Nanotube 02
International Conference on the Science and Application of Nanotubes
Boston College (USA)
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Executive Summary

By Mauricio Terrones

1. Introduction

Following the identification of carbon nanotubes produced in the arc discharge apparatus (by Sumio Iijima in 1991), the new field of Carbon Nanoscience emerged. A clear example of the rapid growth of this area can be visualized by looking at the number of publications devoted to Nanotube research (Fig. 1). From this chart it is observed that more than 1500 publications appeared in 2001. Therefore, I do not doubt that we will soon witness nanotube applications within the next years.

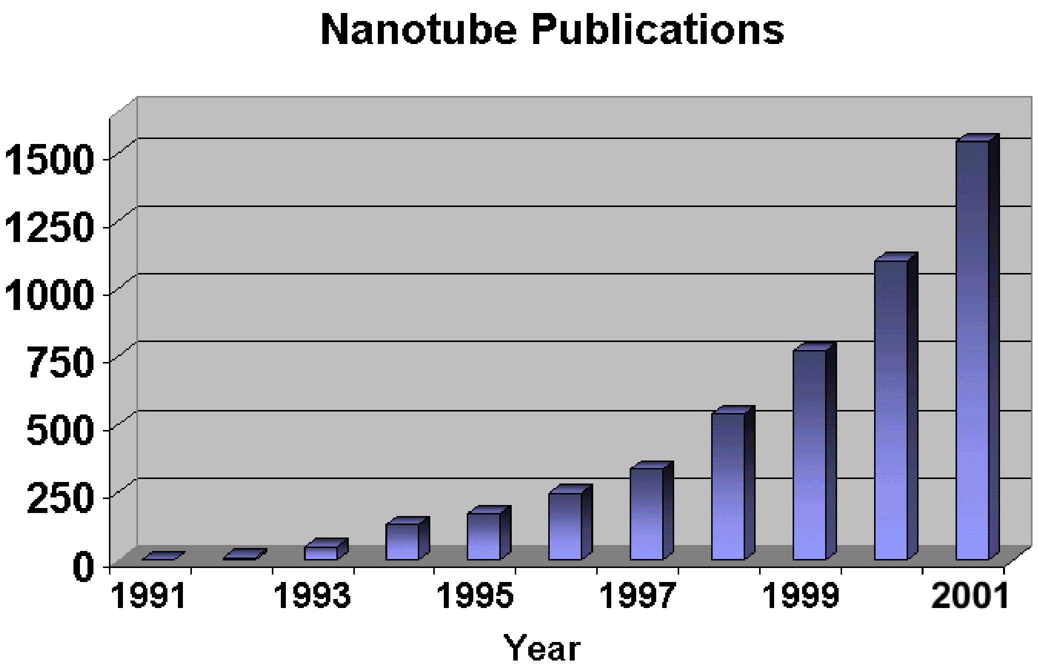

Fig. 1 Number of Publications devoted to Nanotubes in the last 10 years according to the Science Citation Index.

Nanotube 02 is the clear example of the rapid growth and development of nanotube science and technology. This conference was unique not only for the participants' positive response but also for the novel and fascinating advances we grasped in nanotube synthesis and possible emerging technologies. The number of delegates represented from different countries across the world was around 260, and consisted of chemists, physicists, engineers, electron microscopists and material scientists belonging to both industry and academia. The nice and balanced blend of researchers made the atmosphere adequate for discussions and for establishing collaborations.

During the conference, six excellent Keynote lectures were given by leading researchers who have made crucial contributions to the field: Richard E. Smalley (Nobel Laureate), Christian Colliex, Morinobu Endo, Mildred S. Dresselhaus, Phadeon Avouris and Charles M. Lieber. In addition, 19 leading scientists in the nanotube field presented invited talks on various “hot” topics raging from nanotube production to electronics and applications.

I believe that the most important time for discussion occurred during the poster presentations, which was scheduled in the afternoons. Four poster sessions were devoted to Synthesis (99 posters), two sessions to applications (68 posters), two sessions to Characterization (36 posters) and 1 session to electronic properties (27). This reflects the level of activity and the current importance of controlled nanotube production. Applications are coming up, and this will certainly be the next issue that will be discussed during **Nanotube 03**.

