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CNT and Nanodiamond

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Index

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Executive summary

Carbon nanotubes (CNT) represent one of the most research intensive areas within nanotechnology. Their extraordinary material properties have given rise to numerous application scenarios since their discovery in the early 1990s. These include new composite materials, electrode coatings, energy storage, sensors, alternative flat panel display technologies, novel nanoelectronic components, and pharmaceutic-biomedical applications. Due to the wide range of applications, CNTs are relevant for many industries.

In many areas, CNTs are still in an early research stage; however, recently first applications have been leaving the development laboratories. Above all, mechanically reinforced CNT plastics are increasingly being commercialised. Often, these are lifestyle and sports products in which the reference to new high-tech materials can be effectively advertised. Also, the production of electrically conductive composites, coatings, lacquers and paints is gaining importance and are flowing into marketable products.

So far CNT-based products have largely addressed niche markets; however, due to increased industrial production capacities, CNTs are decreasing in cost stimulating further expansion, particularly in the composite sector.

In general CNTs offer considerable innovation and commercialisation potential. Some years ago Europe was in danger of falling behind international competitors. However, due to large research funding projects stimulating innovation and numerous industries expanding their production capacities, there is now the opportunity to overcome such gaps. The associated stimulation effect opens up possibilities for Europe not only to compete effectively with the U.S. and Asia, but also to establish technological leadership positions in particularly crucial areas, and to achieve rapid and targeted implementation into commercial products and applications.[1]

Introduction

Definition

Carbon nanotubes (CNTs) are nanoscale cylindric tubes, which consist of rolled-up layers of graphite. The tube ends may remain open but are often capped with a hemisphere of the fullerene structure. Their diameter ranges from ~1 to ~50 nm and their length is typically in the micron range, but can reach several millimeters. Single-walled carbon nanotubes (SWNT or SWCNT) and multi-walled carbon nanotubes (MWNT or MWCNT) are distinguished. The SWNTs can be formally derived from a seamlessly rolled-up graphite layer. The MWCNTs consist of multiple concentrically aligned single-walled tubes of different diameters. A specific configuration frequently appearing in literature is MWNT consisting of exactly two concentric nanotubes. They are called double-walled carbon nanotubes (DWNT or DWCNT).

Keywords

carbon nanotube, carbon nanotubules, CNT, nanotube, SWNT, SWCNT, MWNT, MWCNT, DWNT, DWCNT

Overview

Carbon nanotubes

Ideal CNTs show a number of extraordinary mechanical, chemical, thermal, electrical and physical properties making them one of the most promising materials within nanotechnology.

CNTs are characterized in particular by the following exceptional properties[2],[3]:

- Electrical conductivity: There is a "ballistic" electron transport in metallic CNTs along the tube axis; upon moving through the transport medium electrons are not scattered on length scales of several microns. Due to quantum mechanical effects there are nearly no collisions with the carbon atoms in the lattice structure. The achievable electric current densities are more than 1000 times higher than those of metal wires made of copper or silver.
- Thermal conductivity: With > 3000 W/(mK) the thermal conductivity of MWNTs considerably exceeds that of diamond (2300 W/(mK)) or silver (430 W/(mK)).
- Mechanical properties: The elastic modulus of MWNTs is given in the literature as ranging from 0.2 to 1 TPa and the tensile strength between 10 and 60 GPa. Thus the tensile strength normalized to the weight is between 60-360 times greater than that of steel.
- Aspect ratio: CNTs have a very high length-to-diameter ratio, making them prone to buckling under compression. However, this high aspect ration is ideal for electron emission applications such as cold field emission in displays or x-ray tubes
- Chemical reactivity: Due to their large surface area and the bending of the surface CNTs are chemically quite reactive compared to graphite monolayers (graphene). This allows for a chemical modification of the CNT surface, which can affect, for example, the solubility of carbon nanotubes in different solvents. In addition, the CNT surface may be functionalised, which is important for applications such as the biomedical sector, electronics and sensors, and for composites processing.

Concerning their electronic properties, single-walled CNTs appear in fractions of conducting (i. e. metallic) and semiconducting nanotubes. The conductivity depends on the structural set-up (i. e. the chirality or “roll- up direction”) of the tubes. Metallic tubes allow for extraordinarily large current densities due to their high carrier mobilities and at the same time show only low electro-degradation of the material. Semiconducting tubes on the other hand give rise for the fabrication of nanoelectronic transistors, which have already been realized as prototypes. Due to their electronic properties and the appearance of both metallic and semiconducting tubes, CNTs are discussed as a promising material in the post silicon era in microelectronics and data storage.

The electronic properties of CNTs give also rise for a number of other applications such as electron emitters in new flat panel display types, electrode materials, fillers for antistatic and conductive plastic composites, electrode materials in electrochemical applications etc.

Based on their chemical properties exposing a large and reactive molecular surface, numerous bio-chemical functionalizations of CNTs have been realized, making them candidates for compound tracers or drug-delivery systems in the biomedical area. However, research is at a very fundamental stage in this sector and issues of biocompatibility and toxicity remain open at the moment.

Significant effort has been spent in the development of large scale production techniques. Meanwhile a series of industrial production plants have been established leading to a decline in CNT-prices[4] and giving rise to more widespread applications. The main consumption will be due to utilisation in novel nano composite materials A number of products based on such composites have already been commercialised such as automotive fuel pipes and car body parts, but predominantly for life style products including tennis and hockey rackets, bicycle frames, and skiing equipment.

CNTs in their various forms are currently at market entry level at least in terms of individual applications. The transfer from lab-scale fabrication to mass production of the raw material has very recently been realized and an increasing number of commercial products contain CNT materials. In addition to composite materials this is also true for electrode materials. However, many of the CNT applications discussed here have not yet been released to market; they are in different states of research ranging from fundamental research to prototypes and lab-models.

Nanodiamond

Metal-diamond galvanic coatings, polishing pastes, lubricating oils and coolants, polymer composites and greases belong to traditional Ultrananocrystalline diamond (UNCD) particulate applications.

Using common galvanic equipment electrochemical deposition of UNCD together with metals has been proven to be useful for coatings of components of transportation units, tools for electronics, watches, medicine and the jewelry industry. The addition of UNCD to galvanic coatings leads to following advantages:

- Increased wear resistance (2 to 13 times depending on the metal);
- Microhardness (may be up to 2 times depending on the metal);
- Increase in corrosion resistance (2 to 6 times depending on the metal);
- Decrease in porosity (pores can be completely eliminated depending on the metal);
- Significant decrease of friction coefficient;
- Considerable improvement of adhesion and cohesion; and
- High throwing power of the electrolyte.

According to interviews[5] the service life of products is increased two to ten times even if the coating thickness is decreased to a half or a third. In many metals that are employed in electronic applications such as silver, gold and platinum the effect of strengthening can be noticed. Mostly in strengthening chromium coatings an electrolytic process UNCD is used in particular. Thereby there is no need for any modification of the standard production line when adding UNCD-containing additives to the chromeplating electrolyte. The operating life of molds, high-precision bearing surfaces and other similar components is higher when using such coatings. The UNCD percentage in a metal coating ranges from 0.3 to 0.5 wt%; 0.2 g/m^2 (1 carat/m^2) of UNCD is required for a 1 mm thick metal layer. Finishing precision polished materials for electronics, radio engineering, optics, medical, and jewelry industries are the fields of application for such UNCD particles.

