Project number: FP6 - 508159

Project acronym: NANOSPARK

Project title: Development of a new machinery for nanotubes mass production based on the Channel Spark Ablation technique

Instrument: Cooperative Research

Thematic priority: Nanotechnology and nanosciences, knowledge-based multifunctional materials, new production processes and devices

Publishable final activity report

Period covered: from 01/11/2004 to 31/01/2007		Date of preparation:	30/04/2007
Start date of the project:	01/11/2004	Duration:	27 months
Project coordinator name:	Marco Mescia		
Project coordinator organisation name:	LABOR Srl	Revision:	0

Summary

SECTION 1 PROJECT EXECUTION

1.1 Project objectives

The NANOSPARK project deals with a new production process for carbon nanotubes production. The aim of the project is to develop a new machinery based on a cheap technological procedure, the Channel Spark Ablation (CSA), to produce high quality single-walled carbon nanotubes (SWCNTs) which should yield the same quality as laser ablation but at much lower costs.

CSA is a technique based on the pulsed electron-beam generation from the glow-discharge plasma environment. It is able to deposit conducting and non conducting materials with deposition rates ranging from 0.01 Å/pulse up to about 100 Å/pulse. This features make CSA a versatile technique able to be switched between epitaxial layers and thin coatings.

The carbon nanotubes (CNTs) produced by this machinery is then used for different applications and in particular as passive electronic elements into innovative solar cells and dye sensitised solar cells exploiting the outstanding properties of conductivity and chemical stability.

The expected results were:

1) the definition and design of the NANOSPARK machinery based on CSA technique;
2) the definition of the process for utilisation of carbon nanotubes in solar energy devices.

During the execution of the project the following activities have been carried out:

1. Design and development of a CSA based machinery for SWCNTs production

Many scientific and technological aspects of the CSA have been deeply investigated in order to make it exploitable for carbon nanotubes production.

a) *Design of an electron-beam generator and the plasma environment characterization*

The CSA is an ablation process based on the pulsed electron-beam generation from the glow-discharge plasma environment. The glow-discharge plasma produced depends on the characteristics of the cathode-anode system therefore a characterization of this component is indispensable to gather cathode information of plasma generation within the reaction chamber.

b) *Reaction chamber design*

The reaction chamber configuration. The configuration of the chamber consisting of the beam generation chamber and the target ablation chamber with the following CNTs formation were studied and designed according to the peculiar operating conditions necessary for plasma formation.

c) *Reduction of the energy consumption*

The energy consumption for CSA system is much lower than laser ablation (about two order of magnitude) and its abatement strongly affects the final products price. Reduction in energy consumption was one of the most important aspect for future exploitation of the NANOSPARK machinery.

d) *Differential vacuum system*

Pressure conditions within the machinery represented one of the major issues. Differential pressure system have been developed in order to create the proper operating conditions. A

Plasma Window has been designed and implemented on the system together with a vacuum system.

e) *Installation cost*

Installation cost for CSA equipment can be 5 times cheaper than commercial pulsed laser deposition set-ups. Conversely to UV-lasers the main advantages of CSA-systems are simplicity and high efficiency in converting electric energy in beam energy. Conversion rate is 50-70%. The possibility to easily scale-up the process using more guns limit cost increase whereas laser ablation which is practically unscalable.

2. Methodology for carbon nanotubes preparation: purification and preparation in different media

CNTs are unique material which can be extremely complicated to be used in industrial applications. Nanotubes can not be used as they are but required of several purification treatments after production. Even the dispersion of the nanostructured material into different media required a deep theoretical and experimental study on the basis of the industrial application desired. CNTs were produced and dispersed in different media according to their final application.

3. Development of new solar systems

Concerning the applications of CNTs the project aimed at designing and developing new solar energy systems with low manufacturing costs, up to 50% lower than traditional crystalline cell modules. The research included the study of the complete process for the deposition of nanotubes and realisation of devices so as the implementation of new deposition processes of SWCNTs suspensions upon substrates to be used to fabricate solar cells.
Two different systems were investigated:

1) Dye sensitised solar cells (Graetzel-like cells);
2) Organic solar cells with bulk hetero-junctions.

1.2 Contractors involved

The NANOSPARK Consortium is made of SMEs and RTD performers operating in different European countries (Italy, Spain, Germany and Austria), in Israel and China with complementary competencies and interests.

In the following table are indicated all the partners involved in the present project.

Partic. Role	Partic. type	Partic. No.	Participant name	Participant short name	Country
CO	RTD	1	LABOR Srl	LABOR	I
CR	SMEP	2	TECNA Srl	TECNA	I
CR	SMEP	3	SINEUROP Nanotech GmbH	SINEUROP	D
CR	SMEP	4	IBE Ingenieria e industria bioenergeticas S.L.	IBE	E
CR	SMEP	5	KONARKA Austria Forschungs und Entwicklungs GmbH	KONARKA	A

CR	OTH	6	Shangai YANGTZE Nanomaterials Co., Ltd	YANGTZE	CHI
CR	RTD	7	Consiglio Nazionale delle Ricerche - Istituto per lo Studio dei Materiali Nanostrutturati	CNR-ISMN	I
CR	RTD	8	TECHNION - Israel Institute of Technology	TECHNION	IL
CR	RTD	9	MAX-PLANCK Institut fur Festkorperforschung	MPI-FKF	D
CR	RTD	10	Organic Spintronics Srl	OS	I

Project Coordinator:

Mr. Marco Mescia
LABOR Srl
Via Giacomo Peroni, 386
00131 Roma (Italy)
Phone: +39 06 40040354
Fax: +39 06 40040357
Email: m.mescia@labor-roma.it

Project's web site: http://www.nanospark-project.eu/

1.3 Work performed

All partners of the project have been deeply involved in the research activities on the basis of their competencies and expertise.

The work performed in the first year was carried out in the following Workpackages:

1) WP1: Preliminary technical study

- ✓ Preliminary study has been focused on the evaluation of CSA technique for SWCNTs production.
- ✓ Definition of the optimal characteristics and processes needed to develop solar energy devices using SWCNTs.
- ✓ The technical characteristics of the final system have translated the users' requirements into technical specifications necessary for the development phase. Technical aspects, risks analysis and safety of the machinery and nanomaterial have been evaluated
- ✓ A market analysis has been carried out by SMEs at the beginning of the project so providing important information for the exploitation of the NANOSPARK machinery and utilization of CNTs produced.

2) WP2: Development of the CSA for SWCNT production

- ✓ A deep analysis of the plasma conditions and deposition phenomena within the reaction chamber was performed over the first year. Chemical-physical parameters identified during the ablation process and CNTs formation were identified for the development and optimisation of process parameters and thus validation of the technology.
- ✓ The configuration of the cathode-anode system was defined and its characterization was performed.

- ✓ The energy supply system was selected among commercial products on the basis of technical specification came out in WP1.
- ✓ Carbon nanotubes analysis methodology was defined by SINEUROP and MPI-FKF. A document on risks concerning nanomaterials exposure and handling was prepared as well. The work integrated information deriving from proceedings of International Conferences and cooperation with other research Institutes.

3) WP3: Mechanical design and prototyping

- ✓ The design of the reaction chamber and the definition of the flow of gas and material were carried out. Part of the research activities, particularly the study on deposition phenomena into the reaction chamber, required additional theoretical investigation and experimentation due to configuration of the chamber.
- ✓ Vacuum system was developed with a double pump system in order to reach the vacuum conditions for electron beam generation and pressure gradient between the first chamber (where the electronic beam is generated) and the second chamber (where plasma generation and CNTs growth occur) which is also called bulb. The system has been realised with two rotary pumps equipped with a filter avoiding the presence of oil in the reaction chamber. The pumps chosen were Leybold pump with a nominal flow rate of 40 m^3/h (vacuum pump) for the chamber and 4 m^3/h for the bulb (turbomolecular vacuum pump).
- ✓ A Plasma Window (PW) has been designed and developed to guarantee the differential pressure condition between the chamber and the bulb. The application of the PW to the system required some changes in the configuration of the reaction chamber and in the general layout of the machinery.
- ✓ The electronics and the remote control for the machinery has been designed. Actuators have been defined and ordered.
- ✓ The electronics and the remote control for the machinery partially designed at the end of the first year was modified and prototyped. Electromagnetic shielding and user's interface were realised as well. The hardware was mounted on the machinery whereas the remote control was installed on a separated PC connected to the machinery.

4) WP4: Tests and refining of the NANOSPARK equipment

- ✓ Testing of the machinery and refining of subsystems (cathode-anode, structure of the reaction chamber, gas injection, etc.) were the major activity carried out during the second year. A complete and accurate experimental phase has been performed to validate the technology. Tests aimed at validating the capability of the machinery to produce CNTs and particularly SWCNTs with a lower energy consumption of laser ablation technique by maintaining the same quality of the final product.
- ✓ Tests demonstrated the capability of the CSA technique to produce SWCNTs with good quality.
- ✓ A great effort was dedicated in preparation of the target material to be used for ablation process. The type and concentration of catalysts into the graphite pellets so as the preparation procedure were deeply investigated.

5) WP5: Field testing on solar energy systems

- ✓ The development of solar energy systems required preliminarily the definition of the formulation of CNTs for deposition processes. Procedures for depositions were defined and tests performed.
- ✓ Prototype of solar energy systems were developed on lab-scale using purified CNTs produced by arc-discharge technique in YAGTZE facility. Purification of the material produced led also to the definition of a methodology for characterization and purification. This work was necessary in order to guarantee the reproducibility of experimental results when test were performed in different laboratories.
- ✓ Development of solar energy systems followed two parallel routes. IBE and KONARKA worked on their systems independently for the development of their devices. Tests were performed to determine the CNTs properties when applied to substrates or merged to polymeric matrices. Secondary tests were indeed devoted to evaluate the performances of the devices in comparison with traditional systems.
- ✓ A first study was performed to evaluate all changes necessary to adapt the pilot lines to production of CNTs based solar cells.

6) WP6: Dissemination and exploitation

- ✓ WP6 was dedicated to the marketing and dissemination actions necessary to transfer the research performed into a marketable result for companies and to enhance the technology state-of –the-art. The first step was the implementation of a website to support information sharing/exchanging. The website is on-line at the following address: http://www.nanospark-project-eu
- ✓ Partners participated in several Conferences and International Workshop on CNTs and nano-structured material in general. Results achieved were submitted to international journals. Three scientific papers have been published:
  - **Plasma Window Characterization**, Ya. E. Krasik et al., published on *Journal of Applied Physics*;
  - **Characterization of a Channel Spark Discharge and generated electron beam**, Ya. E. Krasik et al., published on *Journal of Applied Physics;*
  - **Plasma Window Characterization,** Ya. E. Krasik et al., published on *Plasma Devices and Operations*
- ✓ The NANOSPARK technology has been analysed from a technical and economical point of view. Industrial interests and sectors of SMEs have been taken into account in order to provide a real and complete evaluation. A business plan concerning the new equipment for SWCNT production and nanotubes applications mainly in the field of solar cells has been prepared.
- ✓ Patent feasibility analysis was performed. A patent on process conditions and technological solutions for CNTs production is ongoing.

1.4 Final results

The main results achieved by the NANOSPARK project are:

1.4.1 Development of the CSA technique for CNTs production

The possibility to produce carbon nanotubes ablating graphite by means an electronic beam is strictly related to the operating conditions. The research on physical-chemical phenomena occurring during plasma discharge and nanotubes formation were carried out taking into account:

1. Cathode-anode configuration;
2. Reaction chamber configuration and operating conditions;
3. Vacuum system and Plasma Window
4. Carrier gas and catalysts;

1) Cathode-anode configuration:

Configuration of the cathode-anode system was investigated deeply to understand the effects in the electronics beam generation. An experimental study was performed under different operating conditions.
The cathode was realised with a **graphite-catalyser mixture** requiring a lower voltage discharge (18kV) for ablation and condensation of vaporised graphite to nanotubes. The energy for the sparks is supplied by a **large capacitors unit**, continuously charged by high voltage power supply. **Discharge process is triggered by the spark gap**.
The plasma is generated by the discharge into the quartz tube under vacuum conditions:

- Voltage: **6 - 18 kV**
- Current: **~10 mA**
- Capacitors: **60 nF – 200 μF**

The hollow cathode, 2 mm (inner diameter), is positioned in the head of the quartz tube. Through this hole, the enhanced plasma runs until the target. At the bottom of the quartz tube, an electrode lets enter the gas mixture (electrons beam and ablated carbon) controlled by a Mass Flow Controller (MFC).

The cathode-anode configuration and electrons beam source had to guarantee flexibility of the operating conditions for voltage discharge. The three main parameter were:

- repeatability: **0,1 - 10 Hz**
- amplitude of the discharge current: **up to 100 ns**
- energy: **2 ÷ 10 J**

These operating parameters affected ionisation (plasma formation) of the carrier gas and ablation efficiency (sizes of clusters).

The Channel Spark device (CSD) implemented for testing operated at the discharge voltage of $U \leq 24$ kV and discharge current amplitude $I_d \leq 3.5$ kA. Parameters of the discharge and electron beam were studied by the use of different electrical, optical and spectroscopic diagnostics while changing the amplitude of the discharge voltage, background Ar gas pressure and the CSD geometry. It was shown that the electrons with energy of ~eU appeared prior to the main CSD discharge and that the current amplitude of these high-energy electrons did not exceed $10^{-4}I_d$. Nevertheless, these high-energy electrons were responsible for the initiation of the main CSD

discharge inside the dielectric tube connected hollow cathode with grounded anode electrode. The generation of electron beam with current amplitude up to 3 kA occurred during a fast fall in the discharge voltage. It was shown that electrons with energy 18 keV ≥ Ee ≥ 1.4 keV compose ~ 5% of total amount of electrons with energy of > 100 eV and only 0.5% of electrons had energy 18 keV ≥ Ee ≥ 15 keV. High-current discharge inside the dielectric tube wass accompanied by the formation of the plasma consisting of protons, ArII, ArIII, CII–IV, OII-IV ions. The plasma electron density and temperature were found to be in the range of $10^{15} \div 10^{16}$ cm^{-3} and 10 ÷ 15 eV, respectively. This plasma was not uniform along the insulator tube as well as the electron beam experienced fast growing "hose" instability while travelling outside the tube.

The activity performed has led to a paper submitted to *Journal of Applied Physics* published in 2006.

2) Reaction chamber configuration and operating conditions

- **Plasma conditions:**

The **plasma temperature** for graphite ablation is around **1050 ÷ 1100 °C** while the **target temperature** is approximately **800 °C**.

The vacuum system was initially designed to reduce the residual pressure below 1 Pa. To produce qualitatively good nanotubes it is indeed necessary to reach very low pressure so to avoid material oxidation due to air. Experimental study demonstrated that the plasma density was not sufficient to lead to CNTs formation. Thus higher pressure in the growth chamber were evaluated. The change in pressure conditions required to re-think part of the process and mainly the reaction chamber and composition of the carrier gas.
The configuration of the reaction-chamber and the use of a modified carrier gas allowed to work with higher pressure for plasma generation. The working pressure was about **200 mbar** within the quartz tube.