2. Synthesis

One of the main challenges in nanotube production is the controlled synthesis of nanotubes and nanotube networks. In particular, it has been difficult to control the chirality and length of nanotubes. As Millie Dresselhaus pointed out: “The holy grail would be to turn the right knob and out comes the nanotube of the desired diameter and chirality”. From all the work presented in the conference it is clear that the pyrolytic method involving hydrocarbons and metal particles (also known as chemical vapor deposition –CVD) is the most promising, due to the effectiveness in controlling nanotube growth (*e.g.* patterns of aligned nanotubes on substrates, narrow length and diameter distribution), reproducibility and low cost. It is important to mention the importance of the pioneering work by R.T. Baker and M. Endo in the mid 70’s have contributed to the development of this technique in the nanotube field. Morinou Endo appears to be the first person taking an image of single-walled carbon nanotube (SWNT) in 1975 (Fig. 2). Maybe this image was the first nanodevice fabricated using two crossing SWNTs. Endo gave an excellent keynote lecture on the production, characterization and current applications of carbon nanofibers and nanotubes. According to his lecture, Li ion batteries are now using the so-called Endo fibers (carbon tubular nanostructures) for more efficient performance and long battery lifetimes. He also presented the world’s smallest gears produced by mixing nylon and carbon nanotubes that are now used in the Japanese watch industry (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I17.shtml). However, this is only the beginning since various applications are merging for such tubules, which possess fascinating mechanical, thermal and electronic properties.

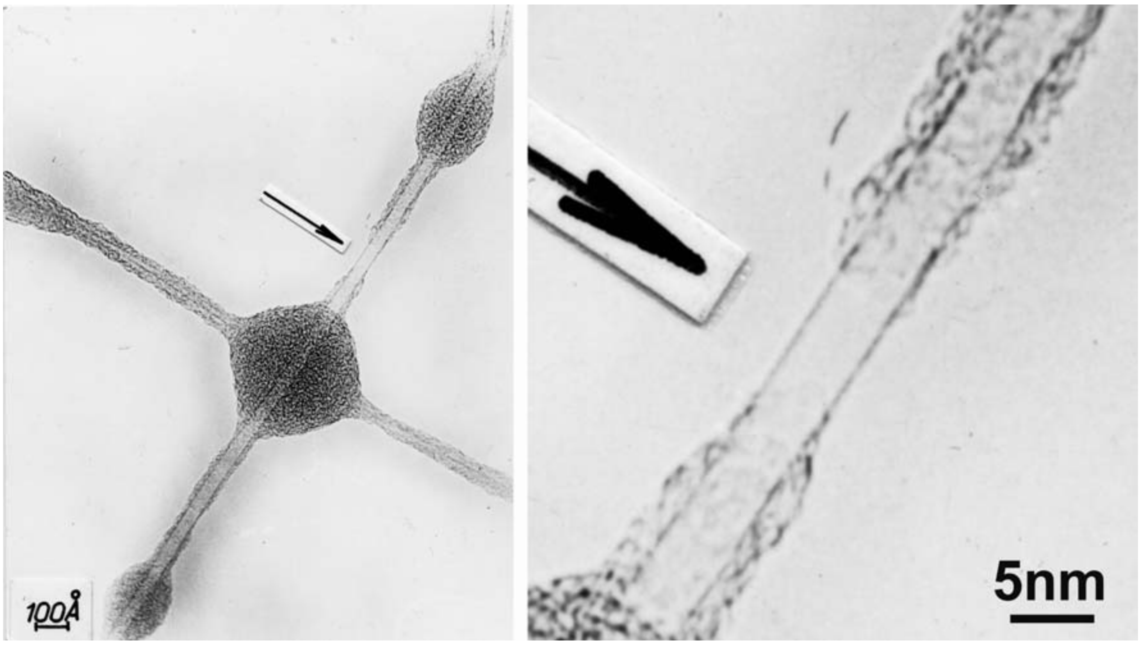

Fig. 2 (left) TEM image of two crossing SWNTs (*ca.* 4nm in diameter) exhibiting amorphous carbon on different sites of their surface; (right) higher magnification showing the individual tubule. The image was taken by M. Endo in 1975 and published in 1976 (see *J. Cryst. Growth* **32**, 335-349, 1976)

Recently, a group at Rensselaer Polytechnic Institute (Troy, NY) leaded by P. M. Ajayan, has proved that CVD techniques can now be used to produce extremely long (*eg.* 20 cm) SWNT bundles (see http://www.rpi.edu/web/News/press_releases/2002/ajayan2.html). An alternative to make long SWNT bundles is the one presented by a French group leaded by Dr. Philipp Poulin. This group extruded a polymer/SWNT in to fibers, which are relatively strong (see http://dielc.kaist.ac.kr/nt02/abstracts/I6.shtml).

