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Carbon Nanotube Fabrication: Patent Analysis

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1. Introduction

Patent documents contain important results of research and development. These documents have long been recognized as a very rich and potentially fruitful source of data for the study of innovation and technological change (Choi et al., 2007). Patent analysis is a valuable method that transfers patent documents into systematic and useful information. The information is helpful to evaluate technological development, monitor technological trends, manage R&D process, and make technological strategies (Chang et al., 2010). In general, patent bibliometric analysis is most commonly used to implement patent analysis (Narin, 1994). Bibliometric data that include such information as patent number, country, inventor, assignee, date of application, and so forth in patents are used to analyze the development and distribution of the patented technology. Furthermore, patent network analysis is an advanced technique of patent analysis suggested by Yoon & Park (2004). This method shows the overall relationship among all patents being studied as a visual network. Researchers can comprehend the overall structure intuitively and identify the influential patents in the patent network.

In the field of nanotechnology, carbon nanotubes (CNTs) possess important roles and technological key factor (Kuusi & Meyer, 2007). CNTs are composed of grapheme sheets rolled into seamless hollow cylinders with diameters within 50 nm. The fabrication of nanotubes is not a difficult task, since they can be found also in common environments such as the flame of a candle. But it is very difficult to control their size, orientation and structure, in order to be able to use them for technological tasks. In 1991, multi-wall nanotubes (MWNTs) were firstly discovered in a carbonaceous stalagmite-like deposit by Iijima (1991), which was the by-product of the fullerene growth process on the electrode. Then, single-wall nanotubes (SWNTs) were discovered in 1993 during the course of synthesizing carbon nanocapsules filled with magnetic fine metal particles (Fe, Co, Ni) (Iijima & Ichihashi, 1993; Bethune et al., 1993). The commonly manufacturing processes of CNTs contain different types of manufacturing technology such as arc-discharge, laser ablation, and chemical vapor deposition (CVD). Arc-discharge and laser ablation methods for the growth of CNTs have been actively pursued in the past ten years. Both methods involve the condensation of carbon atoms generated from evaporation of solid carbon sources. The temperatures involved in these methods are close to the melting temperature of graphite, 3000-4000^{o}C. Recent interest in CVD nanotube growth is also due to the idea that aligned and ordered CNT structures can be grown on surfaces with control that is not possible with arc-discharge or laser ablation techniques.

From recent research, CNTs have been demonstrated to possess remarkable mechanical, electronic and thermal properties with providing strong, light and high toughness traits. On mechanical properties, CNTs have high perfection in their structures and highest modulus of all known materials (Treacy et al., 1996). On electronic properties, CNTs are either metallic or semimetallic depending on the geometry (Saito et al., 1992). On thermal properties, thermal conductivity of CNTs is about twice as high as diamond (Thostenson et al., 2001). Due to these ideal properties, CNTs exhibit unique physical and chemical characteristics as being revolutionary advanced materials. Furthermore, CNTs have been proposed as new materials for single-molecular transistors, catalyst supports, electron field emitters in panel displays, molecular-filtration membranes, gas and electrochemical energy storages, energy-absorbing materials, and scanning probe microscope tips (Kuusi & Meyer, 2007).

Several studies have successfully revealed the use of patent analysis to analyze the development of nanotechnology (Hullmann, 2007; Wong et al., 2007; Chang et al., 2010). Recently, a great deal of attention is being paid to CNTs which represent novel and popular nanomaterials. CNTs have many extraordinary properties and different kinds of applications. Even though CNTs have many advantages and potential, currently some technical bottlenecks need to be solved. Therefore, it is necessary to monitor the current states and the future trends of the emerging technology before the next stage of technological development. This study implements patent analysis to explore the technological states and trends of CNTs in order to assist researchers in executing and managing technology for CNT fabrication.

In this study, patent bibliometric analysis and patent network analysis are used to analyze patents for CNT fabrication. First, we use patent bibliometric analysis to analyze bibliometric data in the patent documents for finding the developmental path of CNT fabrication and its current states. Then, we draw a network graph of the patents regarding CNT fabrication by using patent network analysis. We seek to find the overall relationship among the patents in the patent network and grasp the key technology of CNT fabrication. Finally, we suggest future directions and trends of CNT fabrication based on the results of analyses.