- **Sintering chamber configuration**

The high temperature implies to adopt a quartz tube to bear the operative conditions required by the ablation process. Other suitable materials (ceramic coated steel alloys, stainless steel, etc.) were investigated without success.
The body of the tube is embedded into a **cylindrical furnace** clamped with perforated steel plates. These plates have been included because they provide a radiation shielding. Between the tube and the heater, a chromel-alumel thermocouple was placed and connected to a digital thermometer. Heater power is controlled by a variable voltage transformer.
This new configuration allows to keep the external temperature of the machinery at room temperature because the high temperature is localised in a extremely restricted region of the reaction chamber.
At the outlet of the system a **water cooled condenser** for collection of the material produced by the ablation/gas condensation processes.

Within the reaction chamber the graphite **target is positioned on a rotating disc** in order to use it completely and so reduce material wastes. This target can rotate slowly with a **rotational speed** ranging from **1 to 60 g/min**. To measure the rotation speed it will be necessary to adopt a transducer on the shaft.

The system is entirely protected to avoid direct touch with the operator (electrical discharge) and a fine metal grid is provided. An **UV filter** for protection from the electro-magnetic radiation emitted during the spark processes was also installed on the machinery.

Figure 2: UV shielding for quartz reaction chamber

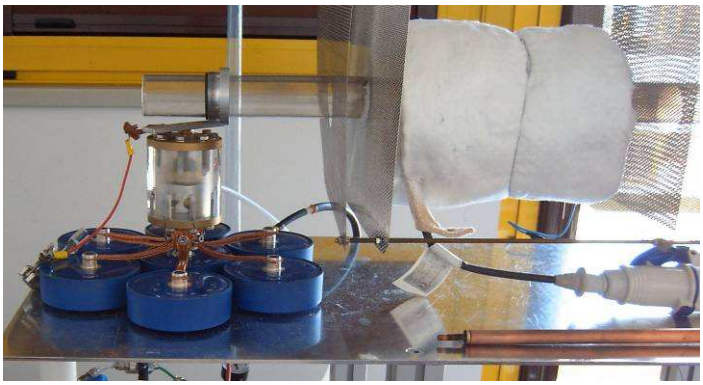

Figure 2: Capacitors unit connected to the quartz reaction chamber

3) Vacuum system and Plasma Window

- **Vacuum system**

The vacuum system was initially designed to reduce the residual pressure below 1 Pa. To produce qualitatively good nanotubes it is indeed necessary to reach very low pressure so to avoid material oxidation due to air. The first system has been studied and realised with two rotary pumps equipped with a filter avoiding the presence of oil in the chamber. The pumps chosen were **Leybold pump** with a nominal flow rate of **40 m^3/h** for the chamber (vacuum pump) and **4 m^3/h** for the bulb (turbomolecular pump).

During tests to simulate ablation conditions the Hollow Cathode volume was pumped, keeping it at a pressure in the range of 1 – 10 Pa, while the pressure in the experimental chamber was maintained as high as possible for the given pumping rate of the Hollow Cathode volume.

Tests demonstrated that the increase in the pressure inside the experimental chamber above 100 mTorr leads to dramatic decrease in the electron beam amplitude.

Activity performed on vacuum system and definition of the operating pressure demonstrated that:

a) the commonly used pumping of only the experimental chamber dictates a pressure almost 10 times larger in the volume of the Hollow Cathode;

b) the use of the differential pumping allows one to make inverse pressure gradient, namely to keep in the volume of the Hollow cathode a 10 times lower pressure than in the experimental chamber;

c) the use of differential pumping required to solve a problem of electrical decoupling of the Hollow Cathode from the pump;

d) the increase of the pressure in the experimental chamber above 0,1 Torr led to dramatic decrease in the energy of the electron beam at the output end of the glass tube.

Data gathered and estimation showed that a Plasma Window could provide 3 orders pressure gradients in order to keep a high (around 10^{-1} Torr) pressure inside the glass tube and around 200 Torr inside the experimental chamber.
According to these results two different developments were carried out:

1. Implementation of a Plasma Window able to generate the proper differential pressure gradient between the electron bean chamber and the growth chamber;
2. Re-design of the reaction chamber configuration with different technical solution for electrodes and for composition of the carrier gas. This new reaction chamber can be integrated with the Plasma Window to improve its efficiency.

- **Plasma Window**

A Plasma Window (PW) is a system able to maintain high gas pressure gradients without introducing mechanical interfaces. The operation of the PW is based on significantly higher temperature and increased viscosity of plasmas as compared with the temperature and viscosity of gases composed of neutral particles. The higher plasma temperature allows to decrease the plasma density while keeping the same value of pressure.
The development of a PW for the NANOSPARK machinery required a complete characterization to evaluate its performances and integration in the CSA based process. Experiments carried out by TECHNION with 2 mm inner diameter and 25 mm length PW showed a ~400 times decrease in the pressure at the output of the arc with a relatively minimal pumping system.

It was shown that the PW arc discharge is characterized by a low-ionized gas with a non-uniform radial distribution of the density, conductivity, temperature, and ionization degree. The maximum in the temperature and conductivity occurred at the axis of the PW. Due to low temperature the conductivity of the gas in the vicinity of the cooling plates is almost zero and therefore a major part of the arc current is transferred in the central region of the discharge channel. It was also shown that the average temperature of the gas was ~10000 K and the ionization degree was ≤ 35%. Calculations of the plasma parameters and their spatial distribution using a simple wall-stabilized arc model showed a satisfactory agreement with the experimentally obtained data. Even a significant decrease in the gas flow through the plasma window occurred due to an increase in plasma viscosity.

Detailed data have been presented in a paper (Ya. E. Krasik and S. Gleizer, *Pressure and electron energy measurements in a channel spark discharge*, Plasma Devices and Operations – accepted for publication in 2007).

Transmission of radiation and charged particle beam from an accelerating gap or drift space that are in high-vacuum into a region with a considerable larger pressure requires introduction of either some interface made of a thin foil or powerful differential pumping. These methods of separation are not always appropriate because of possible particle beam and radiation attenuation and particle scattering.

The experimental setup (see Figure 4) consisted of:

- an anode having a 3 mm diameter hole at the axis
- three 5 mm thick cooling floating plates with a 1 mm thick dielectric film between them and the cathode housing with three cathodes, in the form of sharp cones distributed azimuthally symmetric.

- The cathode tips were inserted up to a radius of ~3 mm from the system axis and at a distance of ~ 8 mm with respect to the first cooling plate.
- the experimental chamber has optical accesses
- a vent for Argon (Ar) gas input and flanges for pressure gauges.
- The PW was connected to the chamber via a ceramic flange in order to decrease the intense heating of the chamber walls by the radiation flux emitted by the arc.
- The low pressure end of the PW is connected to a buffer chamber using a 3 mm diameter and 110 mm long ceramic tube.
- Turbo-molecular pump (Pfeiffer, V70), via a vacuum tube that is 50 cm long and 2.5 cm in diameter (effective pumping rate of ~20 l/s) has been used for maintaining high gas pressure gradients without introducing mechanical interfaces.
- The experimental chamber was filled with Ar gas up to a pressure in the range of 30 - 100 Torr. Pressure in the experimental chamber was regulated by the vent and measured by an Edwards capsule dial gauge CG16K.

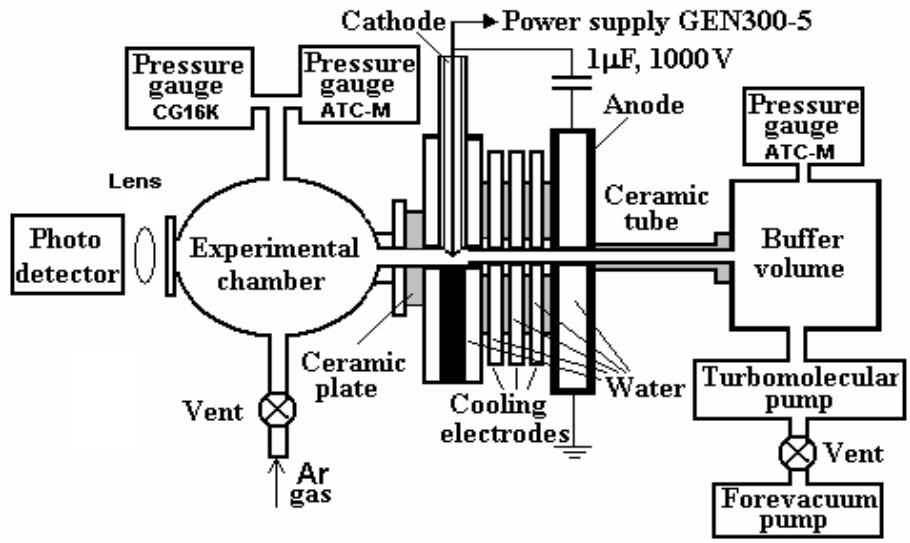

Figure 3: Experimental set-up of the PW.

It is important to note that in all other plasma windows and wall-stabilized cascade arc discharges cathode-tip to first cooling plate distance is about 1 mm or less. Each cooling plate had a hole with a diameter of 2 mm. The anode was placed at a distance of ~3 mm from the last cooling plate. The total length of the PW was ~25 mm. All the parts of the PW were cooled by a water flow delivered through a specially made distribution system.

The cooling plates were manufactured with a system of internal holes for the water flow which significantly simplified their design avoiding brazing or welding which was used in all previous PW designs.

Each PW cathode was supplied by three Gen 1500 power supplies (Lambda America Inc.) connected in parallel, with one power supply as a "master" and the two others as "slaves". Each generator supplied **maximum output voltage of 300 V and current of 5 A**. In order to reduce the electromagnetic noise which appeared during the PW ignition a LC-filter was used at the

output of these power supplies. Resistors of 0.5 Ω made of a 1.5 mm in diameter micron wire were connected in series with each cathode for arc current stabilization.

Experiments showed that when the pressure in the buffer chamber (P2) reached a steady state value of **4×10^{-3} Torr**, the pressure (P1) inside the experimental chamber was equal **2×10^{-2} Torr**, i.e., a pressure ratio of five was obtained. The filling of the experimental chamber with Ar gas up to a pressure of 20 Torr led to an increase in the steady state pressure in the buffer chamber up to 2 Torr because of a decrease in the pumping rate of the turbo-molecular pump. The latter decreases its pumping rate by a factor of almost five because of a decrease in the rotation speed as the gas load increases. Thus, the pumping system allowed to obtain the ratio **P1/P2 = 10**. The dependence of the steady state pressure P2 versus P1 is shown in Figure 5.

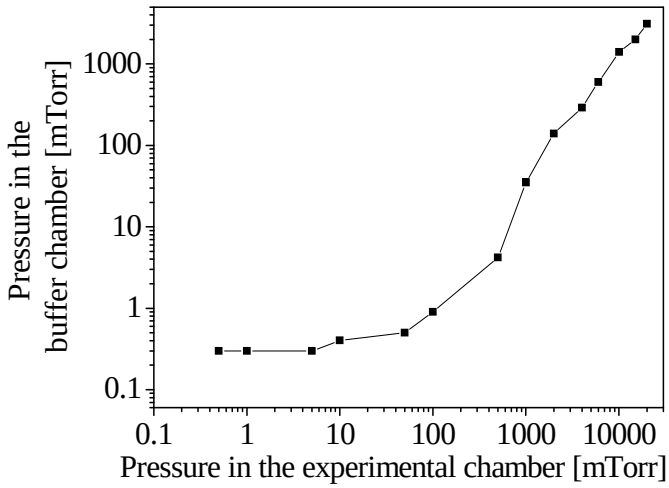

Figure 4: Dependence of buffer chamber pressure on pressure in the experimental chamber without plasma window operation

The ignition of the PW with 2 mm aperture cooling plates at p1 ≈ 30 Torr and P2 ≈ 0.8 Torr and with 300 V initial discharge voltage showed a gradual decrease in the value of P2 down to P2 ≈ 0.08 Torr in the steady state mode. The pressure ratio was therefore **P1/P2 ≈ 375**. The same experiments with 3 mm diameter cooling plates showed that the maximum achieved pressure ratio is **P1/ P2 ≈ 200**.

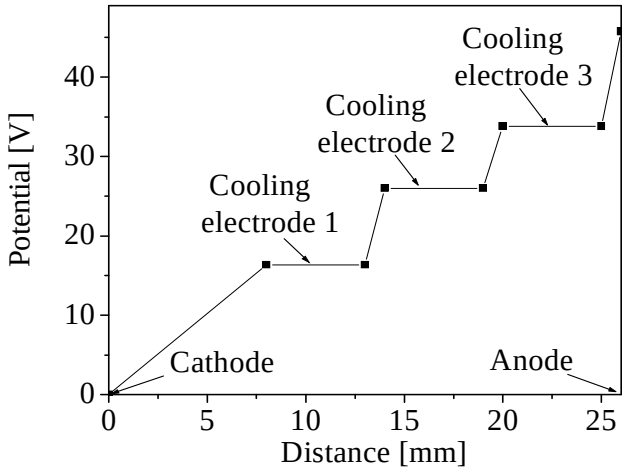

Figure 5: Potential distribution along the PW length.

The potential distribution along the PW floating cooling plates is shown in Figure 6 above. It is possible to see that the potential difference between the cathode and the first cooling plate is $V_{C1} \approx 17$ V, between the first and the second cooling plates $V_{12} \approx 9$ V, between the second and the third cooling plates $V_{23} \approx 8$ V and between the third cooling plate and the anode the potential difference is $V_{3A} \approx 11$ V. The average electrical fields in the discharge channel, i.e., between the cooling plates can be estimated as $E_{12} \approx 15$ V/cm and $E_{23} \approx 13.5$ V/cm.

1.4.2 NANOSPARK system for CNTs production

The specific components constituting the NANOSPARK are:

1. Reaction chamber
2. Vacuum system and Plasma Window
3. Electronics and control system

Following a schematic diagram and pictures of the final apparatus are shown.

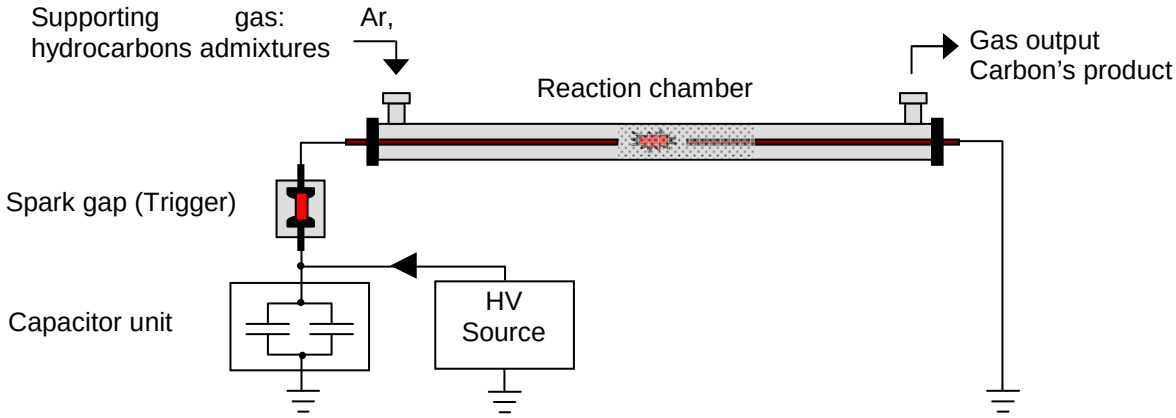

Figure 6: Schematic diagram of new channel spark apparatus.