Professor Xie demonstrated the importance of CVD processes in growing long (*eg.* 2mm) and aligned multi-walled carbon nanotubes (MWNTs), via self-assembly methods. However, there is still some growth control to achieve in the future (URL http://dielc.kaist.ac.kr/nt02/abstracts/I9.shtml). He also demonstrated that pyrolytically grown MWNTs can exhibit relatively high Young's modulus and thermal conductivity.

Some of the poster presentations targeted nanotube production using CVD processes. Advances have been achieved and groups are now working in the purification of SWNTs in order to remove the catalytic particles used during growth. In addition, some groups have now managed to produce double-walled carbon nanotube using this technique (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P170.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P95.shtml http://dielc.kaist.ac.kr/nt02/abstracts/P41.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P4.shtml). It is therefore clear that **self assembly** will be the route to grow nanotube arrays and networks, and I do not doubt that in less than two years we will have excellent growth control of nanotubes and their networks. A schematic representation of future self assembly processes was shown by M. Endo, in which a catalytic nano-spider will be responsible for establishing nanotube networks (Fig. 3).

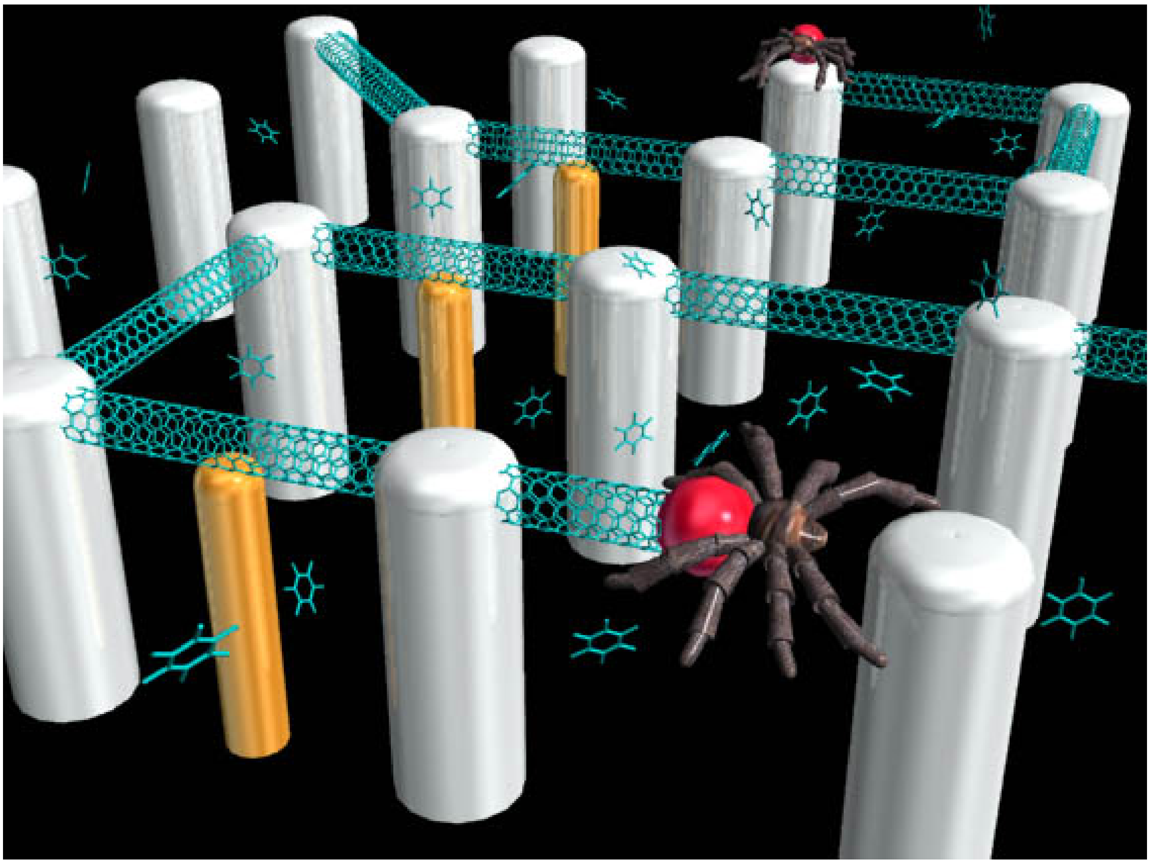

Fig. 3 An illustration showing a catalytic nano-spider building a carbon nanotube network. This picture represents an ideal self assembly process in which nanotubes could grow with the desired length, chirality and diameter (courtesy of M. Endo).

However, another possible route to nanotube arrays could be achieved by growing crossed SWNTs, which could then be annealed and bombarded with electrons or ions. This technique has been able to produce molecular "T", "Y" and "X" SWNT junctions (Fig. 4). This topic is appearing and may be an alternative to develop networks and possibly fabrics using one of the strongest materials in nature (carbon nanotubes). From a theoretical and experimental standpoint, it has been proved that irradiation and annealing is capable of producing intriguing nanotube connections (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P25.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/I8.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/I28.