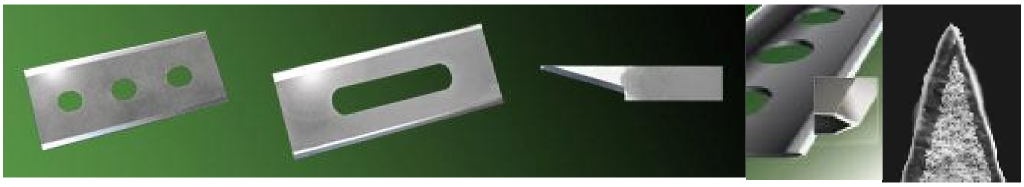

Fig. 1: Plasma sharpened precision tool kits with cutting edges of nanodiamond

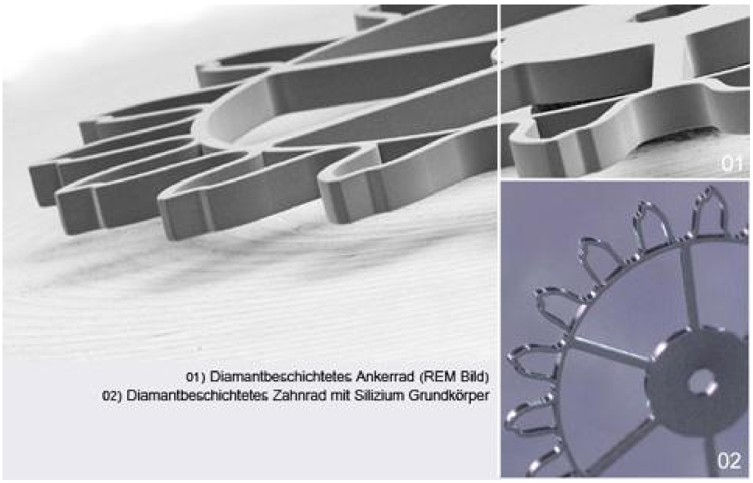

Fig. 2: Nanodiamond coated silicon parts for the clock and watch industry

Comparison of carbon nanotubes and nanodiamonds

CNTs have a diameter of a few nanometers and due to the unique structure have many exciting properties. However, their physical properties are partly comparable to those of diamond.

Physical Properties	Single crystalline diamond	CNTs	Nanodiamond
Grain Size (nm)	up to 10^7	./.	5 to 100
Thermal Conductivity ($Wcm^{-1}K^{-1}$)	22	60	0.06 – 0.1
Min. Resistivity (p-type) (Ωcm)	$< 10^{-3}$	theoretically length independent (but high contact resistance at inter-faces)	$< 10^{-3}$
Fracture Strength[1] (GPa)	4	~100 (theoretical value)	< 5
Vickers Hardness (GPa)	120	./.	88
Young´s Modulus (GPa)	1143[2]	> 1000	~1000

Tab. 1: Some physical properties of single crystalline diamond, CNTs and Nanodiamond

Scientific and technological aspects

To enable a comparable evaluation of nanotechnology related applications, the following "Technology readiness Levels" (TRL) have been defined for scientific or technological evaluations within ObservatoryNANO reports:

- TRL 1: "basic research"
- TRL 2: "applied research"
- TRL 3: "prototype / lab device"
- TRL 4: "market entry"
- TRL 5: "mature market" (mass- or established niche markets)

The TRLs will be used to classify specific applications according to their technological readiness.

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[1] The theoretical value of UNCD fracture stress (σ_f = 100 GPa) is very large compared to that observed experimentally (σ_f < 5 GPa). The fracture stress is strongly depending on defects. Even natural single crystalline diamond is notoriously inhomogeneous.

[2] The Young´s modulus of single crystalline diamond is slightly depending on the crystal orientation.

State of R&D

Due to their outstanding mechanical, electrical, thermal and chemical properties CNTs are considered as promising material in nanotechnology with a wide range of potential applications. However, despite an intensive research only few CNT-based products have already reached the stadium of commercialization and the majority of potential applications are currently still in the research or prototype state. The situation for the different areas of application varies significantly.

Composite materials (TRL 4)

Commercialisation is most advanced in the area of polymer composites. Here the most obvious commercial uses with the highest immediate market potential, especially for Europe, can be seen. First products, for example from the sports and lifestyle sector have already been on market for some time; however, these are still too expensive to compete successfully in the mass market against materials such as carbon fiber reinforced composites. With the expected continuing decline in price of CNT raw material and CNT-based composites a considerable potential will be opening up in this area. Besides mechanically reinforced composites a great potential can be seen particularly for electrically and thermally conductive polymer composites.

Electro-chemical applications (TRL 3 to 4)

Commercial uses have also been identified for electrochemical applications. Here, carbon nanotubes are increasingly utilized as electrode materials in batteries, supercapacitors and fuel cells. New electrode materials play a crucial role due to the growing importance of emerging battery and fuel cell technologies, the increasing demand for efficient energy storage for portable devices, but also in automotive and propulsion technologies.

Hydrogen storage (TRL 2)

Initial expectations regarding the hydrogen storage potential of CNTs have not been realised. The economic relevance threshold of 6.5 weight percent of stored hydrogen as defined by the U.S. Department of Energy has not yet been achieved, despite intensive research. Overall, the activities in the area of the CNT-based hydrogen storage have declined significantly and the use of CNTs as a commercial hydrogen storage medium term appears unlikely.

Displays (TRL 3)

CNT-based field emission displays are currently at an advanced prototype stage. Market launches have been announced several times; however, due to technical implementation difficulties especially in mass production they have repeatedly been postponed. CNT-displays are addressing the rapidly growing market for flat screens, which is currently fully dominated by LCD and plasma displays. CNT-based displays are seen as promising but are in commercial competition with the more established LCD technology. The latter has made great technological progress, especially during the last few years, and now occupies a dominant market position. In addition, organic displays (OLED) are a promising future development; with respect to CNT displays OLED may be regarded as a competing technology. CNT-based displays have only minor commercial relevance for Europe as the major industrial producers, and associated R & D departments and production lines, are largely located in the USA and especially in East Asia.

Nano electronics (TRL 1)

Based on their molecular size and electrical properties nanotubes are ideal building blocks for nano electronics. In a variety of experiments, CNTs have been demonstrated as active electronic devices such as diodes and transistors, as passive interconnects, or as data storage units. All electronic applications of this kind are, however, still at a very early stage of research. While the functionality of individual laboratory models has been widely shown, a transfer into industrial mass production is currently not foreseeable. One of the main difficulties is the fabrication of pure and homogeneous nanotubes with defined conducting properties. The issue is mainly their proper alignment and contacting on substrates particularly with methods of mass production. The further development of micro lithographic methods and the development of targeted growth processes of SWNTs on Si substrates are crucial for advances in CNT nano electronics. A complete replacement of silicon-based electronics by CNT-technologies is currently not foreseeable. This is due to the mentioned difficulties of CNT-electronics and to the profound degree of maturity and the variability of the established silicon technology.

Sensors (TRL 3)

Sensor applications of CNTs are evaluated as very promising. CNT-based heat and gas sensors as well as chemical and biological sensors have been successfully demonstrated; however, so far only lab devices have been developed and broader commercialisation is still lacking. The latter requires uniform CNTs as well as their exact positioning and electric contacting on the substrates. Hence, current drawbacks in the area of CNT-based sensors are similar to those in nano electronics.

Bio-medical applications (TRL 1 to TRL 2)

Bio-medical applications of CNTs have gained considerable interest. CNTs have, for example, been demonstrated as molecular transporters for genes, proteins, and pharmacological drugs ("drug-delivery"). Further applications as implant materials or in purification membranes are also possible. However, the majority of possible applications are currently still at the fundamental research stage. Various bio-molecular and technological difficulties have to be overcome prior to a mature medical or therapeutic utilisation. However, due to Europe´s important position in medical research and medical engineering bio-medical applications of CNTs have promising commercial potential for the future.

Bio compatibility (TRL 2)

The issue of biocompatibility or toxicity is of crucial importance for the use of CNT-based materials in particular in the bio medical area. First systematic studies on the biocompatibility of carbon nanomaterials have been conducted in recent years. However, the results are not yet definite and concluding statements are still not possible. In principle a lung hazard effect of free carbon nanotubes can be assumed. Their hazard potential may be evaluated as lying between other carbon materials such as carbon dust, soot or fullerenes and the more dangerous asbestos. Cytotoxic effects of carbon nanotubes have been shown in cell biological studies; however, various experiments show that the risk is strongly dependent on parameters such as the shape, length, and stiffness of CNTs used for a specific application. Beyond this the question of whether dangerous effects are due to the nanotubes themselves, to impurities contained in them, or to fibre-like agglomerations remains open. For end-users of CNT products hazards may presently be limited. For people working in the immediate environment of CNT production, the hazard potential is similar to that of manufacturing plants of paints and solvents or to the exposure to dusts and fumes; the necessary precautions are therefore similar to the handling of other potentially hazardous substances.