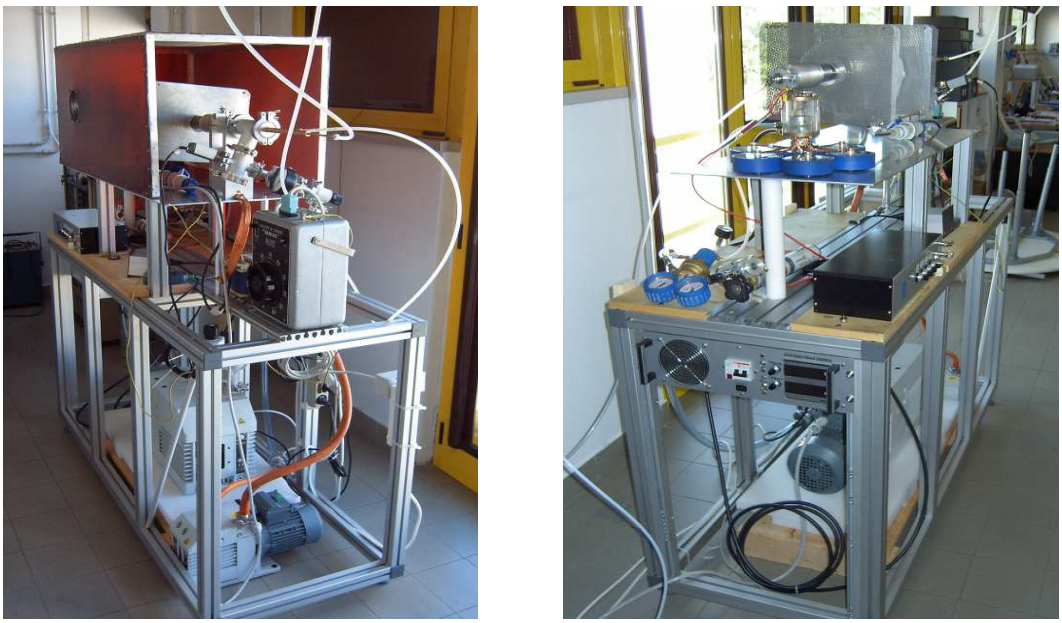

Figure 7: Pictures of new channel spark apparatus with (left) and without (right) electro-magnetic/ high-voltage protection (red screen).

The system is entirely protected to avoid direct touch with the operator (electrical discharge) and a fine metal grid is provided. An UV filter for protection from the electro-magnetic radiation emitted during the spark processes was also installed on the machinery.

1) NANOSPARK prototype

- **Technical specifications and design**

The reaction chamber represent the core f the NANOSPARK system. It was realised with a narrow quartz capillary (inner diameter less than 1.5 mm).

The target and electron gun were unified with two electrodes system longitudinally placed into the quartz tube. A standard electron gun was used for electron beam generation. This was possible because the relatively thick quartz tube could help to focus and drive the electron beam on the target properly. Typical **length and diameter of the tube were 1 – 2 cm and 5 – 10 mm** respectively.

Since the distance between the electrodes was decreased, also the **discharge voltage** during normal operating conditions **was decreased from 20 to 6 kV**. Conversely, the capacity of **capacitors unit** was **increased more than 100 times** to guarantee a high energy spark. The high voltage power supply was modified accordingly to produce the required energy to charge the capacitors unit.
A trigger controls the voltage level and automatically generated the electron beam by discharging the capacitors.

The high energy spark produce and evaporation of the metal catalyst from electrodes. In proper thermodynamic conditions, the metal vapour can form nanoparticles which react with carbon enriched supporting gas. The carbon source in the supporting gas thus represents a seed for CNTs formation and actively contribute to CNTs growth.

Since the melting process of graphite, present in electrodes, required a lot of energy due to its high melting point, volatile hydrocarbons were added to the supporting gas as an additional carbon source due to its low decomposition temperature.

In the following table the characteristics and the main operating parameters of the system have been reported.

Parameter:	Value:
Temperature range:	20 – 1100 °C
Pressure range:	100 – 900 mbar
Charging voltage:	< 6 kV
Charging current:	< 500 mA
Capacitors unit:	< 200 μF
Sparks frequency:	< 10 Hz
Supporting gas:	Argon, Helium
Carbonaceous gas:	volatile hydrocarbons
Gas flow:	< 1500 sccm
Catalyst:	Ni, Co, Y, Fe

Table 1: Characteristics and parameters of the NANOSPARK machinery.

A trigger controls the voltage level and automatically generated the electron beam by discharging the capacitors.

Effects and dependences of process parameters were investigated. Following the classes of tests have been reported:

- ***Temperature***: series of experiments were performed in temperature range from room temperatures up to 950 °C. For some supporting gas containing the gaseous source of carbon, the upper temperature was limited to approximately 600 °C in order to avoid its thermal decomposition. The temperature of gas didn't strongly effected the CNTs fromation.
- ***Pressure***: series of experiments were performed at different pressures, starting from 200 until to 600 mbar, with step of 100 mbar. It was noticed that above 200 mbar which represented the minimum pressure for CNTs formation, no significant changes in results could be observed.
- ***Supporting gas***: two noble gases were tested, namely, argon and helium gas. Since no differences were observed, the argon gas was mostly used due to its low price. In addition to solid form of carbon contained in electrodes (graphite), two gaseous hydrocarbons were introduced into the supporting gas with several volume ratios (10, 20 and 30 by volume.
- ***Catalyst content***: the working electrodes were prepared by compressing a mixture of graphite and metal catalyst powders. The influence metallic catalysts and their ratio in the mixture on a final product was investigated. Two standard metal catalysts have been chosen, namely, a NiCo catalyst with weight ratio of 1:1 and a NiY catalyst with weight ratio of 4:1 as standard ratios recommended by literature.
- ***Electrodes distance***: The experiments were carried out with different distances between the electrodes ranging from 1 to 60 mm.
- ***Diameter of the channel tube***: the main change in the experimental apparatus concerned the diameter of the tube. The effect of diameter and of the ratio diameter to length was investigated. Capillary of the tube was studied: increasing diameter and decreasing the length of the channel quartz tube.

The quantity of nanotubes produced was estimated by ratio of the graphite to defect modes obtained from Raman spectra. All samples produced manifested certain quantity of amorphous carbon which was clearly indicated by the presence of wide and joined G and D modes in Raman spectra, mainly due to sp2 and sp3 bonds.

Production of SWCNTs was optimised by varying some parameters: capacitors unit, distance between electrodes and the diameter of the tube.

From the graph below (Figure 4) is possible to get important information about CNTs composition and temperature effects due to burning procedure. The weight ratio of SWCNTs to others carbon forms is around 50 wt% (grey and light grey bands). After thermal treatment a large amount of metal content more than 80 wt% was removed. This measure could provide a reference value regarding the purity of the product obtained with the NANOSPARK technology.

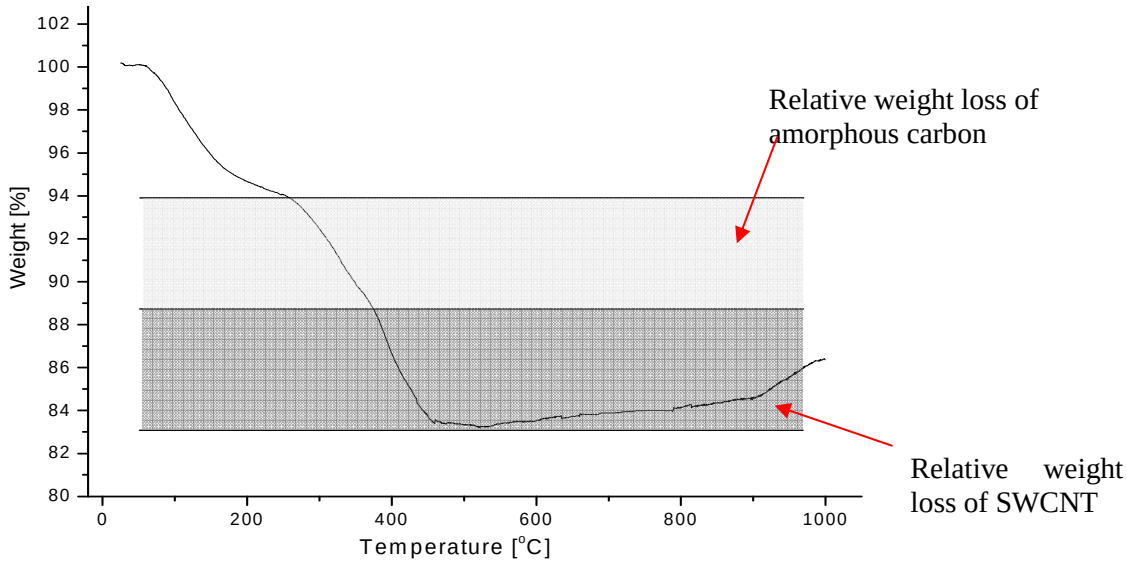

Figure 8: Thermo-gravimetric analysis of SWCNTs produced by NANOSPARK technology.

- **Carrier gas and catalysts**

The carrier gas, **Argon with an admixture of hydrocarbons**, is injected into the chamber and maintained at the operating conditions required by a precise mass flow controller, whereas the gas pressure is controlled by acting on rotary pump and precise valve. The choice of argon as carrier gas guaranteed a good ionisation while the volatile carbon materials with low decomposition temperature represented "nuclei" for carbonaceous material condensation into CNTs by interacting with catalysts.

CNTs are produced by ablation of the target hit by the electronic gun. The high energy of the beam produce an instant vaporization of the target and the formation of a plasma. Different catalysts were incorporated into the graphitic pellets. These material was then ablated by using CSA technology for NANOSPARK prototype validation by comparison with CNTs produced via arc-discharge technique.
The working electrodes were prepared by compressing a mixture of graphite and metal catalyst powders. The influence metallic catalysts and their ratio in the mixture on a final product was investigated. Two standard metal catalysts have been chosen:

- **NiCo** catalyst with weight ratio of **1:1**;
- **NiY** catalyst with weight ratio of **4:1**.

The experiments were then performed with the following weight percentages of catalyst inside the compress pellet (electrode): **2, 3, 4, 20, 30 and 100 wt%** (by weight). Furthermore, two experiments were carried out by using of **10 and 80 wt% of Ferrocene** as a catalyst. This last catalyst required to use Argon atmosphere adding acetylene and NH_3.

- **Performances**

Performances achieved by the NANOSPARK system are:

a) Production rate: **~ 50 mg/h** (raw material)

b) Purity of produced raw material: **80 wt% of metal catalyst**, **10 wt% of SWCNTs**

and **10 wt% of other carbon forms** (mostly amorphous) according to thermo-gravimetric analysis (see Figures 5 and 6)

c) Diameter distribution of CNTs: **1.3 – 2.5 nm** (estimated by Raman analysis and TEM images)

d) Energy consumption: **~ 3 kWh**

e) Possibility to modify process conditions to end-users need

The following Figures show the Raman spectra of raw material produced through target ablation. The curves provided by this analysis clearly demonstrate the presence of SWCNTs by looking at the high graphite's mode (G), very small defect's mode (D) and presence of radial breathing modes (RBM) typical of SWCNT spectrum. Both two samples were prepared in argon atmosphere with admixture of 10 vol% of volatile hydrocarbons. The gas's flow rate and pressure were of 500 sccm and 300 mbar, respectively. In this case experiments were run at room temperatures without use of furnace. The only difference between the two experiments was the catalyst composition. While the first sample (Figure 5) was prepared by using standard NiCo catalyst, the second one (Figure 6) was prepared by introducing stainless steel powder in standard catalyst.

TEM pictures (Figure 7) refer to first sample produced with standard NiCo catalyst and confirm Raman spectra of samples. Dark area are due to pile of carbon and metal compounds which are not transparent to electrons but the fine shape of SWCNTs is clearly identifiable. From this pictures is also possible to estimate the mean diameter of SWCNTs which was estimated to be around 2 nm.

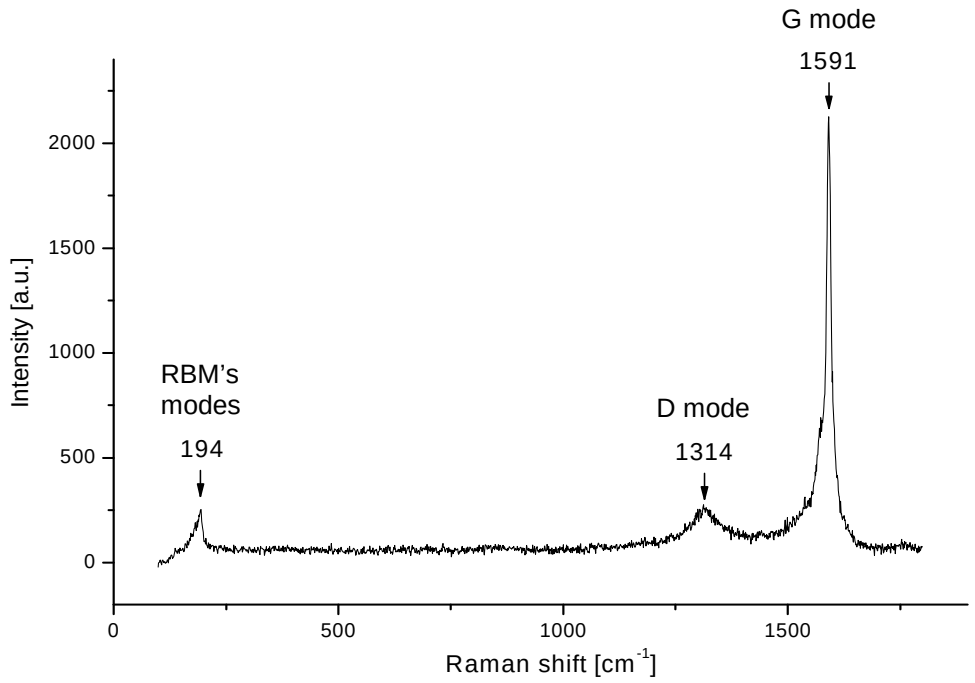

Figure 9: Raman spectrum of SWCNTs prepared by the channel spark method with nickel – cobalt mixture as a catalyst (ratio 1:1).