2. Methodologies

2.1 Data collection

The data of patent documents in the field of CNT fabrication were collected from the U.S. Patent and Trademark Office (USPTO) database available at www.uspto.gov. The search was made by looking for the code “carbon nanotube” or “CNT” in the titles of patent documents in recent ten years. Five experts in the area of CNT then reviewed the search results and eliminated the irrelevant ones. 97 patents issued from 2001 to 2010 were collected. The data set contains patents from U.S. Patent No. 6,331,690 to U.S. Patent No. 7,854,991. However, because the patent numbers are too long to be usable for patent analysis, the patents were sorted by issue date and labeled with serial numbers from 1 to 97, with number one being the oldest patent.

2.2 Patent bibliometric analysis

Patent bibliometric analysis is a research method utilizing bibliometrics to perform patent information analysis in order to evaluate technological activities (Narin, 1994). Bibliometric data such as patent number, document type, date of issue, country, title, inventor, assignee, international patent classification, date of application, and so forth in patent documents are analyzed (Gupta & Pangannaya, 2000). Hence, the researcher can perform statistical calculations on the chosen set of bibliometric data to analyze the development and distribution of the patented technology. In this study, patent bibliometric analysis would be used to analyze 97 patents about CNT fabrication to uncover the developmental path and current states of CNT fabrication

2.3 Patent network analysis

Network analysis attempts to describe the structure of interactions (edges) between actors (nodes). Actors are the given entities in the network. The relationship among actors and the location of individual actors in the network provide rich information and assist the researcher in comprehending the overall structure of the network (Wasserman & Faust, 1994).

In recent, Yoon & Park (2004) used the concept of network analysis in patent analysis, and suggested patent network analysis. Particularly, Chang et al. (2010) applied this method to analyze the technological trends of carbon nanotube field emission display (CNT-FED) technology. This method uses the frequency of keywords occurrence in patent documents as the input base to produce a visual patent network. The relations among patents represent edges in the patent network while individual patents represent nodes. Patent network analysis visually displays all the relationship among the patents and assists the researcher in intuitively understanding the entire structure of the patent database. In addition, because network analysis uses several patent keywords as its input, this method is capable of detecting the internal structure of patent network and thereby produces useful results.

Patent network analysis uses two mathematical tools to present the information from the patent network, namely graph and quantitative technique. Graph can visually display the structure of a set of patents by generating a patent network. However, if too many patents are involved or a wide variety of patent relationship exits, graph will become too complicated to show the exact relationship among the patents. In this case, the indexes calculated from quantitative technique can clearly show the information on the patent network.

Following patent bibliometric analysis, patent network analysis would be used to examine the overall relationship among the patents about CNT fabrication and to find out the key patents. Primarily, this study adopts the below steps to graph the patent network:

Step 1. Technical experts select the relevant patent keywords based on the substance and characteristics of the patented technologies.

Step 2. Calculating the frequency of keywords occurrence in patent documents and integrate the data into keyword vectors. The keyword vectors from patent 1 to patent *m* are as follows:

$$\text{Patent 1: } (k_{11}, k_{12}, k_{13}, \cdots, k_{1n})$$

$$\text{Patent 2: } (k_{21}, k_{22}, k_{23}, \cdots, k_{2n})$$

$$\vdots \quad \vdots$$

$$\text{Patent } m\text{: } (k_{m1}, k_{m2}, k_{m3}, \cdots, k_{mn}) \tag{1}$$

For example, in the document of patent 1, the first keyword occur k_{11} times, the second keyword occur k_{12} times and so on as above.

Step 3. Utilizing Euclidian distance to calculate the distance between the patents and to establish the relationship among patents. If keyword vectors of patent *i* and patent *j* are defined as $(k_{i1}, k_{i2}, \cdots, k_{in})$ and $(k_{j1}, k_{j2}, \cdots, k_{jn})$ respectively, the Euclidian distance value (E_{ij}^d) between the two vectors is computed as follows:

$$E_{ij}^d = \sqrt{(k_{i1} - k_{j1})^2 + (k_{i2} - k_{j2})^2 + \cdots + (k_{in} - k_{jn})^2} \qquad (2)$$

Step 4. Euclidian distance matrix (E^d matrix) is composed of all Euclidian distance values among all vectors. However, the E^d matrix must be dichotomized in order to graph the patent network. It is necessary to transform the real values of E^d matrix into standardized values from 0 to 1 for dichotomizing in the next step.

$$E_{ij}^s = \frac{E_{ij}^d}{Max(E_{ij}^d, i = 1, \cdots, m\,; j = 1, \cdots, m)} \qquad (3)$$

The E^d matrix is interpreted as dividing the all values of E^d matrix by the maximum value of E^d matrix. The all values of E^s matrix are from 0 to 1.