Technical production of carbon nanotubes (TRL 5)

Meanwhile, since carbon nanotubes can now be produced on an industrial scale, there are a number of sources of CNTs available at a reasonable cost per unit.[6] Multi-walled nanotubes (MWNT) are predominantly produced as for these a high purity level is achievable on industrial scale. Due to increased production capacities and profitable production processes the price for MWNT is in a range of 100-150 €/kg, depending on material quality and acquired quantities. For highly pure SWNT in contrast, prices still are in a range of 100 €/g. [7],[8] Over recent years the price decline for MWNTs has exceeded a factor of 100. In case of further enhanced production capacities, prices of below 40 €/kg for MWNT are likely on a medium run.[9] Single-walled carbon nanotubes (SWNT) are more expensive to produce than MWNT. Meanwhile the complex manufacturing process of the SWNT has been transferred into the technical scale (for example by Nanocyl or Thomas Swan). The price of SWNTs are expected to fall by a factor of ten with increased production volumes.

Major CNT-producers such as Bayer Material Science (D), Arkema (F), Hyperion (USA), Nanocyl (B), Iljin Nanotech (South Korea), Shenzhen Nanotech Port (China) and Japanese companies[10] predominantly use catalytic CVD for large scale MWNT-production. For SWNT-production also laser ablation, arc discharge or high pressure CO-processes are utilised.

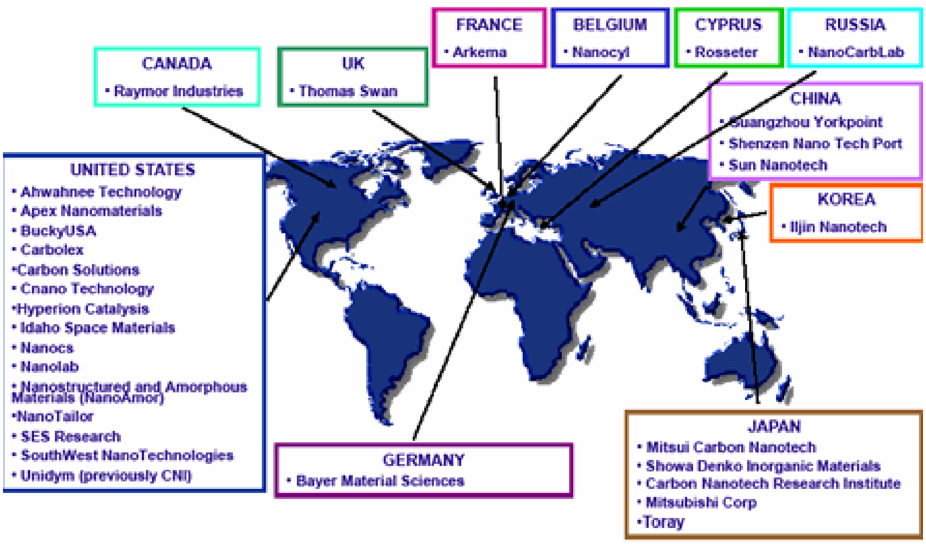

Fig. 3: Global production of CNT (Source Yole Developpement, Electronics.ca)

In 2009 Bayer MaterialScience established a production plant with a capacity of about 200 tons per year. A production capacity of 3000 tons per year is in the target for the medium term. The MWNTs are processed as agglomerates, which are still contaminated with catalyst residues, and have to be "unravelled" before further processing; however, as they are not dusty, they permit easy handling. Bayer MaterialScience is currently expanding its sales and cooperation network. Besides its distributor, Brenntag Schweizerhall, the company has recently completed an agreement with Toyota Tsusho on exclusive distribution rights for its product "Baytubes" in Asia.

Very recently Arkema (France), which started its CNT activities in 2003, announced the construction of a CNT pilot production plant with a capacity of 400 tons per year starting from 2011.[11] As a novelty, this plant will be the only CNT production site in the world that will use an entirely bio-sourced raw material. Arkema started its first pilot laboratory capable of producing some 20 tons per year of CNTs in 2006. Meanwhile they developed a range of innovative masterbatches that are easy to process within various thermoplastic, elastomer and, more recently, thermoset matrices. These masterbatches help to optimize the application properties of end-products.

Bayreuth based Future Carbon (Germany) goes one step ahead in the value chain. The company also offers products in form of CNT dispersions and functionalized CNTs for further processing in respective applications.[12] Even other companies and institutes, such as Amroy, Nanocyl, Hyperion, EMPA and Polymaterials AG are increasingly investigating industrial scale processing of functionalized CNT, to provide reasonable prices for industrial end producers.[13]

Production of polymer composites (TRL 4)

A major challenge concerning the economic exploitation of the positive properties of MWNTs their occurrence in the form of agglomerates, which often prevents a good dispersion in composites. Recent research expects that neither CNT-agglomerates nor short, mechanically sheared CNTs may transform the desired positive properties of nanotubes into the composites. Hence, it is also the processing of the composites, which plays an important role. The procedure consists of two steps: firstly, based on chemical surface functionalization or by use of suitable dispersants, the CNTs have to be prepared in a way that is principally allowing for a dispersion within the compound. For the utilisation of nanocomposites in an application, a second step requires the adjustment of the recipe to the specific property profiles through the use of further additives, fillers, processing aids, stabilizers, etc.

Due to the numerous interactions between the polymer matrix, the functionalized CNTs, and further additives and auxiliaries, complex processes and lengthy formulation task are mostly required.

In principal there are three ways for the production of thermoplastic matrix composites:

- Mixing of CNTs in polymer solutions and pouring as (thin) films;
- In-situ polymerisation of polymer monomers in presence of CNT; and
- Compounding of thermoplastics with CNT via masterbatches or direct mixing processes.

For industrial applications the compounding with existing techniques is of particular importance. For mixing mainly twin screw extruders are used but even alternative extruding techniques are utilised.[14]

The first practical implementations of thermoplastic polymers have been successfully carried out by the Leistritz Extrusion Technology (Germany). They used co-rotating twin screw extruders, since the required shear can be well realized. As a result of shear stress the CNT primary agglomerates are broken and the majority of the CNTs is dispersed in the polymer. It turned out that the quality of the dispersion of CNTs within thermoplastic polymers depends on several parameters;

- screw stocking (kneading elements)
- extrusion speed
- CNT concentration (> 10% favourable)
- polymer material (e. g. CNTs are easier dispersed in polycarbonate than in polyactide acid.)

Components made of CNT composites can be produced either directly from the extruder or by injection molding. The incorporation of CNTs into different polymers may be made either by a compound or a masterbatch.[15]

Additional demand for research

Within the nanomaterial family, carbon nanotubes probably represent the most prominent and the most promising species. In some respect they are even representative of the whole range of carbon based nanomaterials; however, there is a different R&D-state ranging from fundamental research to market maturity for CNTs depending on the application. A multitude of open questions and a variety of research items remain to be addressed.

In general CNT applications, even within the industrial sector, are expanding rapidly with the first mass production plants now installed. The predominant and most widespread applications are in the composite material sector; however, there is a large number of other applications for CNTs at varying states of development. The most critical applications with respect to the utilization of CNTs are the ones demanding a high purity of specific nanotube types. For electronic applications for example it is crucial to have either pure semiconducting or pure metallic lots of single-walled tubes (SWNT); however, manufacturing pure CNTs remains a challenge. This is also true for the controlled arrangement or a controlled deposition growth of CNTs.

Whereas CNT-based nanoelectronics are still at an early stage, hydrogen storage is somewhat beyond the hype. Original expectations to store significant amounts of hydrogen in CNT-materials have not been realised.