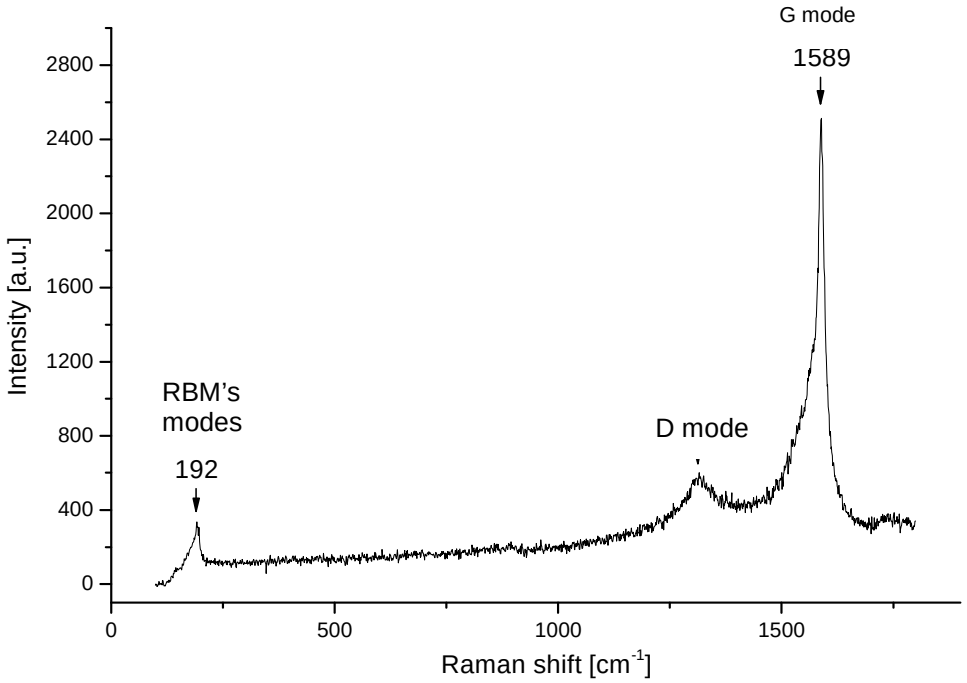

Figure 10: Raman spectrum of SWCNTs prepared by the channel spark method with Fe as a catalyst.

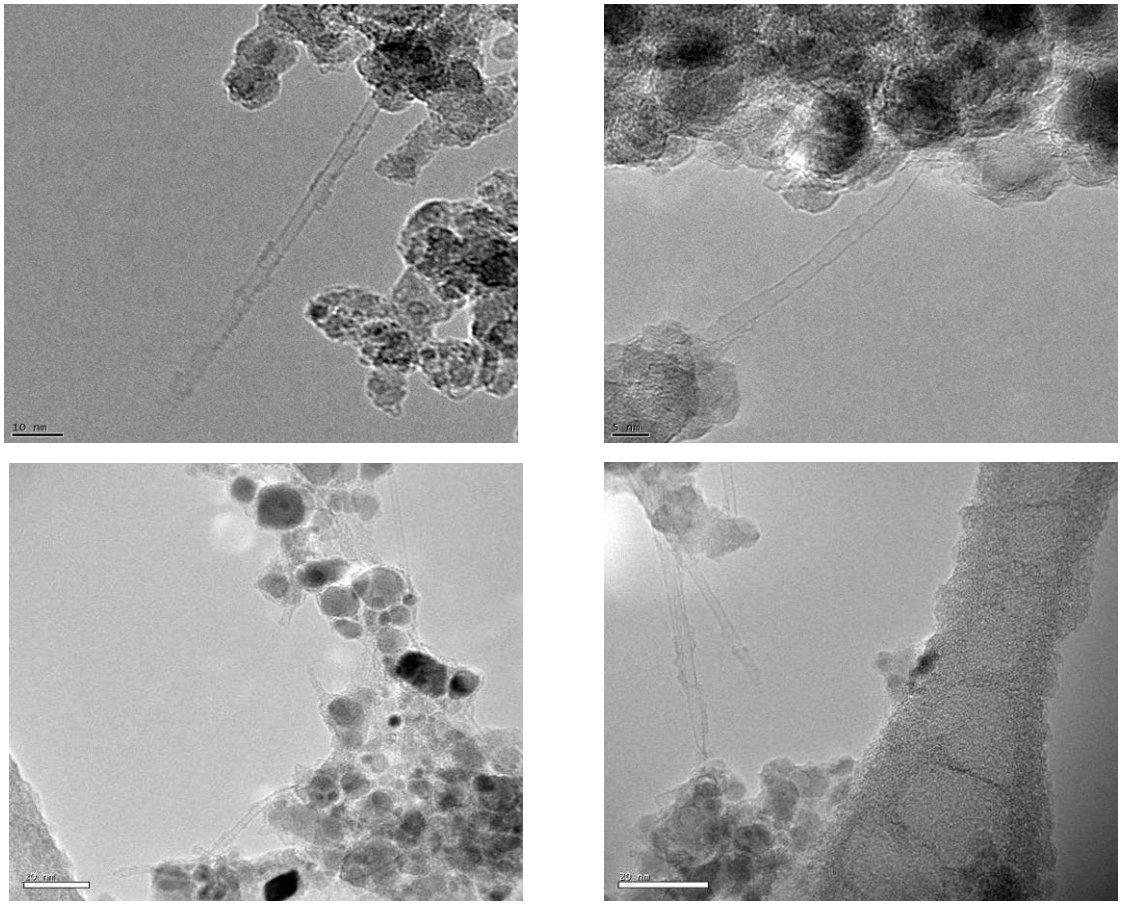

Figure 11: TEM images of SWCNTs prepared through NANOSPARK technology with nickel – cobalt mixture as catalyst (ratio 1:1).

2) Electronics and control system

The electronics has been realised on the basis of the technical specifications

- **Electronics**

The electronics (Control Board) has been realised with a **MCU board with a watch-dog built in**, two I2C boards and an auxiliary board AC Main.

A specific firmware for MCU has been programmed to set and manage all processing parameters through the **serial interface RS232 optoisolated**. It performs different actions: measurements, monitoring the status and tune parameters. All connection have been isolated to avoid electromagnetic noises transmission and signal failures. Details about shielding have been provided in the following section whereas in Figure 8 wiring of electronics have been presented.

Below a block diagram of the electronics is reported. The MCU is the core of the system and it manages each components and auxiliary board.

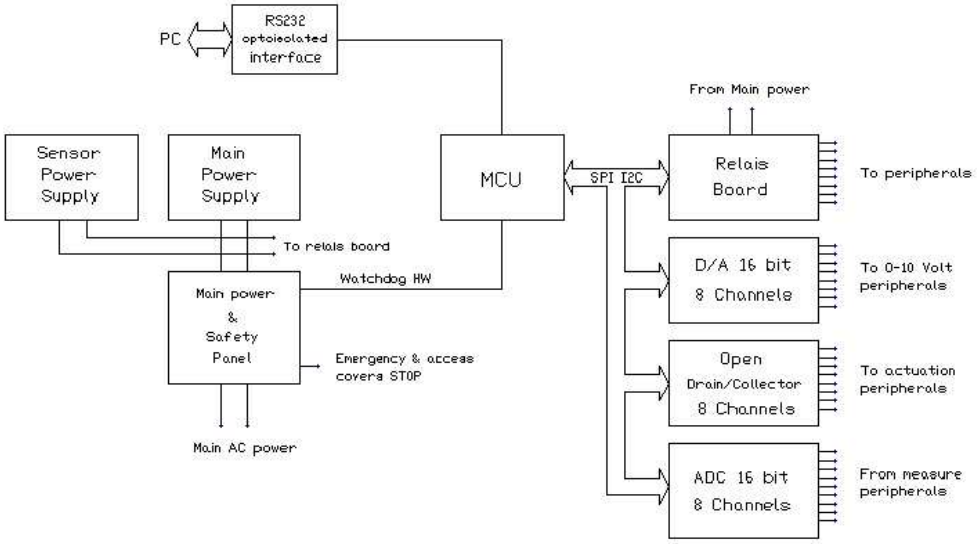

Figure 12: Block diagram of the NANOSPARK electronics.

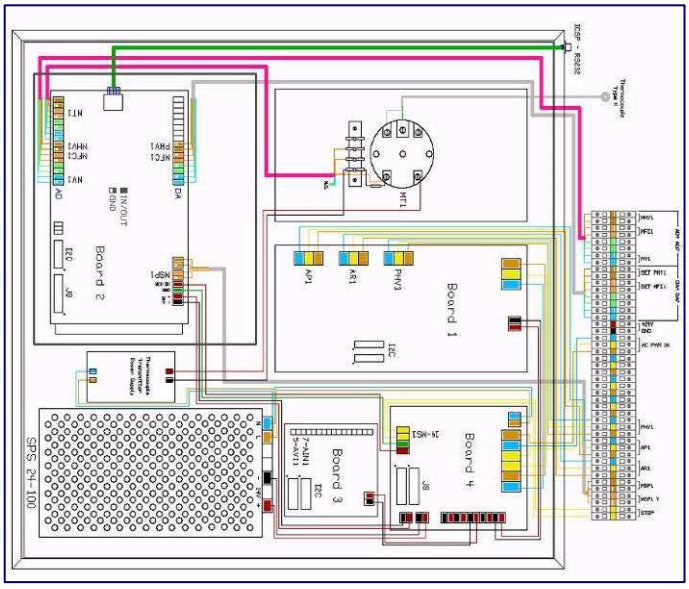

Figure 13: Wiring of electronics.

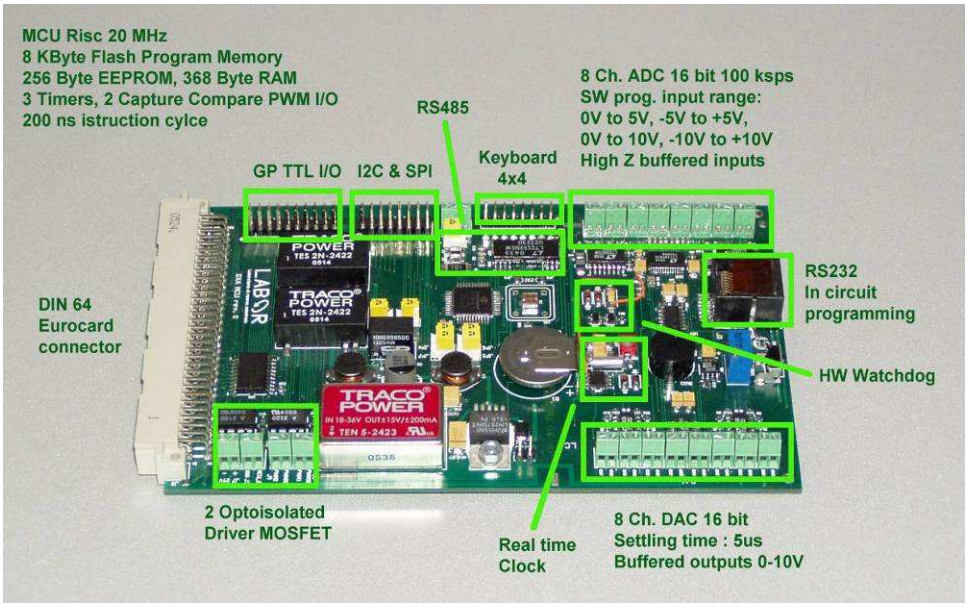

Figure 14: MCU board (BOARD 2)

- **Remote control**

The NANOSPARK system has been equipped with a remote control for machinery control acting on the electronics. The remote control is performed by a user-friendly software implemented by using Visual Basic.

The control system has been installed on a **Travla C134** (Mini-ITX case for EPIA M) with **1GHz, 512 Mb RAM and LVDS** (Low Voltage Differential Signaling) **interface** for flat panel displays, at signal rates as high as 655 Mbps. The PC has been also equipped with a 40 Gb Hard Drive and a DVD-K05 slim.

The SW performs the following actions:

a) set-up and tune-up process parameters while the system is ON.

b) Register a LOG file of the process parameters configuration

c) Monitor the status of the system

d) Measure process data

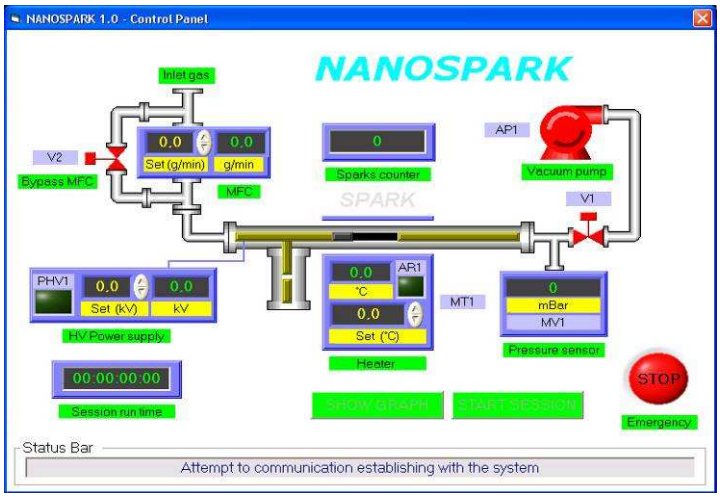

Figure 15: Control Panel – check of the system before the experimental run.

Figure above shows the main view the control panel.
When the system starts the SW communicates with the hardware (control board) to check out all the electronic devices before the experimental run. The status is reported on the *Status Bar* in the lower part of the window.
Then the check has been completed the system is put in *HALT* mode and it is ready to start the experimental runs. All parameters can be tuned up at this stage particularly the High Voltage set-point, the mass flow controller and the Heater.
Experimental session can be started by clicking on the *START SESSION* button. See Figure 11 below.

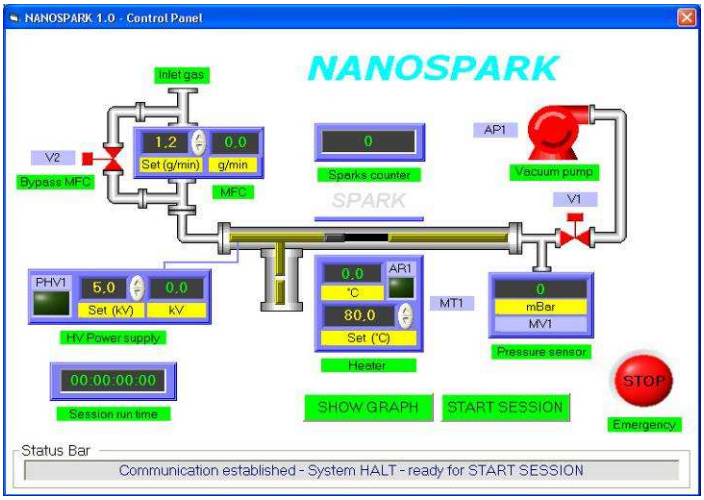

Figure 16: Control panel - session in progress.