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P6.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P46.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P181.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P202.shtml). In addition, these networks could also be used as transistors or nanotube processors containing various transistors.

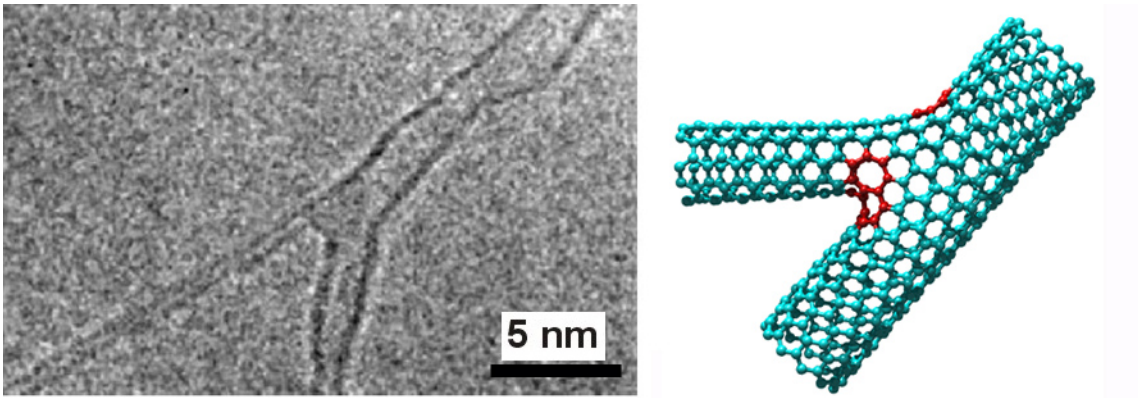

Fig. 4 HRTEM image of a SWNT "Y" junction exhibiting nanotubes of different diameters, produced inside the microscope during heat treatment and electron irradiation of two crossing tubes. The right model represents a "Y" junction of carbon nanotubes of different chirality. It has been demonstrated theoretically that such junctions could behave as nanoswitches.

3. Other Nanotube materials

During the conference, other type of nanotube systems, besides carbon, was also discussed. In particular, the effects of B and N together with carbon (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I28.shtml). Various groups around the world are working on such systems from a theoretical and experimental point of view. Regarding synthesis, Golberg's work (from Bando's group in Japan) has demonstrated that carbon nanotubes serve as efficient templates for producing BN and BCN nanotubes after reacting MWNTs with boron oxide at high temperatures (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P31.shtml). However, other CVD methods have proved efficient to grow BCN nanosystems and theoretical calculations have also been performed (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P154.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P54.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P45.shtml http://dielc.kaist.ac.kr/nt02/abstracts/P190.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P105.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P177.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P191.shtml).

In addition, Charles Lieber demonstrated that other type of nanowires could be used in nanotechnology (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I27.shtml). This opens new research avenues in the development of emerging technologies. In particular, he showed that semiconducting nanowires could be used in the fabrication of novel optoelectronic devices, bio-chemical sensors and multicolor photonic devices.