Another promising application is the flat panel display sector. CNTs are discussed as one of the future technologies. First prototypes have already been presented; however, efficient display sealing in mass production has not been achieved yet and even homogeneity of large area CNT-distribution is still an issue. In addition, among future display technologies, CNT-based flat panels face strong competition from both the ever improving LCD technology and the promising OLED approaches. Research effort and funding spent in CNT-display development has been drastically reduced recently. However, it is mainly Asia, that is concerned by this decline, as there are no major display industries located in Europe.

Further demand for intense research may also be seen in biomedical applications. Numerous applications discussed are temporally far ranging and a number of challenges remain to be addressed. One of the most crucial items is biocompatibility. After all biocompatibility and toxicity of nanomaterials, and in particular carbon nanotubes, remain an issue and are up to further investigation.

Commercial realisations and economic potential of CNT-based applications appear different depending on the particular application. In general, there is considerable additional R&D-demand for all areas. Major hurdles for numerous applications are currently lacking purity and homogeneity as well as the difficult production reproducibility of the fabricated raw material. The further development and optimisation of suitable analysis methods for quality control is urgently required. In addition suitable mass production compatible alignment, configuration and contacting methods are still lacking, which is a particular drawback for nano electronics and sensor applications.

Another major challenge is the suitable dispersion of CNT in particular in composite materials and in display technology.

Applications and perspectives

Applications for carbon nanotubes are numerous. According to their stage of development they are already utilized as, or discussed for;

- matrix materials or fillers in composites (large scale utilization, mechanical reinforcement, conductive and antistatic materials/polymers) [TRL 4 to TRL 5]
- lightweight construction [TRL 4]
- electronic devices (large area flat panel displays, nano-electronic transistors, logic circuits, computer memory, quantum information technologies etc.) [TRL 1 to TRL 4]
- opto-electronics (photonic crystals, solar cells) [TRL 1]
- energy storage (hydrogen storage, electrode materials for supercaps, batteries, fuel cells etc.) [TRL 3 to TRL 4]
- sensors (gas, heat, chemicals etc.) [TRL 3]
- actuators (e. g. artificial muscles) [TRL 3]
- medical applications (implants, probes, prostheses, orthopedic equipment, surgical tools, “drug delivery systems” etc.) [TRL 1 to TRL 2]
- nanoscience nanotechnology (AFM-tips, molecular tweezers etc.) [TRL 2]
- chemistry (catalysts, gas adsorbents etc.) [TRL 3]

Current situation within the EU

Within the EU numerous research institutions and groups are involved in carbon nanotube research and development. From a qualitative view they frequently belong to the front end of worldwide research in their respective fields. However, the quantity of research as well as the transition from research to commercial applications often appears much weaker when compared to other world regions. Taking the situation of CNT research and applications, the number of scientific publications and patent applications as well as of public funding activities ranges far behind those of the US and Japan.

European companies appear to be clearly reserved concerning both the utilization of carbon based nanomaterials and investments into appropriate R&D. Whereas in the electronics sector, including displays, Japan and other east Asian countries, as well as the US, are fundamentally dominating applied and transfer research, the European position appears to be more promising in the areas of energy storage, environmental applications, composite materials and nano-toxicity research. Meanwhile, a number of European companies has shown an increasing interest in new electrode materials as well as in carbon based composite materials. In recent years the first large scale CNT production plants have been installed and scaled up. The production capacity meanwhile has been enhanced to several hundred tons per year.

The quality of CNT research in Europe is consistently assessed as being highly valuable. However, research activities are more extensive in the U.S. and East-Asia. This situation, in addition to the technological barriers described above, are currently addressed by larger funding projects for applied research in European states. Examples for these are the "Genesis" program in France or the "Innovation Alliance CNT" in Germany. Thus, further progress and breakthroughs as well as an improvement of the patent situation may be expected from European CNT-activities in upcoming years.

Economic aspects

General market description

This subsection deals with two types of carbon based materials: Carbon Nanotubes (CNTs) and Nanodiamond. Carbon Nanotubes and metal oxides are mentioned to have the best prospect of success concerning nanomaterials in nanotechnology in 2009 to 2014[16].

Carbon nanotubes have always been considered as a future mass market for several applications. However, there has not been a significant commercial breakthrough up to now. Commercially available market studies and future prognoses are most likely science driven and overoptimistic. At least in some fields, e.g. microelectronics, it is very questionable if there will ever be a significant market for CNTs. Furthermore, technological problems, such as control of the chirality and therefore the required physical properties, remain to be solved. A similar discussion was ongoing 20 years ago with polycrystalline diamond films.

Today it appears that polycrystalline diamond can serve some niche markets only, even when polycrystalline diamond films have extreme physical properties, which are at least comparable with diamond, when compared with conventional materials. One key issue of both diamond films, including nanocrystalline diamond films, and CNTs is the exorbitant price of these materials. This was almost overlooked by the scientific community, who were most likely blinded by the excellent physical properties of CNTs.

For the sake of comparison, the experimentally reported physical properties of diamond and single-wall carbon nanotubes (SWCNTs) in relation to silicon are shown in Fig. 4. According to this comparison of physical properties of diamond with SWCNTs, it does not seem appropriate to talk about better properties of CNTs. Only concerning the diameter-to-length ratio and the lower density nanotubes are superior compared to diamond. This leads to the conclusion that the variety of applications where the use of nanotubes exceptionally promises major advancements is limited to a few applications. Examples are reinforcement of polymers or rubber, SPM tips or emitter materials for field emission displays (FEDs).

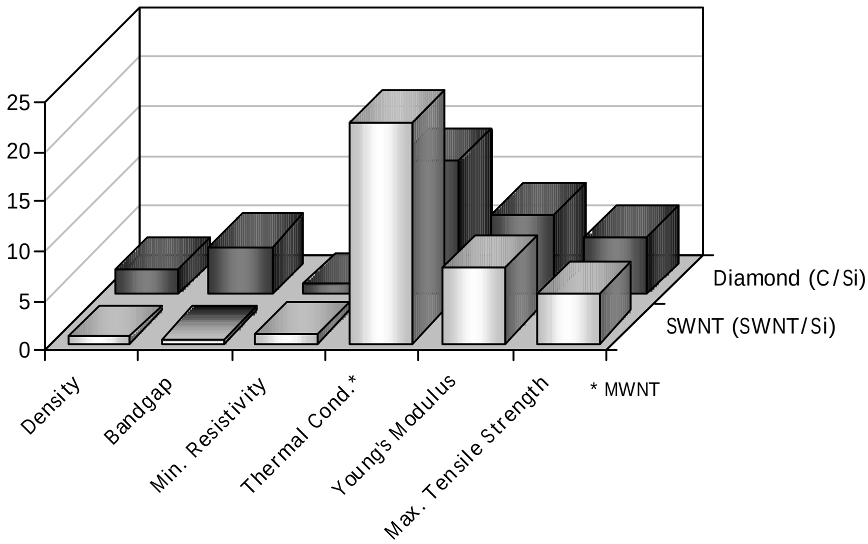

Fig. 4: Selected physical properties of CNTs and diamond normalised to the properties of silicon. (Source: NMTC)

Depending on the quality of carbon nanotubes in terms of purity, defects, single- or multi-wall CNTs etc., current prices of CNTs vary roughly between 1.5 and 1000 $US/g with an average price of 180 $US/g for SWCNTs and 100 €/kg for MWCNTs compared with that of synthetic diamond ranging between 0.5 and 7500 $US/g depending among other things on the fabrication method, quality and size of the crystals. Most of the discussed applications do not take into account the high price of CNTs or possible alternative technologies. Therefore, a large number of possible applications will not be possible due to the high price of CNTs.

	SWNT	MWCNT	Carbon Black[17]	Gold[18]
Price US$/ g	180	0.135	0.001	28

Tab. 2: Material Costs of SWNT and MWNT in comparison to Carbon Black and Gold (only average prices were considered). (Source: NMTC)

According to a market forecast of BCC Research concerning Carbon Nanotubes[19] nearly $51 million was spent on them in 2006. This value should rise up to about $80 million in 2007. Four years later, in 2011, it is estimated that $807.3 million could be reached, but only if a CAGR (compound annual growth rate) of about 74% exists. Taking a look at the fields where CNTs are established, one can see that composites are the biggest sector with a value between $40 million and $45 million in 2006 hence accounting for over 80% of the whole industry in the world. The field of composites is going to rise up to around $450 million in 2011. In the energy sector, Carbon Nanotubes were used only for a very small percentage in 2006 and 2007, but it is estimated that in 2011 this field will reach $53 million, an increase of over 300%.