When the machinery is working the firmware of the MCU board performs periodically a check on the process parameters and adjust process conditions according to mismatches between set-points and parameters values measured by sensors. At the end of the cycle the firmware generates a record containing all the information regarding electronic devices, sensors and parameters of the system. This file is also used by the SW to automatically update values on the control panel and save data in the *LOG* file. Each run produces a new and different log file. These logs file are stored in the PC hard disk and are available off-line. It is important that data can not be overwritten; each new status is recorded in a new log file so to maintain all the information of the process.

When the operator starts a session the system executes the following operations:

1. *Opening of the decoupling vacuum valve;*
2. *Ignition of the vacuum pump;*
3. *Ignition of the HV;*
4. *Voltage set-up;*
5. *Trigger capture;*
6. *HV measurements;*
7. *Pressure measurement;*
8. *Set point mass flow controller with feedback on pressure;*
9. *Mass flow measurement;*
10. *Temperature measurements;*
11. *Ignition of heater with feedback on temperature;*
12. *Safety check on panels lock*

- **Electromagnetic shielding**

The electronics has been protected into an **aluminium alloy box** for electromagnetic immunity (IP54) see Figure 12. Connections among control board and auxiliary boards have been realised with **optoisolated wires**. Also the remote control (PC) has been then connected by means of RS 232 connection optoisolated.
A double shielding for connections from the actuators and probes to Control Board was also adopted: cable shielding protection and external spiraflex stainless steel.
These technical solutions has guaranteed the proper shielding and avoided interferences due to the electromagnetic noises generated by the electrons pulses. Test were performed on the NANOSPARK prototype at CNR.
In the following figures is possible to notice the electronics open and closed. In figure 12 is evident the aluminium box containing the MCU board (lower part). Cables are also protected with **ferrites nuclei** which concentrate the magnetic field lines saving electric cables from noises transmission.

Figure 18: Internal view of the electronics - MCU board shielding and general layout.

Figure 18: Shielding of the electronics.

1.4.3 Characterization and purification of CNTs

- **Characterization**

A standard procedure was defined to characterize the bulk material, analyze the content of Single Walled Carbon Nanotubes purity and improve different methods of purification of carbon nanotubes such as dry-oxidation in air, to remove amorphous carbon and wet chemical treatment by acid to remove metallic nanoparticles.

This work was requested for:

a) preparation of different suspensions containing SWCNTs.
b) definition of experimental systems for dye solar sensitised cells and PV cells prepared with SWCNTs.

SINEUROP has optimised and applied an optical method to determine in a quantitative way the concentration of single-walled carbon nanotubes in the presence of other carbonaceous components (like amorphous carbon and graphitic particles) to samples from arc discharge and laser ablation synthesis. A methodology for carbon nanotubes analysis has been established in cooperation with the MPI-FKF.

The protocol requires different phases for samples preparation and measurement techniques:

- Homogenisation
- Measurement of electrical conductivity
- Preparation of pressed pellets
- Preparation of films of SWCNT composites
- Electrical measurements
- SEM characterisation
- X-rays powder diffraction
- Optical spectroscopy

The Quality Control protocol can be requested to SINEUROP.

Methods for processing nanotubes composites were investigated. Homogeneous films, about 1 mm thick and 14 cm in diameter, were prepared by a spray technique.

The following methods have been exploited for carbon nanotube analysis:

1) *Raman spectroscopy*: tested for suitability to detect small amounts of nanotubes in a qualitative way, tested for determination of defects in nanotubes
2) *X-Ray Powder diffraction*: developed so far that graphitic contaminations can be determined in a quantitative way. To this end a marker of Fullerene C60 powder is added in known amount to the sample.
3) *Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM)*: developed so far that they help in collecting evidence for the presence of nanotubes (not useful for quantitative determinations).
4) *Thermogravimetric Analysis*: Allows determination of metal particles from catalyst remains, in some cases nanotubes can be distinguished from graphite and from amorphous carbon, but very often the burning temperatures are not sufficiently separated.
5) *Elemental Analysis*: Induction-Coupled Plasma: allows precise determination of metal content.

These 5 methods have been developed, tested, and calibrated on single-walled carbon nanotubes from laser ablation and from carbon arc synthesis. Then they were applied to nanotubes produced by Channel Spark Ablation.

- **Purification of CNTs for deposition processes**

Purification route based on thermal and acid treatment was developed at MPI and consisted of a partial burning of the raw product followed by an acid treatment with HCl.

The burning method, consisting in **air oxidation**, was essentially a large-scale version of thermogravimetric analysis (TGA), plus a **final acid washing and filtration**. Following (Figure 19) TGA of a typical raw product is shown. The various components burn off at different temperatures

because of their different stabilities. In particular, the amorphous carbon burns off at a lower temperature than CNTs. Any graphite left can be filtered off at the end after acid has removed the catalyst. The final residue is metal catalyst which does not burn off.
The samples of SWCNTs were characterized by scanning electron microscopy and Raman spectroscopy. Optical absorption spectrum was also used to investigate the separation of SWCNTs according to their metallic and semi-conducting types.

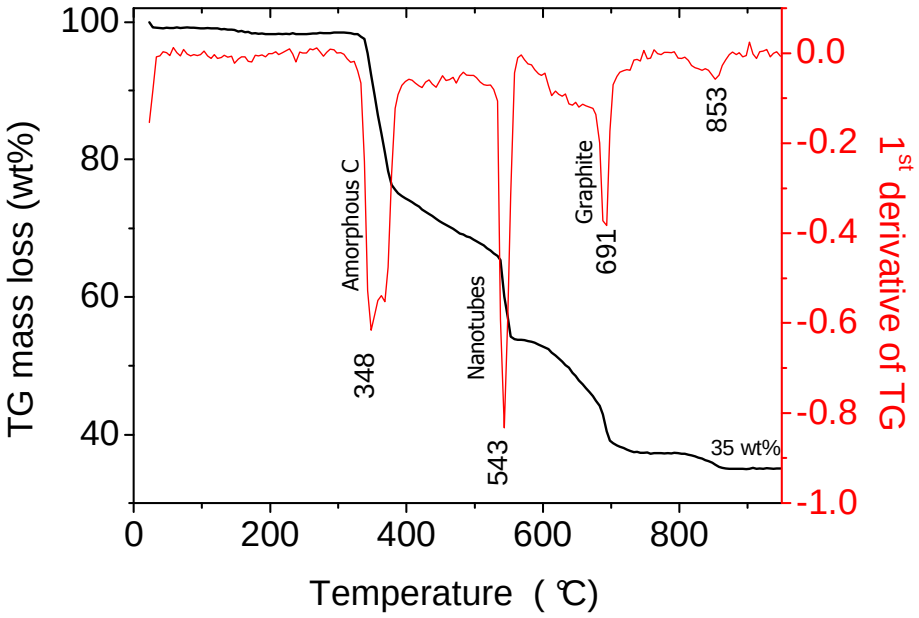

Figure 19: Thermogravimetric analysis (TGA) of a raw product.

The following electron micrographs are taken on bucky paper prepared from carbon arc soot after various steps of purification.

Quantitative evaluation of SWCNTs purity by solution phase NIR spectroscopy gave following results:

1. **raw material** contained approximately **30% SWCNT**s;
2. **after burning off** a part of amorphous carbon the amount of **SWCNTs increased up to 50%;**
3. **acid treatment** removed the metallic impurity whereas the **SWCNTs content remained constant**.

For large material throughput a modified purification procedure was applied for CNTs produced at MPI. Carbon nanotubes raw material were moved by a rotating transport spiral through a tubular oven as shown in the following Figures 23 and 24. Thus heating the raw material in air could remove most of the amorphous carbon by-product and enriched the **nanotubes concentration from 15 up to 50%**.

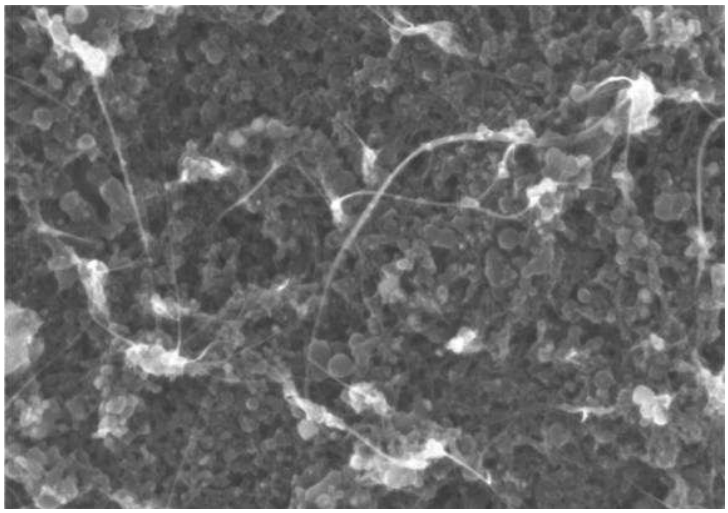

Figure 22: Raw material.

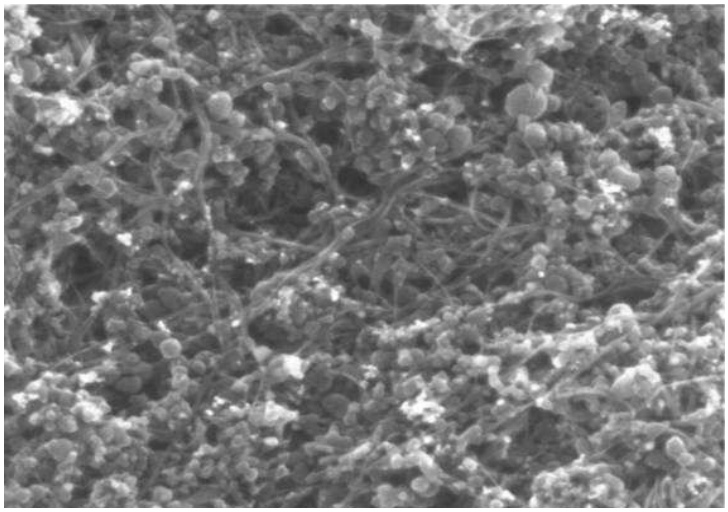

Figure 22: After dry oxidation (30 min at 370°C in air).

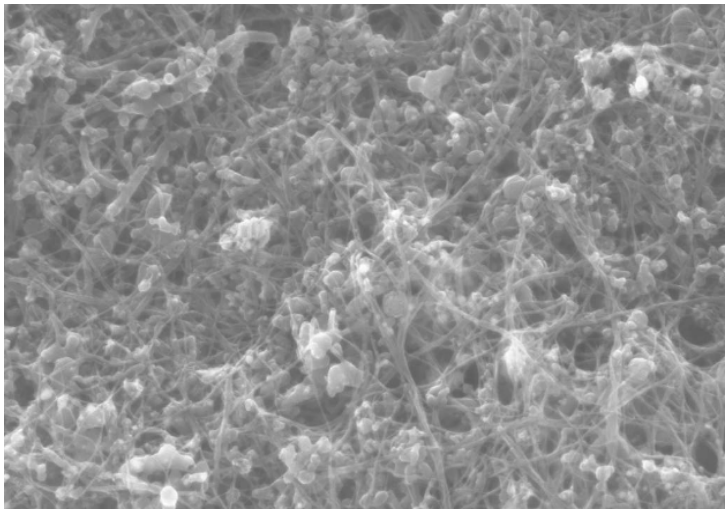

Figure 22: After dry oxidation and centrifugation.