4. Composite materials

Another important aspect that was dealt during the conference was the fabrication of various types of composites using carbon nanotubes. In this context, robust and conducting composites can be produced using either single or multi-walled carbon nanotubes. However, two main problems are still present in such systems: (a) The good “bonding” between the matrix (polymer) and the filler (nanotubes), and (b) the good dispersion of nanotubes in the polymer matrix. This is because a perfect rolled graphene sheet is inert to reactions, and it is very difficult to anchor a polymer on the tube surface. In addition, the tubes always tend to aggregate and homogeneous dispersions have proved difficult to obtain (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P201.shtml). Until these problems are addressed, we will not see the best performance of carbon nanotubes in composite materials. However, Blau’s group in Ireland has done some good progress and reported an 80% increase in Young’s modulus and 60% in hardness for PVA-nanotube composites (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P167.shtml). An approach used in order to activate the carbon nanotube surface is by using plasma etching (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P176.shtml). Unfortunately, some mechanical properties may be reduced due to some tube damage. Nevertheless, this work is very important for taking advantage of the excellent mechanical properties of carbon nanotubes. Other type of composites exhibited good performance as gas sensors (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P112.shtml). Physco-chemical properties of nanotube composites such as thermal and ferroelectric (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P106.shtml), electrical (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P93.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P161.shtml) and mechanical (URL http://dielc.kaist.ac.kr/nt02/abstracts/P198.shtml) were also presented. It was also seen in a poster by Smalley’s group that certain polymers attached preferentially to SWNTs of defined chirality, the method might be implemented for achieving nanotube purification according to chiralities and electronic properties (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P141.shtml).

Researchers have now started to work on ceramic composites involving nanotubes and Al_2O_3, SiO_x or $MgAl_2O_4$ (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P94.sht), and this demonstrates the versatility of nanotube composites exhibiting different mechanical performance.

Peapods also form a carbon-carbon composite material, in which fullernes (or endohedral fullerenes) fill SWNTs. David. E. Luzzy and co-workers were the first to identify these structures, and various groups are now working on this material. Shinohara’s group presented the synthesis and electronic properties of $(Gd@C_{82})_n@SWNT$ (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I20.shtml), which could well be used as transistors. Another experimental talk dealt with the mapping of electronic states in fullerene peapods using Scanning Tunneling Microscopy (STM). Here it was shown that C_{60} molecules alter the electronic structure of SWNTs (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I18.shtml).

5. Theory

Theoretical calculations have played a crucial role in Nanotube science. In particular, the prediction of the electronic and mechanical properties of carbon nanotubes, which depend upon chirality and diameter, is a clear example of the importance of computer calculations. A few years later, these properties were confirmed experimentally. **Nanotube 02** is not the exception and excellent and exciting theoretical work was presented.

Theory on nanotube devices in electronics (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P192.shtml), stability of defective and narrow tubes using tight binding molecular dynamics (TBMD) calculations (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I2.shtml), junction creation with SWNTs using TBMD (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I8.shtml), electronic properties of nanotube junctions (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I1.shtml) and semimetallic nanotubes (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I13.shtml), were discussed during the during this meeting.

Peapod formation was also discussed theoretically and some models are in good agreement with experimental results (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P8.shtml). In addition, theoretical scenarios for fullerne coalescence in nano peapods were nicely presented (URL http://dielc.kaist.ac.kr/nt02/abstracts/P19.shtml). The symmetry, transport, electron confinement and electronic structure in fullerene peapods was also discussed (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P79.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P203.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P66.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P135.shtml).

Electronic properties calculations using first principles were also introduced for nanotubes and other carbon systems (see Electronic properties section).

6. Characterization

In order to establish the physico-chemical properties of carbon nanostructures, it is vital to determine their structural, electronic, thermal and mechanical properties. **Nanotube 02** had a wide variety of state-of-the-art characterization techniques. Transmission electron microscopy (TEM) and their associated spectroscopy techniques such as electron energy loss spectroscopy (EELS), electron dispersive X-ray (EDX) analysis are commonly used in the field. In addition, electron diffraction is another tool used to establish the crystal structures (chiralities) of individual nanotubes (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P156.shtml).