Drivers and barriers

Looking at the value chain in the Nanomaterials sector, nanotechnology has a big influence in the materials development[5].

Drivers of the materials industry are clearly chemical companies. Through the controlled size-selective synthesis and assembly of nanoscale building blocks a change and manipulation of nearly all material properties can be done in a very strong way. However, the wide ranging synthesis approaches have a number of key challenges that may be summarised as follows:

- The ability to scale-up synthesis and assembly strategies for low-cost, reproducible, large-scale production of nanostructured materials, while maintaining control of critical feature size and quality;
- Control of the size and composition of both Nanodiamond and CNTs; and
- Control of the interface and distribution of nanocomponents within the fully formed materials.

However, the most significant problem is the potential health and environmental risks of nanomaterials. Currently, very little is known about the pathways into the human body and the possible impact of nanomaterials to health. Up to now several kinds of nanomaterials like fullerenes are used in commercially available products such as cosmetics. The impact on health and the environment is not sufficiently clear yet and that this is the reason why the German Federal Environmental Agency (UBA) has most recently given the warning to use products with nanoparticles inside until the effects on the human health are not better explored[20]. This overreaction has produced a lot of protest from the nanocommunity and other ministries. However, if the public is not completely informed this could have an enormous negative impact on nanotechnology related products.

An international research team investigated how carbon-based nanoparticles interact with cells. They found strong biophysical evidence that nanoparticles may alter cell structure and pose health risks depending on the exposure conditions and the interaction between nanoparticles and other compounds in the human body[21]. This can also have significant implications for the commercialisation of products. As long as the consequences of using nanomaterials in commercially available products are unknown some industrial players have serious reservations to use these materials[5] in products even when nanomaterials for specific applications promise a better performance. The same properties that nanomaterials are designed for may cause health and environmental problems. One example is that with decreasing particle size the surface area to mass ratio becomes greater. Therefore, the specific surface and reactivity increases. This property is desired, for example in the case of catalysts, but can also lead to greater toxicity for living organisms.

Due to lack of information, up to now there are many uncertainties as to which conditions nanomaterials are likely to pose health and environmental risks. From this arises an important hurdle for the commercialisation of nanotechnology related products. In addition, other commercialisation aspects can also represent significant hurdles.

Another current challenge is the economic/financial crisis which can be assumed to be far from over. Harper summarised five possible influences of the economic crisis on Nanotechnology in a white paper[22]. He has given arguments that especially venture capital funding of nanotechnology start ups is thin on the ground. Beside a number of possible negative effects the white paper points out positively that now many companies have a clear market focus and address real and critical needs in a cost effective manner.

Recent survey results[23] of European micro, nano and materials enterprises indicate that almost half of the responding small and medium-sized high-tech companies were affected by a decrease in orders and in sales. About two thirds of the responding companies are expecting negative effects on their businesses development in 2009.

At the current stage it is virtually impossible to predict all consequences of the economic crisis on nanotechnology related products. This includes also the nanomaterials sector. According to the authors view, it can be expected that the future development will slow down further and will not only affect small and medium-sized companies but also global players.

Potential health risks that people are concentrating on, appear to be a substantial barrier to carbon nanotubes (CNT)[5]. CNTs had started to be processed and synthesised in massive amounts, but being long, thin and bio-persistent, it is now assumed that they can be carcinogens, which could be the commercial end of CNTs[24]. However, especially health risks of CNTs are widely discussed in the community. One key point for a further understanding could be the surface termination of CNTs. It should be underlined that there are only indicators available which indicate the possible risk of this material. Furthermore, it should be noted that CNTs will most likely have no influence on health if they are incorporated as fillers in composite materials (like polymers) as long as there is no abrasion. Up to now CNTs and health are still an open question which is widely discussed. However, concrete results are still missing.

Nanodiamond thin films are supposed to be completely safe[5] without any negative impact on health. Nanodiamond scalpels are used for eye surgery applications in medicine. However, the production process of diamond is relatively slow and requires a significant amount of energy which makes these films relatively expensive. Furthermore, chemical-vapour deposition of diamond was a scientific hype in the 1990s. After missing success stories and products many companies left this field. Some of these companies concentrated on diamond like carbon films which are currently more mature at least for hard coatings. Therefore, the topic diamond is sometimes considered as an exotic field which makes it more difficult to realise real world applications. Therefore, the “new material” Nanodiamond was clearly overlooked. The physical and chemical properties of this material are clearly outstanding and extreme and offer therefore a wide range of possible applications in the future.

Boundary conditions

An extremely high modulus and elastic strain, in addition to a tensile strength in an order of magnitude higher than that of conventional carbon fibres, make carbon nanotubes the ultimate reinforcement in polymer matrix composite materials and perhaps also in light metals. Additionally, CNTs may be capable of meeting requirements for anti-electrostatic filler for an insulating polymer matrix or for applying electrostatic painting processes. The use of carbon nanotubes as filler materials is expected to increase the electrical conductivity of polymers together with the desired improvement in mechanical properties. Given the predicted annual average growth rate of more than 200 % of polymer nanocomposites, this seems to be a very attractive field in the short term. However, the success of carbon nanotubes in this area will also depend on their price competitiveness compared with other filler materials such as layered silicates, metal nanoparticles or nanofibres.

Other possibly attractive markets for carbon nanotubes include fillers for paints and lacquers in order to increase the electrical conductivity and to avoid electrostatic charging. As already mentioned above, composites filled with carbon nanotubes can be used for light weight tanks and pipes (e.g. for automotive applications). In the case of composites advantage can be taken from the electrical, mechanical and thermal properties of carbon nanotubes. The advantage of taking carbon nanotubes as filler materials is that only small amounts of CNTs have to be used. This fact can compensate the high costs of the CNTs.

Nanofibres are generating great interest in certain industry segments, where alternative materials are characterised by limited performance or much higher unit prices.

Economic information and analysis

Carbon based materials offer a wide range of possible applications. However, carbon as a material with a number of potential applications has been frequently overlooked in the EU. Japan concentrates research and funding on the application of several carbon based materials. A number of Japanese funding approaches illustrate that; one example is funding of CNT research with about €15 million per year[25]. However, even in Europe CNT research has been intensified during recent years. This is indicated among others by large national funding and innovation programs such as "Genesis" in France, which started in 2008 or the "Innovation Alliance CNT" initiated by the German Ministry of Education and Research in 2008/2009.

The current market for CNTs is estimated to a total of approximately $US 10 million for predominantly research grade nanotubes with production quantities of several kilograms[26]. The partly very optimistic future prospects of nanotubes have to be treated very carefully. In most applications discussed, the future progress of CNTs in mass markets depends critically on their price development and price competitiveness compared with alternative materials. Global players like Mitsui & Co., Japan, have announced the start of mass production in the range of 120 tons per year. This massive increase in CNT supply will certainly contribute to bringing down prices and promote the substitution of conventional materials like carbon fibres by CNTs. In a similar way Bayer MaterialScience (Germany) very recently started a CNT-production plant with a capacity of 200 tons per year and wants to increase this to 3000 tons p. a. in the medium term. Arkema (France) announced the construction of a CNT pilot production plant based on entirely bio-sourced raw material with a capacity of 400 tons per year starting from 2011.