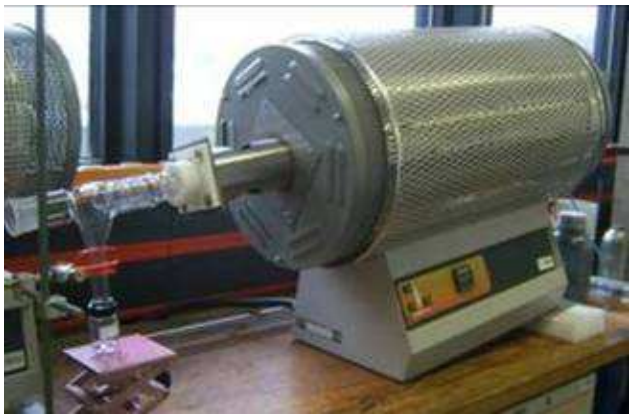

Figure 23: Tubular oven for purification

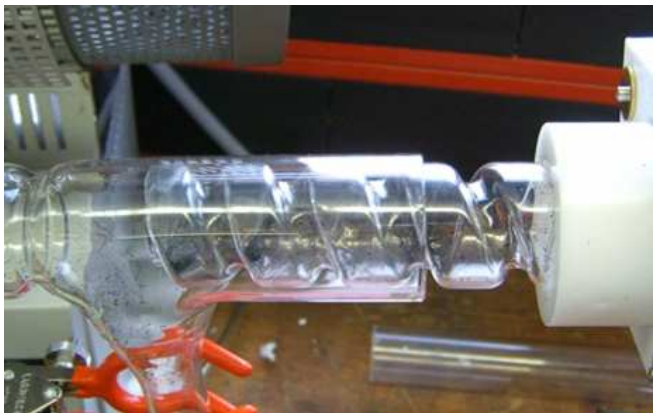

Figure 24: Rotating spiral

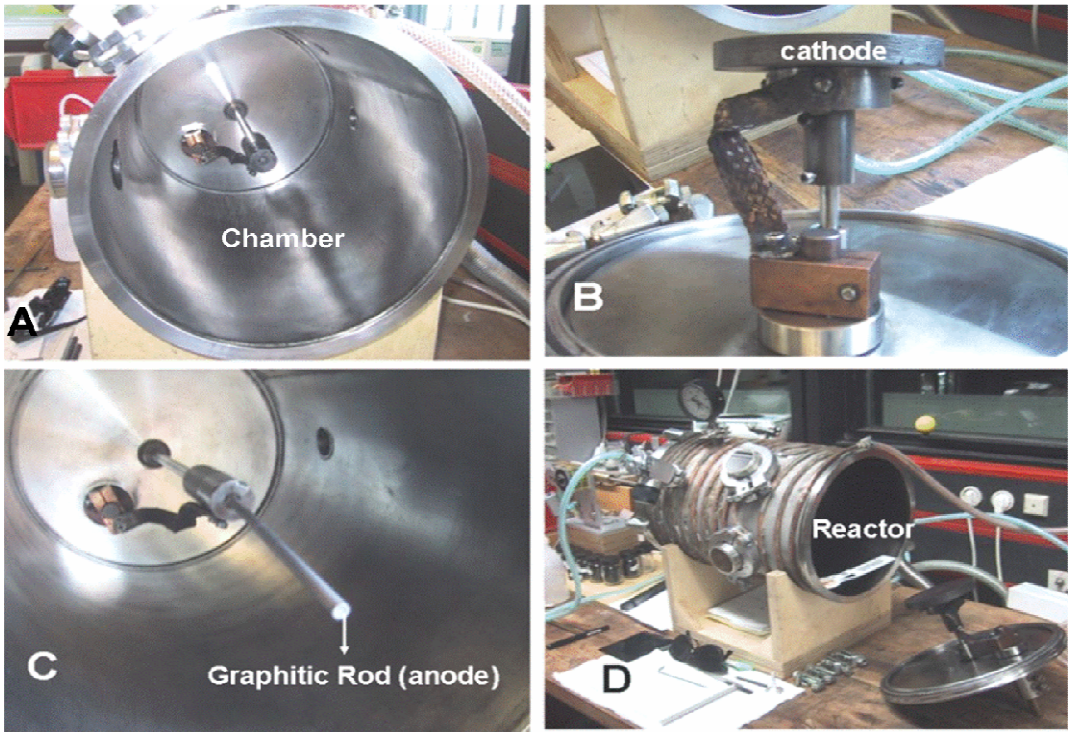

Figure 25: Kraetschmer generator for arc-discharge synthesis of SWCNT

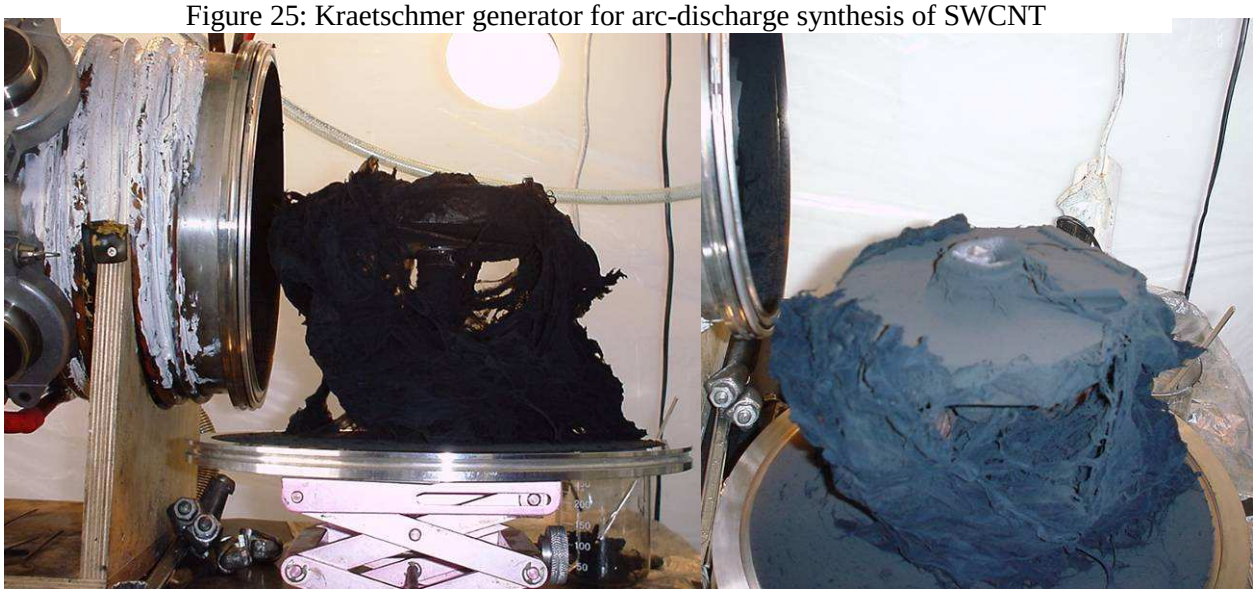

Figure 26: Nanotubes produced by arc-discharge at YANGTZE.

1.4.4 Solar energy systems

SWCNTs have been used for implementation of solar energy systems. The choice of carbon nanotubes as alternative material for the development of photovoltaic devices was mainly due to the outstanding properties of conductibility showed by this carbon product. In addition organic solar cells are potentially much cheaper and easier to make than their inorganic counterparts but their efficiencies and lifetimes remain an issue.
In the NANOSPARK project two different technological solution for solar cells have been investigated:

1. Dye sensitised solar cells
2. Organic solar cells

The main problem to solve to produce CNTs based solar cells was the preparation of material (suspensions and powders) and identification of proper deposition procedures in order to get good thin layer: optically transparent and highly conductive.
The material was prepared in form of powder as well as dispersed in organic solvents and then sent to partners, IBE and KONARKA, to investigate its application in solar cells.

1) Dye sensitised solar cells

In Graetzel-type solar cells nanotubes were as transparent electrodes, as thermal leads and thermal sinks for heat management, and as active material when combined with a n-type organic semiconductor. To raise the conductivity rate of the thin film coated glass which act as substrate for dye sensitised solar cells (DSSC), highly conductive carbon nanotubes grid was realized on the glass surface in order to create a preferential fast path for charge transfer, reducing remarkably the sheet resistance. In this application CNTs substitute the current solution of a SnO2 layer and a metallic grid, typically made of Argentums.

Transparent thin films of single-walled carbon nanotubes on various substrates were prepared and tested. Such networks have been prepared on:

- Glass
- FTO coated glass (samples from IBE)
- flexible plastic foils (like that of PET)

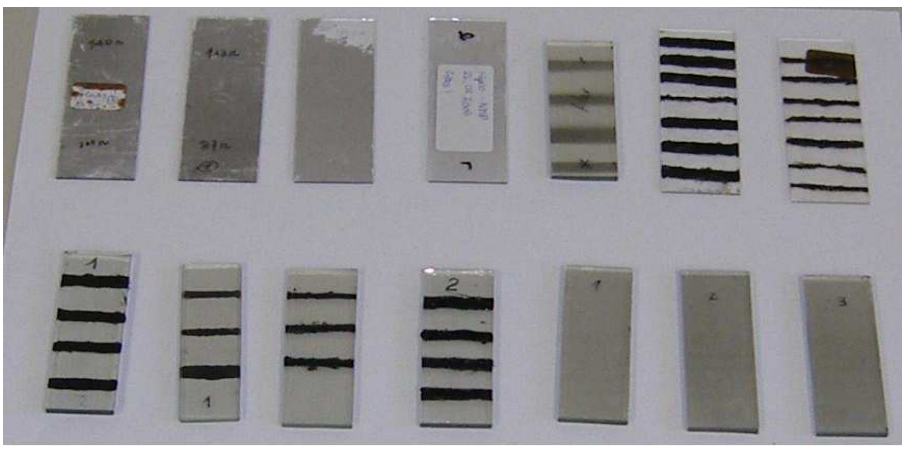

Figure 27: Samples of carbon nanotube networks and painted leads on glass and FTO coated glass prepared for testing on solar energy systems.

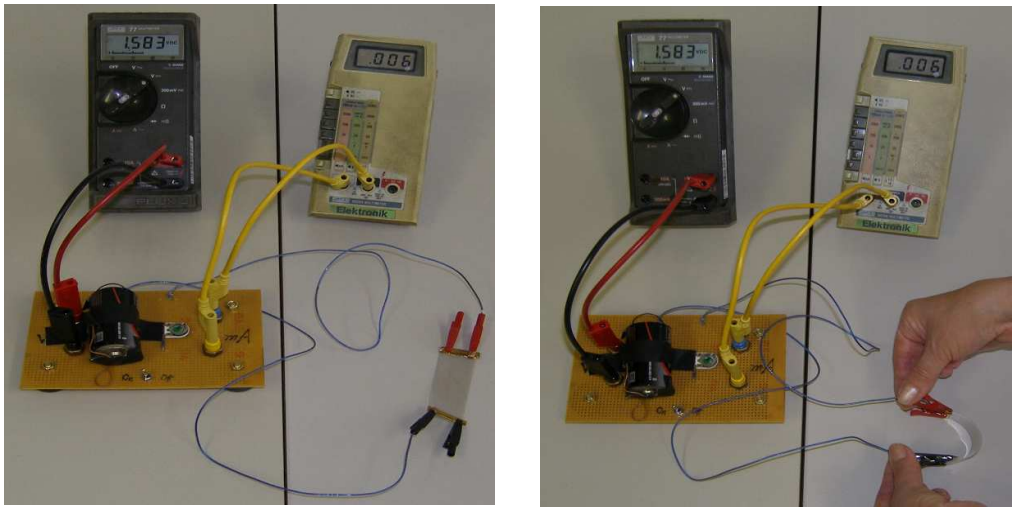

Figure 28: Electrical resistivity measurement on carbon nanotubes network deposed on a flexible PET substrate using copper-tin foil as contacts.

The influence of organic solvents on the electrical conductivity of carbon nanotubes based electrodes deposed on substrate was evaluated. Special attention was paid to the influence of the iodine solution in acetonitrile, which is actual solution used in its IBE dye sensitised solar cells. The iodine solution used during tests was a 0.5 M LiI/0.05 M I2 solution in acetonitrile.
The surface resistivity measured in air was about **1 kΩ/square**, while **after 48 h exposition in iodine solution it increased up to 10 kΩ/square**. If the thin nanotube layer is not fixed on the glass, the surface tension of liquid causes small breaks in the network, which is the main reason for the observed enhancement of resistivity after contact with organic solvent.

The transparent layer of CNTs deposed on glass demonstrated scarce mechanical stability and resistance to scrape. Various deposition methods for improving adhesion were investigated, including air brush spraying, painting of electrodes from nanotubes and different polymeric binders.

Surface treatments applied were:

- **silanization** of glass surface with aminopropylsilane (APS)
- **dip-coating** of glass with polymer polymethylmathacrylate (PMMA)
- **spin coating** of nanotube-polymer composite

Silanization is a method for deposition of nanotubes from surfactant solution. Although the network of nanotubes sprayed on the silanized glass surface was conductive (surface resistance 190 Ω -1.2 MΩ) it was not satisfactorily fixed to the surface. Also the nanotubes network on top of PMMA layer was not sufficiently adhesive to guarantee mechanical stability in a liquid. Since PMMA interlayer was dissolved in acetonitrile solution, a glass coating with carbon nanotube-acrylic resin-composite was used to improve the adhesion significantly. The resulting **composite layer was mechanically stable in air and conductive** (surface resistance 2kΩ - 2 MΩ).

The nanotube thin network deposed on glass was protected with a thin layer of polymer to avoid peeling off due to acetonitrile. The samples were dipped in an aqueous solution of polyvinyl alcohol (PVA) (3 wt %) and dried in a flow of argon. The resulting coating could fix the nanotube network to the glass substrate and showed the surface resistivity in the range of 100 - 160 Ω/sq. Afterwards the samples were exposed to the iodine solution for 24h at enhanced

temperature of about 50 °C. The treatment in organic solvent did change neither the morphology of the composite layers nor their electrical conductivity.

For the development of DSSC was important the improvement of working transparent metal oxide electrodes by adding highly conducting carbon nanotube lines. These lines are supposed to help collecting the photo-generated charges increasing the overall conductivity. In a Graetzel-type solar cell these lines are in contact with the organic solvent (acetonitrile) and with iodine (elemental iodine and iodine ions). Therefore it was important to investigate the electrical conductivity of the nanotubes leads in the environment of iodine solution. For this purpose 0.5 M lithium iodide LiI and 0.05 M iodine I2 were dissolved in acetonitrile simulating the working electrolyte in the dye sensitized solar cells used at IBE.

Several electrode wires (length/width/thickness 2 cm/0.15 mm - 0.3 cm/0.1 mm) were prepared from suspension in organic solvent (NMP), or epoxy polymer.

The **electrical resistivity** of nanotubes lines painted from solution **varied between 0.2 and 0.5 Ωcm**. One order of magnitude lower resistivity was measured for strips of bucky paper glued on glass. Exposure of these samples to **iodine solution reduced the resistivity again by factor of 5**. Nanotube wires prepared from **acrylic resin** composite showed **resistivity in the range of 50 - 150 Ωcm**. However, these electrodes were not **stable in the iodine solution** because the resin dissolved in acetonitrile. Wires based on **epoxy composite were stable in iodine solution** even at enhanced temperature (up to 50 °C) and their **volume resistivity varied between 1 kΩcm and 7 kΩcm**.

CNTs were also fixed on glass by PVA layer and painted nanotube leads. In this case the thick carbon nanotube leads had a function of contact electrodes for the transparent thin layers.

Several similar devices were prepared by spray and painting method followed by coating with a protecting layer of PVA. Finally, the electrical resistivity was measured. Tests performed have shown that thin **nanotube networks and nanotube leads assembled into all-carbon devices** with the abovementioned method **were chemically and mechanically stable** in the environment of DSSC.

The following table provides an overview of the values gathered during tests and allow to compare different preparation methods.

Sample	Surface resistivity	Volume resistivity
SWNT+NMP (N-methyl-pyrrolidone) paste on glass in air	-	0.25 Ωcm
solution of 0.5 M LiI/0.05 M I_2 in acetonitrile	-	2.5 Ωcm
SWNT+NMP in acetonitrile	-	0.20 Ωcm
SWNT+NMP in 0.5 M LiI/0.05 M I_2 in acetonitrile	-	0.01 Ωcm
SWNT+Epoxy glue on glass in air:		
#1	-	3.7 kΩ
#2	-	3.4 kΩ
#3	-	2.6 kΩ
#4	-	1.7 kΩ
#5	-	3.8 kΩ
#6	-	0.7 kΩ

SWNT+Epoxy glue in acetonitrile	-	4.0 kΩ
SWNT+Epoxy glue in 0.5 M LiI/0.05 M I_2 in acetonitrile	-	0.85 Ωcm
SWNT+Epoxy glue kept 10 min in 0.5 M LiI/0.05 M I_2 in acetonitrile and dried	-	0.16 Ωcm
SWNT+NMP paste on FTO in air	-	0.01 Ωcm
SWNT+Epoxy glue on FTO in air	-	0.10 Ωcm
SWNT+Epoxy glue on FTO in 0.5 M LiI/0.05 M I_2 in acetonitrile	-	0.06 Ωcm
SWNT- BP stripes in air	-	0.05 Ωcm
SWNT- BP stripes after treatment in 0.5 M LiI/0.05 M I_2 in acetonitrile	-	0.01 Ωcm
SWNT network on glass	1 kΩ/	-
SWNT network on glass kept 48 h in 0.5 M LiI/0.05 M I_2 in acetonitrile and dried	10 kΩ/	-
SWNT network on FTO	7 Ω/	-
SWNT network on glass covered by PVA with BP stripes as contact electrode:		
#1	340 Ω/	-
#2	360 Ω/	-
#3	280 Ω/	-
#4	240 Ω/	-
SWNT network on glass with BP stripes as contact electrode covered by PVA after treatment in 0.5 M LiI/0.05 M I_2 in acetonitrile sample	420 Ω/	-
SWNT network on glass covered by PVA with SWNT-epoxy-glue contacts:		
#1	610 Ω/	-
#2	270 Ω/	-
#3	410 Ω/	-
#4	60 Ω/	-
#5	580 Ω/	-
#6	570 Ω/	-
#7	640 Ω/	-
#8	400 Ω/	-
#9	410 Ω/	-
#10	160 Ω/	-
SWNT network on glass covered by PVA with SWNT-epoxy-glue contacts after treatment in 0.5 M LiI/0.05 M I_2 in acetonitrile:		
#1	330 Ω/	-
#2	200 Ω/	-

Table 2: Measured results of electrical resistivity for single walled carbon nanotubes thin layers and painted leads.