Christian Colliex gave an excellent lecture on EELS characterization on individual tubes of different elemental compositions (*e.g.* CNx, WS2, BN, C, etc.) in spots of 0.5 nm (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I7.shtml) Very recently, image reconstruction using real high resolution-TEM images in atomic nanowires encapsulated in SWNTs was reported by the Oxford group. Jeremy Sloan talked about this new technique and demonstrated that that the lattice parameters of halide nanowires (encapsulated in SWNTs) are larger when compared to the bulk dimensions (URL http://dielc.kaist.ac.kr/nt02/abstracts/I11.shtml). The technique is novel and could be used on other atomic systems.

Raman spectroscopy is one of the most powerful techniques used to determine the chirality and electronic properties of SWNTs. In this context, Millie Dresselhaus reveled that it is now possible to perform Raman spectroscopy on individual SWNTs (URL http://dielc.kaist.ac.kr/nt02/abstracts/I15.shtml). She demonstrated that it is possible to obtain enough Raman signal from individual nanotubes (something amazing!). This technique can now be used to characterize individual carbon nanostructures and appears to be extremely helpful.

In addition, H. Kuzmany and R. Saito gave excellent presentations on Raman spectroscopy and characterization of carbon nanotubes, peapods and annealed peapods (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I12.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/I16.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P63.sht, http://dielc.kaist.ac.kr/nt02/abstracts/P125.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P51.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P189.shtml). Various posters also discussed the importance of Raman spectroscopy in doped and BN nanotubes (see http://dielc.kaist.ac.kr/nt02/abstracts/P38.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P190.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P210.shtml)

Raman is also used for determining the mechanical properties of carbon nanotubes by observing frequency shifts in particular active modes (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P198.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P190.shtml)

STM and STS are very important techniques for determining the atomic structure and electronic properties of nanotubes (*eg.* density of states-DOS). Ali Yazdani presented fascinating results on the importance of these techniques in nanopeapods (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I18.shtml). Density of states of doped nanotube systems were also presented, and it was shown that B and N could replace the trigonal sites of carbon nanotubes, thus leading to doped systems exhibiting different performances in field emission devices and composite materials (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I28.shtml).

Finally, a poster by Zettl's group reported on STM techniques used to identify functional groups and defects deposited on the nanotube surfaces (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P196.shtml)

7. Electronic properties

Fascinating theoretical and experimental work on the electronic properties of nanotubes and devices were widely presented. From the experimental point of view, Phadeon Avouris described various types of devices that could be constructed with SWNTs such as carbon nanotube field effect transistors (CNTFETs) and logic gates, which can be produced by doping or by heat treatments on SWNT devices (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I22.shtml)

Charles Lieber briefly discussed the performance of electronic nanotube devices, he showed that certain and specific nanowires can be better candidates for making specific nanoelectronic devices, when compared to SWNTs.

Superconductivty in carbon nanotubes is an important issue, which was addressed by Helene Bouchiat (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I3.shtml). Her group performed transport on SWNT bundles and observed superconductivity. Theoretical work on the superconductivity in carbon nanotubes was also presented during the poster presentations (see URL http://dielc.kaist.ac.kr/nt02/abstracts/P207.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P21.shtml). In this context, last year Tang's group in Taiwan observed superconductivity of 4 Angstroms diameter nanotubes (at ca. 10-20 K). In this context some attempts to produce very narrow SWNTs was presented by G. Amaratunga (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I24.shtml).

Other posters described a wide variety of results on transport, quantum conductance and electronic properties of carbon nanotubes (see posters for Tuesday Afternoon).

8. Applications

Some of the nanotube applications that were envisaged a few years ago have become a reality. **Nanotube 02** presented some new applications and potential uses of carbon nanotubes. One of the most promising nanotube applications is the fabrication of TV displays and Lamps with high intensities, operating at low voltages. In this context, Jean-Marc Bonard summarized the work along this line, and presented encouraging results (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I14.shtml). Otto Zhou also presented important results in field emission devices using a triode-type field emission apparatus (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I19.shtml).

Very recently, it has been reported that an X-ray source can be fabricated using nanotubes by Otto Zhou's group (see http://www.sciencenews.org/20020706/fob1.asp, http://dielc.kaist.ac.kr/nt02/abstracts/I19.shtml). This result demonstrates that novel applications in medicine can arise.