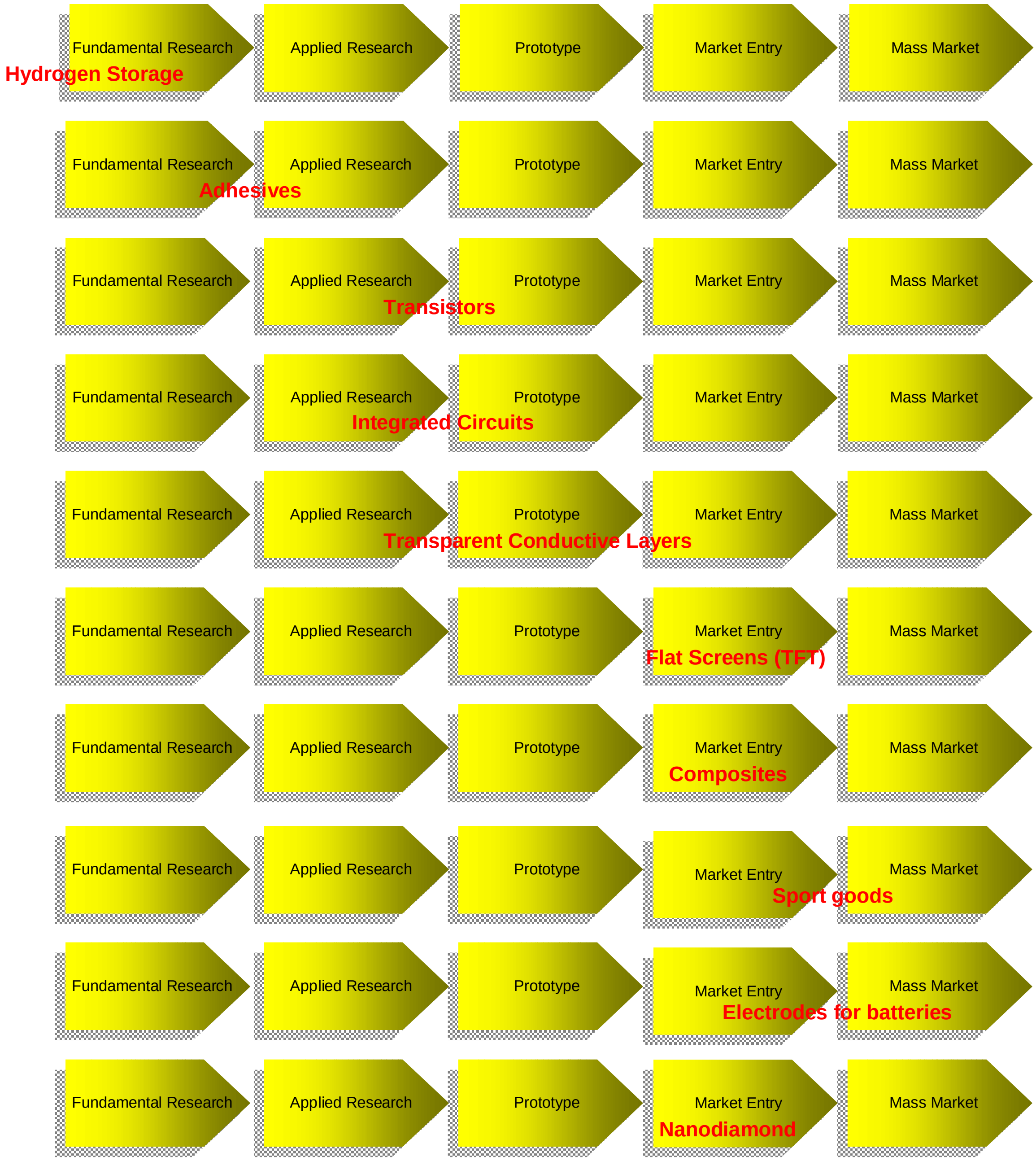

Fig. 5: Value-Added Chain of Carbon Nanotubes and Nanodiamond

The application of Carbon Nanotubes and Nanodiamonds in various fields is shown in Fig. 6. It can be seen as a value-added chain where the products using Carbon Nanotubes and Nano-diamonds are listed according to their stadium of application. Carbon nanotubes for example can be used for sport goods, transistors or flat screens.

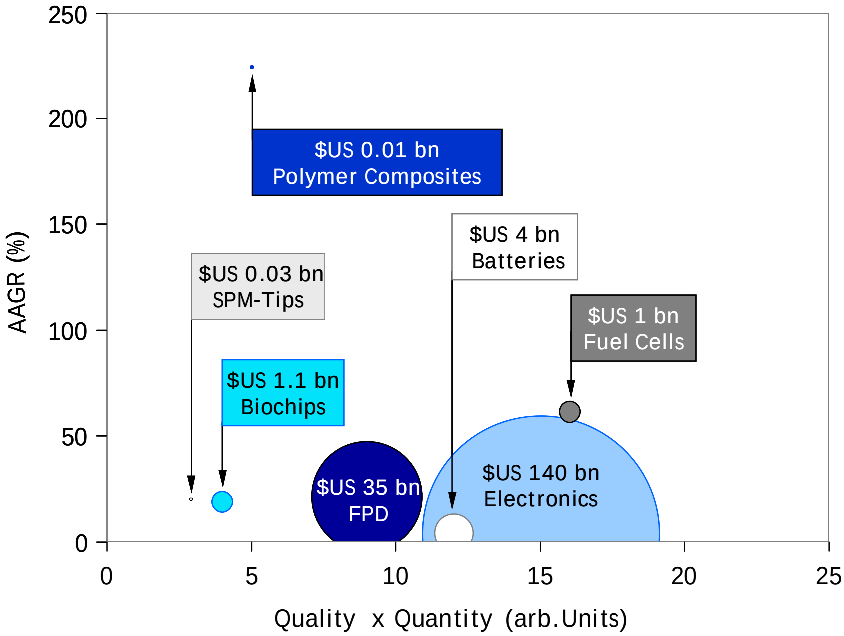

Fig. 6: Market sizes and growth rates versus market requirements of possible end markets for CNT products

Patent analysis

Carbon Nanotubes

To get an overview of patents with reference to carbon nanotubes, which were published during the last years, both the patent database of the World Intellectual Property Organization (WIPO) and the European Patent Office´s (EPO) free online service "esp@cenet" were analysed. "esp@cenet" showed 3500 hits regarding European patent applications[27].

Fig. 7 and Fig. 8 focus on WIPO applications.

As shown in Fig. 7 the number of patent applications published each year was nearly constantly growing from 1 in 1995 to 309 in 2008. The number of applications in 2009 is not yet fully available. Due to the publication delay correct numbers will not be available before late 2010.

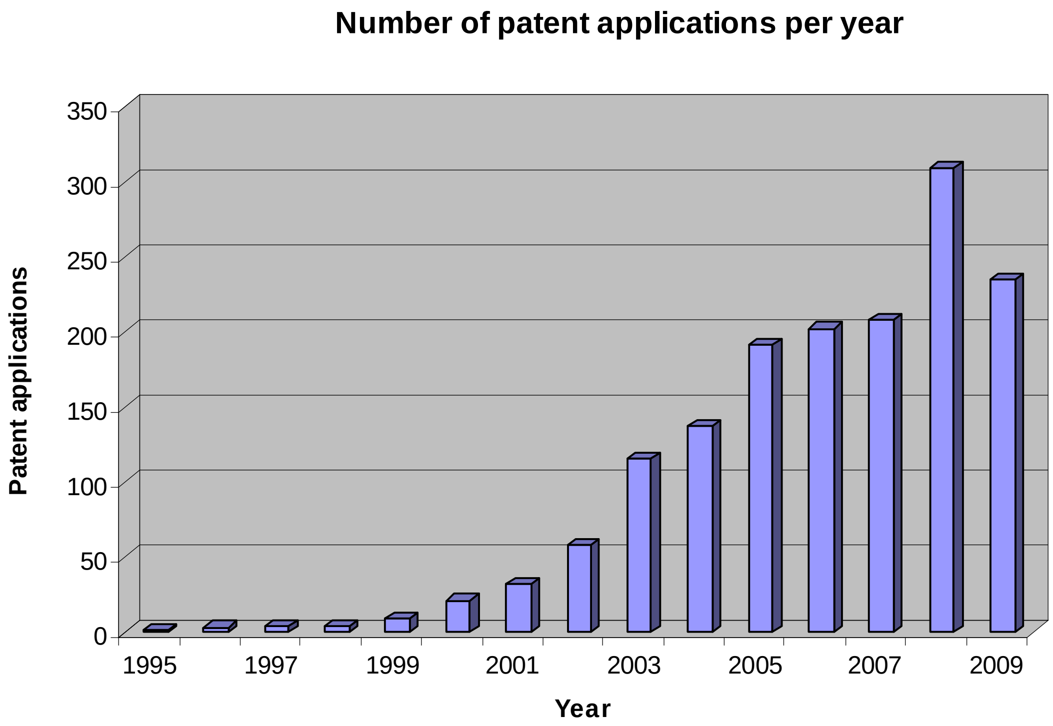

Fig. 7: Number of patent applications per year concerning Carbon Nanotubes (Source: WIPO patentscope; keyword search; date of data acquisition: 2009, 29th November)

The WIPO patentscope[28] offers the possibility of a country assignment of patent applications to the first applicant´s country giving a rough impression on where the new invention has been made. Fig. 8 illustrates the number of patent applications assigned to individual countries from 1995 until now.