Since CNTs are extremely different from material typically used for DSSC production, a procedure to deposit the material was defined on the basis of the protocol firstly prepared by SINEUROP and MPI on how depositing CNT as a "thick" conductive grid.
Epoxy resins was used to disperse CNTs and so deposit them on glass. The choice of the most suitable epoxy resin was extremely important because the resin matrix strongly affects the response in term of resistance and easy handling. **Sikadur31 CF** was chosen. CNTs mixed into resins were handled within 3 hours to avoid polymerization and drying.

Different ratio CNTs/resins by weight were tested: 1:1 , 2:1 , 3:1 , 4:1 , 10:1.

Deposition were carried out by manual deposition to firstly evaluate the coating effect and then by using a **screen printing technology**. Printing technology allowed to control thickness in order to respect a **20 microns limit** and the desired regularity.

For testing **180 MESH steel tissues with 55 microns thick strings and a 20 microns thick emulsion on the printing side were used**.

Tests performed were aimed at evaluating resistance of CNTs layer to corrosion over time and effects of size on deposition process to scale-up the prototype cell. Experimental results allowed to get only a first evaluation on systems.

The scale-up of the process presented some problems mainly related to the electrical resistance of the transparent electrodes (proportional to dimension) which is the limiting factor.

The typical lab glass used for testing had an **area of few square millimetres**.
Conductibility was almost comparable to silver grid cells but lower anyway. Conductibility of CNTs grid was almost inexistent as the size of cell increased over **10 x 10 cm area** even using a mixing ratio **CNT/resin 10:1**. This fact pointed out the limit of the adopted technology for DSSC and imply to redefine the technological approach.

Tests on CNTs based cells were only partially performed and are still ongoing at IBE.

2) Organic solar cells

For the development of polymeric solar cells by KONARKA, SWCNTs were provided as powder and solution into organic solvent.
CNTs were used to prepare thin layers which were analysed by:

- UV-VIS spectroscopy
- Sheet resistance measurements
- Atomic Force Microscopy (AFM)
- Chemical stability of CNT under elevated temperature and illumination
- OPV (organic photovoltaic) devices (as electrodes)

Thin layers were deposed onto different substrates:

- Glass,
- Glass covered with ITO,
- glass covered with ITO and CNT,
- glass covered with CNT (colour code described in inset).

For all these substrates it was possible to find in literature data for transmission spectra. In addition these materials were chosen because they show similar transmission spectra.

The experiments performed have showed that a thin layer of CNTs may serve as semitransparent electrode in organic photovoltaic (OPV) devices. The measurements were carried out in van-der-Pauw geometry which is a standard procedure to determine the sheet resistance of thin conductive layer. The measured sheet resistance values were rather high (in the kΩ range) suggesting that **a single thin CNTs layer was not sufficient to serve as an electrode in OPV devices**.

It has been noticed that the roughness of layers played an important role for OPV devices. As all layers are very thin (50 - 250 nm) rough electrodes or buffer layers had be very smooth to avoid short wiring. Due to the shape of CNTs (thin and very long) one may expect rather rough surfaces of CNT films. Conversely in AFM measurements very smooth regions and area covered with spikes (height >100 nm) were found.

Experiments with CNTs provided the information for the preparation of multilayers to be applied to solar devices. As a final test, a series of devices were prepared with CNTs substrates. As the sheet resistance of simple CNTs layers was too low only **glass/ITO/CNT substrates were used for device preparation**. In this case ITO supports the conductivity of the CNTs layer. The layer arrangement is shown in the picture below.

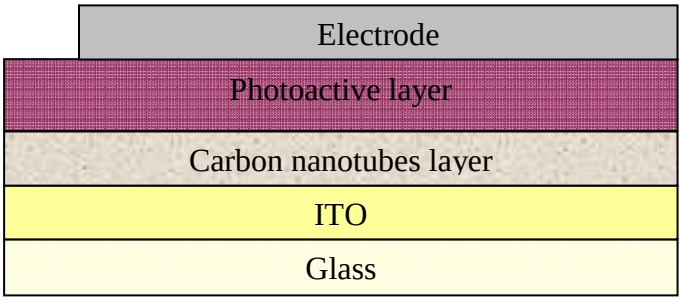

Figure 29: Scheme of layers in CNTs solar devices

In a second trial the **Glass/ITO/CNT substrates** were first covered with a planarization-layer to reduce the roughness of the substrate. Baytron PH, a well know conductive polymer which is often used in organic light emitting diodes and organic solar cells, was used. The introduction of the interlayer reduced the shunting problem. The use of this conductive polymer allowed to prepare devices with a diode-like behaviour but the observed current-voltage curves were degraded by micro-shunts which are still present in the device. To solve the problem the Baytron PH layer thickness was increased to reduce the shunting problem further. This solution was indeed not feasible because thick Baytron layers reduced the transmission of the electrode significantly and thus abating the performance of the solar cells.

In Figure 30, it is shown the schematic layer arrangement of a typical organic solar consisting of a transparent packaging (e.g. glass, polymer foil) coated with a transparent electrode (e.g. a transparent conductive oxide). On top of the transparent electrode the ‘Active Material’ was deposited. In the work performed the ‘Active Layer’ was a conjugated polymer–fullerene blend. The cell was then finalized with a second electrode (primary electrode in Figure 29).
All the different layers were investigated in order to identify the properties and best solutions to realise organic cell based on CNTs according to the NANOSPARK work-programme.

The deposition process has been realised by preparing a transparent electrode on transparent substrate. Then the active material was deposited on top of the transparent electrode and finally the primary electrode applied on top of the active material.

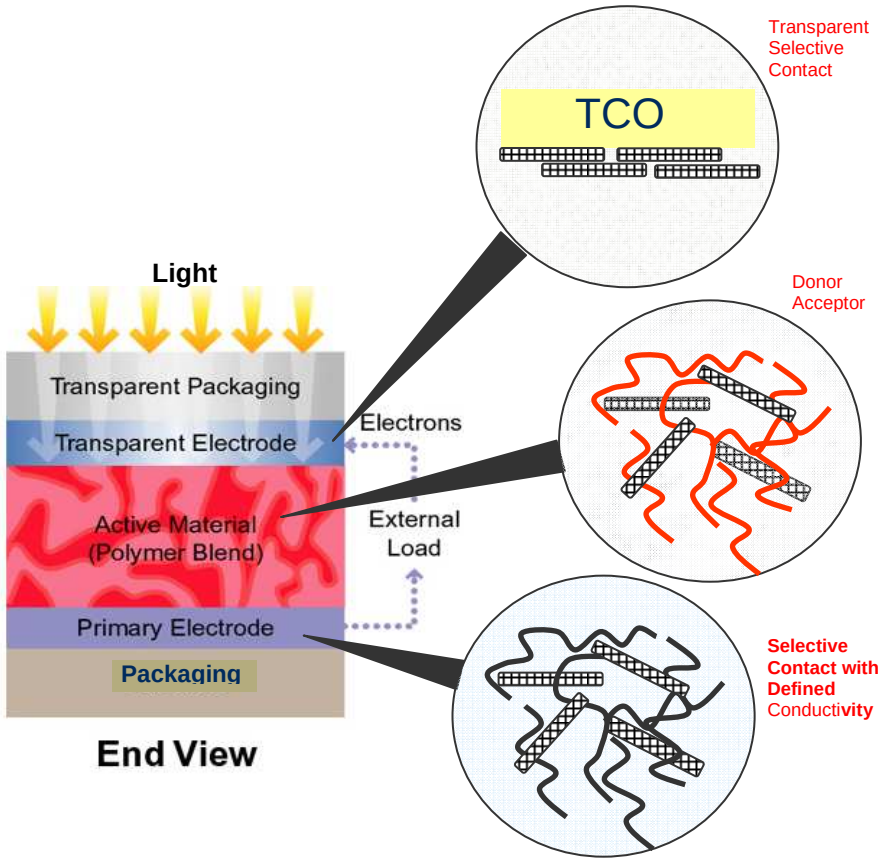

Figure 30: Schematic drawing of an organic solar cell, application of SWCNT in different layers.

- **Transparent selective electrode**

SWCNTs were tested as transparent electrode. Ideally they could replace transparent conductive oxides (TCO) like indium-tin-oxide exhibiting a better transparency in the visible in near infrared region of the solar spectrum and also a better conductivity. Unfortunately CNT materials available at the moment did not allow the preparation of superior transparent electrode systems. To study the basic applicability, SWCNTs were coated from solution on glass substrates with a thin TCO layer. Standard devices were processed on top of the SWCNTs layer and tested under solar illumination. Results were negative because the prepared devices did not work as solar cells. All of them were electrically shunted suggesting that the surface roughness of the SWCNTs-layer significantly exceeds the layer thickness (~ 200 nm) of the photoactive layer. Therefore upon applying a conductive primary electrode the two conductive layers (primary electrode and transparent electrode) were connected and the solar cell is short-circuited.

- **SWCNTs as acceptors**

SWCNTs were also used as acceptors molecules replacing the standard fullerene acceptors but no charge transfer could be demonstrated. Therefore the charge generation efficiency of the prepared solar cells was very low (~1000 times lower compared the standard acceptor molecule).

This result was expected because similar observations have been published earlier. Tests carried confirmed that SWCNTs are not good candidates for replacing smaller fullerenes as electron acceptors.

- **Selective contact with a defined conductivity**

SWCNTs were also tested as selective electrode material by applying

a. SWCNT from solution on top of the active layer;

b. A mixture of SWCNTs and a conductive polymer on top of the active material.

Devices with a SWCNTs primary electrode showed a lower performance. The SWCNTs films applied out of a water/surfactant/SWCNT dispersion were rather inhomogeneous leading to a non-perfect primary electrode. Primary electrodes based on SWCNTs-conductive polymer composites gave indeed nicely working devices. One of the key-issues for optimizing the device performance was the formulation of the SWCNTs-conductive polymer dispersion. As the surface energy of the active layer is very low, soap-type surfactants were needed to get a homogenous coating on the active material. During the optimization process different formulation were tested. In Figure 54 typical current-voltage curves measured under illumination are shown for a device with SWCNTs and a reference device without SWCNTs.

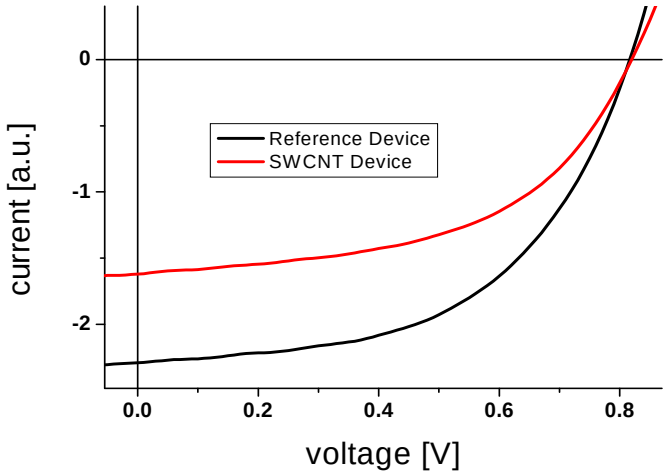

Figure 31: Current-voltage curves measured under sun illumination. Typical devices with and without SWCNT have comparable efficiency in the range of 3-4 %.

Based on two formulation of the SWCNTs-conductive polymer dispersion, a set of devices was prepared for lifetime testing. After preparation devices were sealed with a thin glass slide and mounted in a home-made degradation holder. The holder was placed under a solar simulator (Steuernagel 1500) and current voltage curves were acquired every 100 - 200 hours.

In the following Figures (32 and 33) the evolution of the most important solar cell parameters are shown for the devices with and without SWCNTs. For the two formulations these results were gathered:

a) devices with carbon nanotubes prepared according to Formulation 1 are more stable compared to the reference devices. While devices with SWCNTs showed ~75 % of the

initial efficiency after 1200 hours of illumination, the output of the reference device was only 68 % of the initial performance.

b) when Formulation 2 I used for CNTs deposition, devices stabilities were comparable. After 1200 hours the device performances decayed to ~65 % of the initial value.

c) SWCNTs can be successfully incorporated as one of the electrode materials in organic solar cells and the energy conversion efficiency of devices with and without CNT material was found to be comparable.

d) lifetime tests demonstrated a dependence on the formulation of the coating dispersion, nevertheless devices with and without SWCNTs showed comparable stabilities under sun illumination.

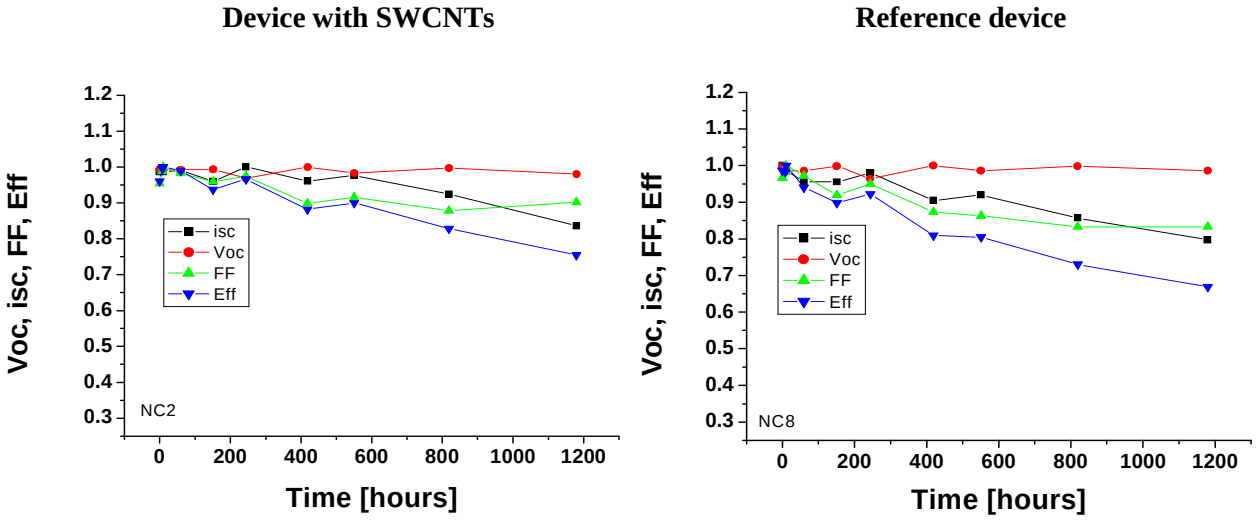

Figure 32: Comparison of devices with and without SWCNT electrodes in the lifetime test realised with Formulation 1; isc – short circuit current, Voc – open circuit voltage, FF – electrical fill factor, Eff. – power conversion efficiency.