Various researchers in Industry and Academia thought that carbon nanotubes could be one of the best alternatives for hydrogen storage. In this context, Michael Hirscher gave an excellent talk on the possibility of storing H_2 in nanotubes (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I4.shtml).

Unfortunately, his results, which were convincing and very well presented, demonstrate that the hydrogen uptake is lower than 2%, being the highest for HipCo Produced SWNTs. He showed that the influence of impurities such as Ti (coming from the sonication probe) might be responsible for the results reported previously with uptakes up to 7%. It seems that nanotubes may not be the best material for storing hydrogen, but additional experiments should be carried out.

The adsorption of other gases such as He, H_2, N_2, SF_6 in nanohorns, double-walled tubes, SWNTs, carbon foams was presented by Katsumi Kaneko (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I21.shtml). He proved that it is indeed possible to store certain gases in nanohorns. However, further studies need to be accomplished and verified for developing novel gas storage devices. Results on hydrogen Storage in peapods (URL http://dielc.kaist.ac.kr/nt02/abstracts/P33.shtml) were also presented,

The fabrication of supercapacitors using nanotubes, Li-ion batteries, composite microgears was also discussed during the conference (see http://dielc.kaist.ac.kr/nt02/abstracts/P161.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/P83.shtml, http://dielc.kaist.ac.kr/nt02/abstracts/I17.shtml)

The fabrication of Nanoelectronic devices is another fascinating possibility that nanotubes can offer. However, if a computer processor nowadays carries more than 40 million transistors, we should think of an efficient way to create nanotube networks that could emulate nanochips, operating at high speed without overheating the device. I believe that self-assembly processes will be the solution to grow tube networks that can behave as efficient processors. In this context, there is still a long way to go but I can hardly doubt that some day we will see some nanotube electronics in our laptop computers.

Fullerene Endohedrals in peapods may also offer some alternatives in quantum computing or memory devices, in which the atoms encapsulated in the fullerenes could be position in desired locations, thus carrying some specific information.

Regarding memory devices, it was shown that aligned Fe filled carbon nanotubes and Fe-doped CN_x nanotubes could behave as bits of information (see URL http://dielc.kaist.ac.kr/nt02/abstracts/I28.shtml). Here each nanowire would be an individual bit of information, because it can be magnetized only with two different orientations, thus associating a “1” or a “0”. For example we could store 10,000 Gbits/square inch in ferromagnetic nanowires of diameters of *ca.* 8 nm.

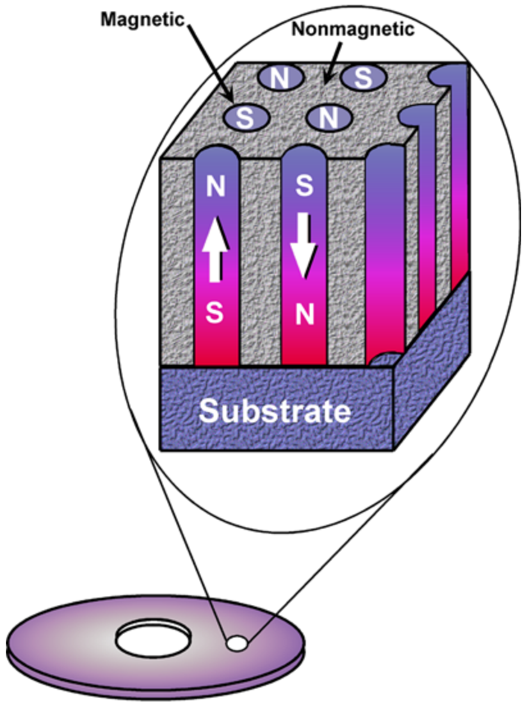

Fig. 5 Schematic of quantum disk containing aligned ferromagnetic nanowires in which each nanowire would be an individual "bit" of information

Sixty-eight posters were devoted to applications and this indicates that the nanotube technology field is only starting, and numerous exciting results have appeared rapidly over the last 10 years. The filed is growing fast, and in the next years we will witness novel technologies using nanotubes. This is only the tip of the iceberg and numerous unexpected results will turn carbon nanostructures in the new Silicon of the 21st century.

Finally, I will quote Prof. Endo, who said, "Carbon is burning HOT!!!!"