Raman sprectroscopy", *Phys. Stat. Sol. (b)* **243** *13* 3238-3241 (2006)

18.) Kovac, P., I. Husek, V. Skakalova, J. Meyer, E. Dubrocka, M. Hirscher and S. Roth: "Transport current improvements of *in situ* MgB2 tapes by the addition of carbon nanotubes, silicon carbide or graphite", *Superconducting Science and Technology* **20** (2007) 105-111

19.) Dettlaff-Weglikowska, U., V. Skakalova, J. Meyer, J. Cech, B.G. Mueller and S. Roth: "Effect of fluorination on electrical properties of single walled carbon nanotubes and C60 peapods in networks", *Current Applied Phyiscs* **7** (2007) 42-46

20.) Skakalova, V., J. Maultzsch, Z. Osvath, L.P. Biro and S. Roth: "Intermediate frequency modes in Raman spectra of Ar+-irradiated single-wall carbon nanotubes", *Phys. Stat. Sol. (RRL)* **1**, *4*, 138-140 (2007)

Further information
on the project and on the future development of the topic can be obtained from the homepages of the partners:

www.fkf.mpg.de/klitzing/nano
www.sineurop-nanotech.com
www.danubiananotech.com