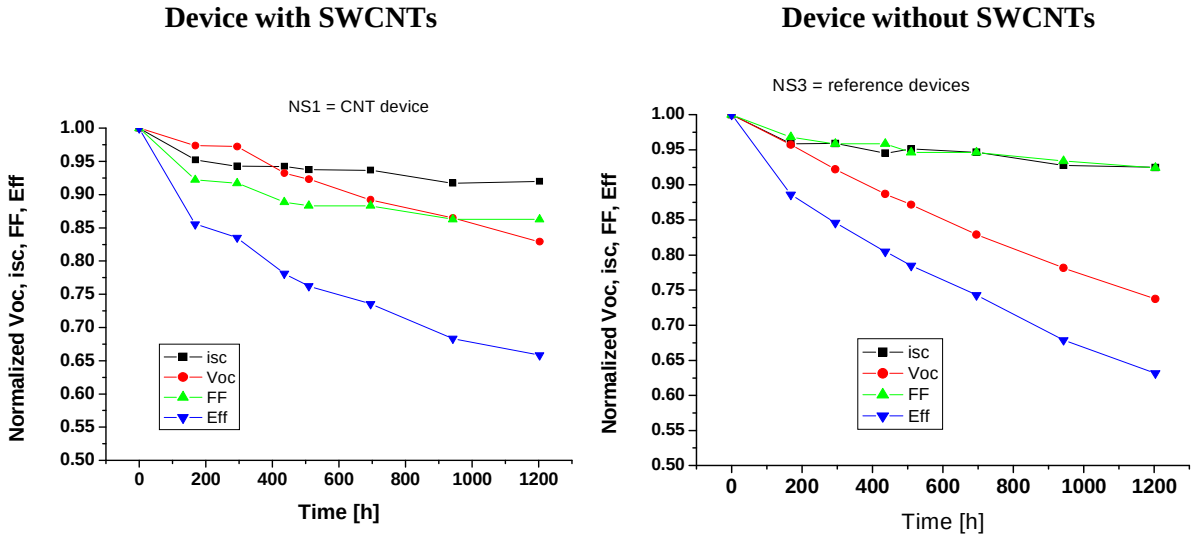

Figure 33: Formulation 2; Comparison of device with and without SWCNT electrodes in the lifetime test, isc – short circuit current, Voc – open circuit voltage, FF – electrical fill factor, Eff. – power conversion efficiency.

SECTION 2 DISSEMINATION AND USE

The main publishable results and their possible exploitation are described:

2.1 *Overview table*

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s) of application**	**Time for commercial use**	**Patents or other IPR protection**	**Owner & Other Partners involved**
CSA technology and characterization	To be defined	Nanomaterials production processes	2007	Patent application on	CNR and OS
NANOSPARK machinery design	Reaction chamber; auxiliary components	Machinery for nanomaterials production	2007 - 2008	Patent application on	OS and TECNA
Plasma Window	Mechanical-electronic components for industrial machineries	Components for Plasma based machinery	2008	-	TECHNION, CNR and TECNA
Methodology for CNTs characterization	Purification of nanostructured materials, procedures for nanomaterials handling	Nanomaterials production and purification processes	2007	-	SINEUROP, MPI and CNR
Deposition processes for CNTs and solar cells development	Deposition processes; Solar cells exploiting SWCNTs properties	Renewable energies; PV devices	2008 - 2009	Patent application on-going	IBE, KONARKA and SINEUROP

2.2 *Description of exploitable results*

2.2.1 CSA technology and characterization

2.2.1.1 Result description

The NANOSPARK project has demonstrated that the Channel Spark Ablation is capable of producing carbon nanotubes from graphite with a lower energy consumption and high quality of the final product. Nanotubes produced can be commercialised at a lower cost as different products: nanotubes powder, suspensions or dispersed in polymeric thins film, etc.

Development and characterization of the Channel Spark Ablation have been carried out focusing on:

- definition and optimisation of the plasma conditions generated during target ablation within the reaction chamber;

- design and development of the reaction chamber as core of the NANOSPARK system;
- design and development of mechanical components, electronics and control system;

The result consists in the characterization of the Channel Spark Ablation for carbon nanotubes production. Experimental results and theoretical explanation of plasma deposition phenomena have been published in two papers on *Journal of Applied Physics*:

- ***Characterization of a Channel Spark Discharge and generated electron beam***
  Ya. E. Krasik, Svetlana Gleizer, Konstantin Chirko, Joseph Gleizer, Joshua Felsteiner, Vladimir Bernshtam, Cino Matacotta

- ***Pressure and electron energy measurements in a channel spark discharge***
  Ya. E. Krasik, Joseph Gleizer, P. Nozar, C. Taliani

2.2.1.2 Possible market applications

The possible exploitation of the NANOSPARK technology is related to nanotubes and thin films production. The material developed could be applied to different products, firstly to electronic applications, production of nanostructure material based on CNTs and solar cells as presented by the intended project.
In addition, technical solutions adopted for the reaction chamber, could be exploited in different machineries for nanostructured material preparation by pulsed beam ablation at industrial level.

2.2.1.3 Stage of development

The technology has been developed and characterized. The results achieved during the experimental phase have been used for optimisation and validation of the NANOSPARK prototype. The machinery is available at the CNR in Bologna and partners are going on with the implementation of the system to pass from a working equipment on lab-scale to an industrial system ready for the market. The machinery is currently operating at CNR for production of CNTs and specifically single-walled carbon nanotubes.

2.2.1.4 Collaboration sought or offered

The work performed and the results achieved did not require or imply any collaboration or agreement with external companies or Research Institutes. Partners are available for commercial agreement for using the NANOSPARK technology for CNTs production.
Cooperation with Research Institutes is sought for refining of the machinery and possibly transfer the technology to other nanostructured materials and applications.
Partnership with private companies (both Small and Large) will be evaluated for commercial exploitation of the technology worldwide.

2.2.1.5 Intellectual property rights granted or published

Two papers regarding the characterization of a Channel Spark discharge phenomena and generated electron beam have been submitted to international Journals.
Design of the reaction chamber and subsystems have been protected and could be licenced to thid parties by OS.

2.2.1.6 Contact details

Prof. Carlo Taliani
Via Gobetti, 101
40129 Bologna - Italy
Phone 1: +39 051 6398531
Fax: +39 051 6398539 / 40
Em@il: C.Taliani@bo.ismn.cnr.it

2.2.2 NANOSPARK machinery

2.2.2.1 Result description

The result of this activity was the NANOSPARK machinery able to produce high SWCNTs with a energy consumption lower than Laser Ablation technique.

2.2.2.2 Possible market applications

The possible exploitation of the NANOSPARK machinery is related to nanotubes and thin films production. The technical solutions developed for this machinery could be transferred to other vacuum machineries exploiting plasma for material transformation. This equipment thought for carbon nanotubes production could be used for different kind of nanotubes or complex oxides production at nanoscale.

2.2.2.3 Stage of development

The NANOSPARK prototype demonstrator has been developed and tested. Part of the technology used in the machinery is already patented but some technological solution need to be protected before disseminating any information

2.2.2.4 Collaboration sought or offered

Licensing of the patent and of know how to producers of vacuum and/or plasma based machinery will be evaluated.

2.2.2.5 Intellectual property rights granted or published

Partners neither published any information regarding the machinery nor granted any intellectual property right to third parties. Patenting of some technological solutions of subcomponents is under evaluation.

2.2.2.6 Contact details

Prof. Carlo Taliani
Via Gobetti, 101
40129 Bologna - Italy
Phone 1: +39 051 6398531
Fax: +39 051 6398539 / 40
Em@il: C.Taliani@bo.ismn.cnr.it

2.2.3 Plasma Window

2.2.3.1 Result description

The Plasma Window (PW) is a system able to maintain high gas pressure gradients without introducing mechanical interfaces between two different chambers. The operation of the PW is based on significantly higher temperature and increased viscosity of plasmas as compared with the temperature and viscosity of gases composed of neutral particles. The higher plasma temperature allows to decrease the plasma density while keeping the same value of pressure.
The development of such component required a complete characterization to evaluate its performances and integration in the Channel Spark Ablation based process.
Experimental results and estimation showed that the PW could provide three orders pressure gradients in order to keep a high pressure inside the first chamber and a very low pressure inside the second one. This result was of paramount importance for pressure condition for CNTs production.

The work carried out and experimental results regarding the PW developed and applied to CSA machinery have been published in a papers on *Plasma Physics and Operations*:

- ***Characterization of a Channel Spark Discharge and generated electron beam***
  Ya. E. Krasik[1], Joseph Gleizer[1], V. Gurovich[1] and I. Kronhaus[1], A. Hershcovitch[2], P. Nozar[3] and C. Taliani[3]

2.2.3.2 Possible market applications

Since the Plasma Window is able to generate a differential pressure between two chambers, it could be used in all equipments which require a precise pressure control in presence of high energy beams.

2.2.3.3 Stage of development

The Plasma Window has been realised and installed on the NANOSPARK machinery. It has been tested and it is currently under refining to improve its performances. The system can be adapted to different equipments and can be supplied to customers on the basis of requirements and data sheet of the process used.

2.2.3.4 Collaboration sought or offered

Currently the work performed and the results achieved implied a strict cooperation between TECHNION and an US Research Centres.
The Plasma Window is a patented technology. The system developed for the NANOSPARK project represented a modification of a pre-existing patent. By the way some changes and innovation have been introduced for this specific application. Cooperation with companies specialised in machinery design and construction in the field of advanced materials production will be evaluated.
Project partners would like to investigate different applications of the Plasma Window at industrial level with Research Institutes and companies.

2.2.3.5 Intellectual property rights granted or published

Partners published a paper provided a complete characterization of the Plasma Window since all sensitive technical information are already patented.
Patents on innovations realised for the NANOSPARK system on PW will be evaluated.

2.2.3.6 Contact details

Prof. Yakov Krasik
Technion City – Department of Physics
32000 Haifa - Israel
Phone 1: +972 4 8293559
Phone 2: +972 4 8293666
Fax: +972 4 8226641
Em@il: fnkrasik@physics.technion.ac.il

2.2.4 Methodology for CNTs characterization

2.2.4.1 Result description

The result of the activity performed was a protocol for characterization of CNTs and preparation of the material for different applications, mainly for integration into solar cells.
The NANOSPARK project aimed at using carbon nanotubes, produced by Channel Spark Ablation technique, for solar cells development. The choice of CNTs as alternative material for the development of photovoltaic devices was mainly due to the outstanding properties of conductibility showed by this material.

Single-wall carbon nanotubes (and carbon nanotubes more in general) can be produced by a variety of techniques like arc discharge, laser ablation, chemical vapour deposition and other techniques. But the as-produced material is known to be inhomogeneous and contains a variety of impurities such as metal catalyst, amorphous carbon, and graphite particles. So it is very important to determine the purity of samples of CNTs and the separation of CNTs into the metallic and semi-conducting fraction from electronics perspective.
Carbon nanotubes prepared were properly purified and characterized. In order to guarantee a constant standard of the material a methodology for carbon nanotubes analysis was established in cooperation with MPI-FKF.
SINEUROP has optimised and applied an optical method to determine in a quantitative way the concentration of single-walled carbon nanotubes in the presence of other carbonaceous components (like amorphous carbon and graphitic particles) to samples from arc discharge and laser ablation synthesis. The protocol requires different phases for samples preparation and measurement techniques:

1. Homogenisation
2. Measurement of electrical conductivity
3. Preparation of pressed pellets
4. Preparation of films of SWCNT composites
5. Electrical measurements
6. SEM characterisation
7. X-rays powder diffraction
8. Optical spectroscopy

2.2.4.2 Possible market applications

The result achieved can be virtually apply to all industrial sectors which imply the use of carbon nanotubes. Possible refining of the procedures could be necessary according to requirements for material.

2.2.4.3 Stage of development

The work performed led to the definition of a protocol for characterisation of carbon nanotubes samples and quality control. The idea was to develop a general procedure to guarantee reproducible results when nanotubes characterisation is performed at different laboratories.

This procedure was applied upon commercial nanotubes produced for solar cells development and upon NANOSPARK nanotubes when they have been available for testing. It is constantly updated and optimised by SINEUROP in cooperation with MPI-FKF.

2.2.4.4 Collaboration sought or offered

Partners involved in this activity strictly cooperated with several Research Centres as result of pre-existing relationship among parties and participation in other European projects.
Partners involved in this activity are going on with the refining of the methodology and cooperation with other Research Institutes will be evaluated.
This methodology can be provided by SINEUROP on request.

2.2.4.5 Intellectual property rights granted or published

Partners neither published any information regarding the procedures for characterization and purification nor granted any intellectual property right to third parties. Publication of results will be evaluated, meanwhile information will be provided to selected customers or partners outside the NANOSPARK Consortium.

2.2.4.6 Contact details

Dr. Siegmar Roth
Heisenbergstrasse 1
70569 Stuttgart - Germany
Phone 1: +49 711 6891434
Fax: +49 711 6891010
Em@il: SgmrRoth@aol.com

2.2.5 Deposition processes for CNTs and solar cells development

2.2.5.1 Result description

Nanotubes produced with Channel Spark Ablation were not tested for new solar cells. Partners used commercial products to develop solar systems and so carrying out tests. CNTs produced by partners were characterized and purified according to the protocol outlined within the project. This way CNTs produced via NANOSPARK machinery could be virtually compared with commercial product and thus evaluated potential performances in industrial products.

IBE and KONARKA carried out the development of two different solar energy systems making use of CNTs. So far the results achieved were not successful and allowed to implement only lab-scale systems for testing.

2.2.5.2 Possible market applications

The work aimed at developing two innovative type of polymeric solar cells and dye sensitised solar cells.
New solar cells with nanotubes were not yet developed thus it is extremely difficult to evaluate correctly the potential market. Work performed and results achieved didn't allow to produce solar cells based on CNTs and additional work is necessary to overcome technological problems and limits due to production systems.

2.2.5.3 Stage of development

Carbon nanotubes produced by arc-discharge have been tested for the preparation of solar cells. Different techniques for suspensions and solutions preparation have been investigated. Deposition process for photovoltaic applications and particularly onto sensitised solar cells support and organic-conductive layers have been investigated. Results were not successful and the overall methodology need some refining. The most critical aspects of the research was the deposition process which drastically affected the performances of the cells.

The potential results are extremely important and publication will be taken into account only in a secondary step when IPR protection will be outlined.

2.2.5.4 Collaboration sought or offered

SMEs are interested in cooperating with Research Institutes for the development of solar cells based on CNTs as active amterial.

2.2.5.5 Intellectual property rights granted or published

Patent on preparation of solar cells and deposition process is ongoing. All the information have been kept confidential by the SMEs interested.

2.2.5.6 Contact details

Dr. Siegmar Roth
Heisenbergstrasse 1
70569 Stuttgart - Germany
Phone 1: +49 711 6891434
Fax: +49 711 6891010
Em@il: SgmrRoth@aol.com