According to Fig. 8 the United States published about half of the patents during the last 14 years, in comparison to the rest of the world. They are followed by Japan, South Korea, France and Germany. If the numbers of inventions made by all of the European countries (France, Germany, Great Britain, the Netherlands, Belgium etc.) are summarized into one representative amount, it can be seen that Europe takes third place after the USA and Japan.

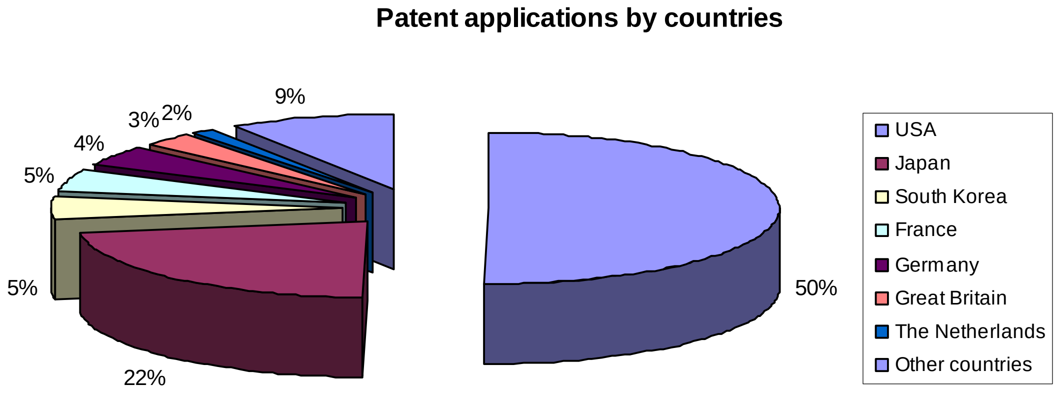

Fig. 8: Patent applications by countries concerning Carbon Nanotubes (Source: WIPO patentscope; keyword search; date of data acquisition: 2009, 29th of November)

Nanodiamond

Nanodiamond or Ultrananocrystalline diamond (UNCD) is currently less attractive when compared with CNTs; at least according to the number of patent applications. The database of the European Patent Office shows only 113 hits when searched for patent applications with variations of the keyword "Nanodiamond".

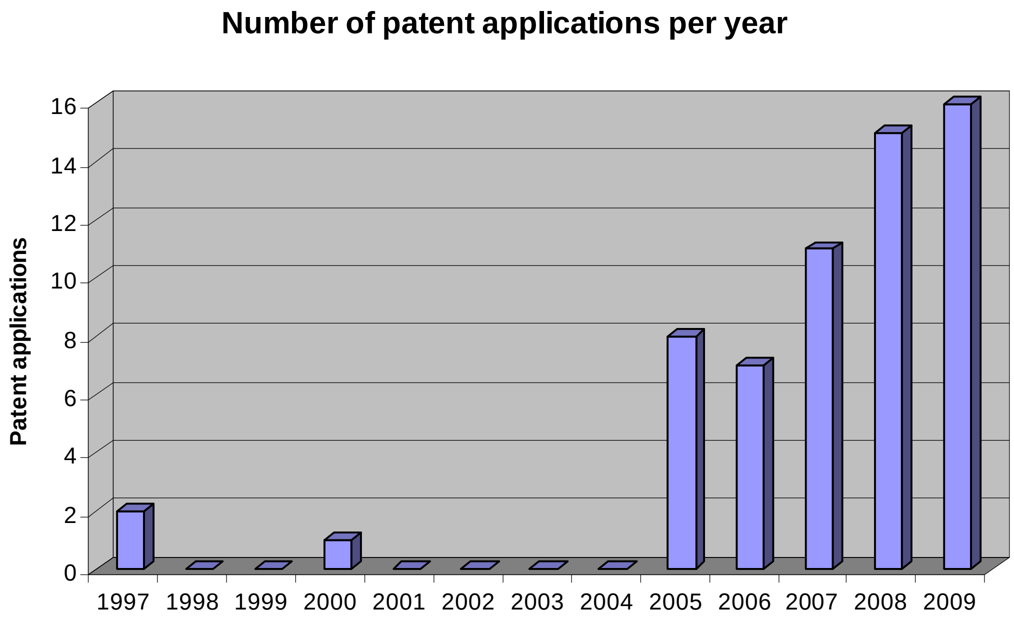

Fig. 9: Number of patent applications per year concerning Nanodiamonds (Source: WIPO patentscope; date of data acquisition: 2009, 21st of October)

An overview of international patent applications in the field of nanodiamonds concerning their quantity during the last few years, as well as their country of origin, is visualised in Fig. 9 and Fig. 10. The relating figures have been extracted from the patent database of the World Intellectual Property Organization (WIPO).

Looking at the number of published patents per year it can be asserted that the amount of patents is nearly not recognisable until 2005. Afterwards there was a more or less constant growth of the number of patents until now.

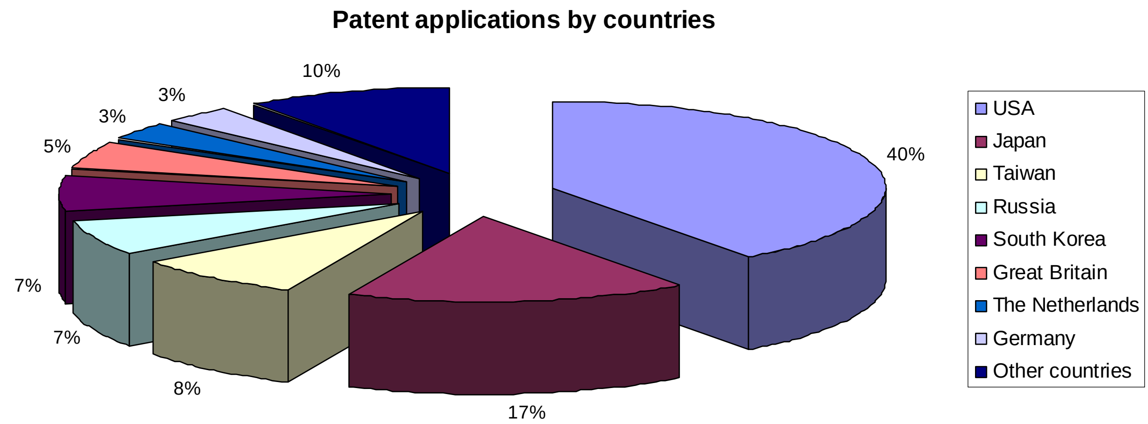

Fig. 10: Patent applications by countries concerning Nanodiamonds (Source: WIPO patentscope; keyword for the advanced search: Nanodiamond; date of data acquisition: 2009, 21st of October)

Fig. 10 illustrates that the United States published most of the patents since 1993 followed by Japan and Taiwan. Summarising the number of patents in Europe during the last 16 years results in the second position for Europe directly following the USA and ranking in front of Japan.

Selected company profiles

Arkema

Arkema[29] is a global chemical company and France´s leading chemicals producer, Arkema consists of three businesses: Vinyl Products, Industrial Chemicals, and Performance Products. Arkema reports sales of 5.6 billion euros. Arkema has 15,000 employees in over 40 countries and six research centers located in France, the United States and Japan. Arkema is one of the leading European producers of CNTs. A 400 tons per year production plant is currently planned to start in 2011 in southern France.

Bayer MaterialScience AG

The Bayer MaterialScience AG (BMS) is the subsidiary of the Bayer AG with the main focus on materials research[30]. It was founded in 2004 due to a restructuring of its parent company and has its headquarters in Leverkusen, Germany. The BMS is one of the leading manufacturers in the field of plastics and polymers. The company can be divided into three sections; coatings/adhesives/specialties, polycarbonates and polyurethanes. In 2008 the volume of sales accounted for € 9,738 billion. Chemical products that are produced by the BMS are for example waterbased dispersions like Hydroxy functional polyurethane dispersions (PUD) - Bayhydrol® U 241 or aromatic isocyanates like Desmodur® RFE.

Donaldson

The company Donaldson was founded in 1915 and is a leading provider of filtration systems[31]. Concerning the section of materials Donaldson is operating in the development of nanofibres and filtration using nanofibres. Products of Donaldson are Ultra-Web® filters, Spider-Web® filters and Donaldson EnduranceTM air filters. This company also produces membranes using the polymer PTFE. Those products are distributed under the trade name Tetratex® [28].

Nanocyl S.A.

Nanocyl is Belgium based chemical enterprise and a leading global manufacturer of CNT-Technologies[32]. The focus is on CNT production, engineering and services. Nanocyl offers a variety of CNT-based products such as synthetic materials, automotive and electronic components, lifestyle products etc. The company co-operates with scientific organisations and other high-tech companies. Nanocyl´s R&D-effort is currently nearly 40 % of the total budget.

Hyperion Catalysis

The foundation of Hyperion Catalysis International was in 1982[33]. The company is leading in the field of Carbon Nanotubes. The developed nanotubes are distributed under the name FIBRIL™ nanotubes. The company produces composites consisting of nanotubes and plastics where the tubes make the plastic electrical conductive.

Thomas Swan & Co. Ltd.

Thomas Swan & Co. Ltd. has existed since 1926 and is a leader in the manufacturing section[34]. One of its product fields are materials for the future, including carbon nanomaterials. Since 2004, the company is producing single-wall carbon nanotubes (Elicarb SW) and multi-wall Carbon Nanotubes (Elicarb MW).

FutureCarbon GmbH

Based in Bayreuth (Germany) FutureCarbon[35] is a high-tech company focused on production of carbon based nanomaterials such as carbon nanotubes and nanofibers. Goals are application oriented production of raw materials and material refinement in industrially relevant volumes. Both synthesized carbon nanomaterials and natural graphite are processed. Specific application foci are on dispersions, composites (resins), powders, granules and metallic systems (e. g. carbon-metal composites).

GFD - Corporation for diamond products (Gesellschaft für Diamantprodukte mbH)

Founded in 2004 in Ulm (Germany), GFD is one of the leading enterprises in micro-structuring of diamond and fabrication of diamond layers[36]. One of the most important products is plasma sharpened diamond coated carbide blade edges (Diamaze PSD). Other activities are on the manufacturing of pure diamond micro parts and with nanocrystalline diamond coated silicon parts. The micro components are distributed by Diamaze Microtechnology SA, a subsidiary of GFD based in La Chaux-de-Fonds (Switzerland).

References and Literature

[1] Brand L., Gierlings M., Hoffknecht A., Wagner V., Zweck A.: Kohlenstoff-Nanoröhren - Potenziale einer neuen Materialklasse für Deutschland, Schriftenreihe Zukünftige Technologien Band 79, ISSN 1436-5928, Hrsg. VDI-Technologiezentrum Düsseldorf, Jan. 2009.

[2] Baughman, R.H., Zakhidov, A., de Heer, W. A., Carbon Nanotubes - The route toward applications, Science, 297, 787-792, 2002.

[3] Coleman, J.N., Khan, U., Gun'ko, Y.K., Mechanical reinforcement of polymers using carbon nanotubes, Advanced Materials, 18, 689-706, 2006

[4] Available at http://www.electronics.ca/presscenter/articles/743/1/Carbon-Nanotube-Production-Dramatic-Price-Decrease-Down-to-150kg-for-Semi-Industrial-Applications/Page1.html (Feb. 6th, 2008)

5 Interview result

[6] A. M. Thayer; Carbon Nanotubes By The Metric Ton; C&EN Vol. 85, 46, p29, Nov. 2007 (http://pubs.acs.org/cen/business/85/8546bus1.html)

[7] Cheaptubes (http://www.cheaptubesinc.com/, July 2009)

[8] Arry Nanomaterials, Nanotechnology (http://www.arry-nano.com/, July 2009)

[9] Electronics.ca "Carbon Nanotube Production Dramatic Price Decrease Down to 150kg for Semi Industrial Applications" Feb. 18, 2008

[10] "Nano Tech 2008" Vol. 1/Sangyo Times Inc

[11] Chemie.de information service; "Arkema to build Carbon Nanotube pilot plant in France" Sep. 21, 2009.

[12] http://www.future-carbon.de/index.php?id=45

[13] http://www.empa.ch/plugin/template/empa/1173/*/---/l=1

[14] U. Wagenknecht, B. Kretzschmar, P. Pötschke, F. R. Costa, S. Pegel, K.W. Stöckelhuber, G. Heinrich, Chemie Ingenieur Technik 2008, 80 No 11, p 1683

[15] VDI Conference "Plastics Processing Technologies 2008", Cologne

[16] Interview result

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17 The carbon black price depends very much on the quality. Therefore, the price can be only considered as a guideline.

18 The gold price showed a dramatically increase over the past few months due to the economic crisis. The value was taken from the Bundesverband Deutscher Banken. The gold value is $ US 870 per ounce (compared with $272 per ounce in the year 2000)

19 Available at http://www.bccresearch.com/report/NAN024C.html (Nov. 6th, 2009)

20 Available at http://www.spiegel.de/wissenschaft/mensch/0,1518,656362,00.html (Nov. 6th, 2009)

21 E. Salonen, S. Lin, M. L. Reid, M. Allegood, X. Wang, A. M. Rao, I. Vattulainen, P.-C. Ke. Real-time translocation of fullerene reveals cell contraction. Small, 4, 1986-1992 (2008)

22 T. Harper, Nanotechnologies in 2009 – Creative Destruction or Credit Crunch?, Cientifica, 2009; Available at http://www.cientifica.eu/attachments/054_Nanotechnologies%20in%202009.pdf (Nov. 6th, 2009)

23 Available at http://www.ivam.de/index.php?content=mitteilung_details&mitteilung_id=1424&typ=presse (Nov. 6th, 2009)

24 Available at http://epa.gov/ncer/publications/workshop/10_26_05/abstracts/hurt.html (Nov. 6th, 2009)

25 L. Brand et al., Kohlenstoff-Nanoröhren: Potenziale einer neuen Materialklasse für Deutschland (in German), VDI Technologiezentrum GmbH, Düsseldorf, 2009.

26 Interview result

27 Available at http://**Fehler! Hyperlink-Referenz ungültig.** (Nov. 16th, 2009)

[28] WIPO patentscope available at http://www.wipo.int/pctdb/en/

29 www.arkema.com

30 Available at http://www.bayercoatings.com/bms/db-rsc/bms_rsc_cas.nsf/id/en_portal (Nov. 6th, 2009)

31 Available at http://www.donaldson.com/ (Nov. 6th, 2009)

32 www.nanocyl.com

33 Available at http://www.fibrils.com/ (Nov. 6th, 2009)

34 Available at http://www.thomas-swan.co.uk/ (Nov. 6th, 2009)

[35] http://www.future-carbon.de/

36 Available at http://diamaze-gfd.com/ (Nov. 27th, 2009)

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