Step 5. The cell of the E^s matrix must be a binary transformation, comprising 0s and 1s if it is to exceed the cut-off value *p*:

$$I_{ij} = \begin{cases} 1, & \text{if } E_{ij}^s < p \\ 0, & \text{if } E_{ij}^s \geq p \end{cases} \qquad (4)$$

The *I* matrix includes binary value where I_{ij} equals 1 if patent *i* is strongly connected with patent *j*. I_{ij} equals 0 if patent *i* is weakly connected with patent *j* or not at all connected. That is, if the E^s value is smaller than the cut-off value *p*, the connectivity between patent *i* and patent *j* is regarded as strong and the I_{ij} value is set to 1. Otherwise, the connectivity is considered weak and the I_{ij} value is set to 0. The determination of cut-off value is a task of trial-and-error. The researcher has to select a reasonable cut-off value so that the structure of the network becomes clearly visible. Then, the *I* matrix can be employed to develop a patent network.

Subsequently, the quantitative technique which contains two indexes can be utilized to examine the structure of the patent network. The first index that finds out the relatively important patents in the patent network is technology centrality index (TCI):

$$TCI_i = \frac{C_i}{n-1} \qquad (5)$$

$$C_i = \sum r, \; r\text{: ties of patent } i$$

where n denote the number of patents. TCI of a patent network is interpreted as the ratio of the number of tied links to all n-1 other patents. It measures the relative importance of a subject patent by calculating the density of its linkage with other patents. That is, the higher the TCI, the greater the impact on other patents. TCI can be used to identify the influential patents in the field of the technology being studied. Moreover, detailed information on these influential patents needs to be obtained. Technological and strategic implication can be deduced from the information as well.

Moreover, the second index called technology cycle time (TCT) index can be used to measure the trends of technological progress in overall network. Let T_i be the application date of patent i, and the formula for calculating TCT index of patent i is shown below:

$$TCT_i = \underset{j}{Median}\left\{ \left| T_i - T_j \right| \right\} \tag{6}$$

where patent j and patent i are connected. It is defined as the median value of age gaps between subject patent and other connected patents. Shorter cycle time reflects faster technology progress; longer cycle time reflects slower technology progress. Thus, patents relating to a rapidly progressing technology should have a smaller TCT index than patents relating to a slowly progressing technology. The changing trends of technological advancement can be detected through calculating TCT index.

3. Results of patent bibliometric analysis

The bibliometric techniques were used to analyze the status of technological development for CNT fabrication in this study. Looking at the different aspects of patenting activities such as growth in patents, country analysis, assignee analysis, co-inventors analysis, and productivity of inventors; the main goal of this investigation is to comprehend the developmental path and current states of CNT fabrication.

3.1 Growth in patents

Figure 1 indicates the growth in the number of patents in the field of CNT fabrication. The earliest patent was issued in 2001 among the collected 97 patents. The patenting activity is mostly presented from 2007 to 2010 by the issue dates, and the majority of patents are filed from 2003 to 2006 by the application dates. In general, it takes about 2-4 years to move from patent application to patent issue. Either the date of issue or application shows that CNT fabrication is still attracting much interest in nanotechnology after 2000. This is confirmed by the fact that Sumio Iijima of the NEC Laboratory in Japan reported the first observation of MWNTs in 1991. After that, significant research efforts in efficient and high-yield CNT growth methods were continually described. The success in CNT growth has led to the CNT related patents. Nevertheless, the number of patent application decreased after 2007, the reason for the phenomenon may be due to the basic science issues needed to be understood and technological bottlenecks needed to be overcome. Currently, the main bottleneck in CNT fabrication is probably one of the main issues either to develop a mass production process or to control growth in order to obtain well-designed nanotube structure. If the trouble is solved, the growth can be expected for the patents and products.

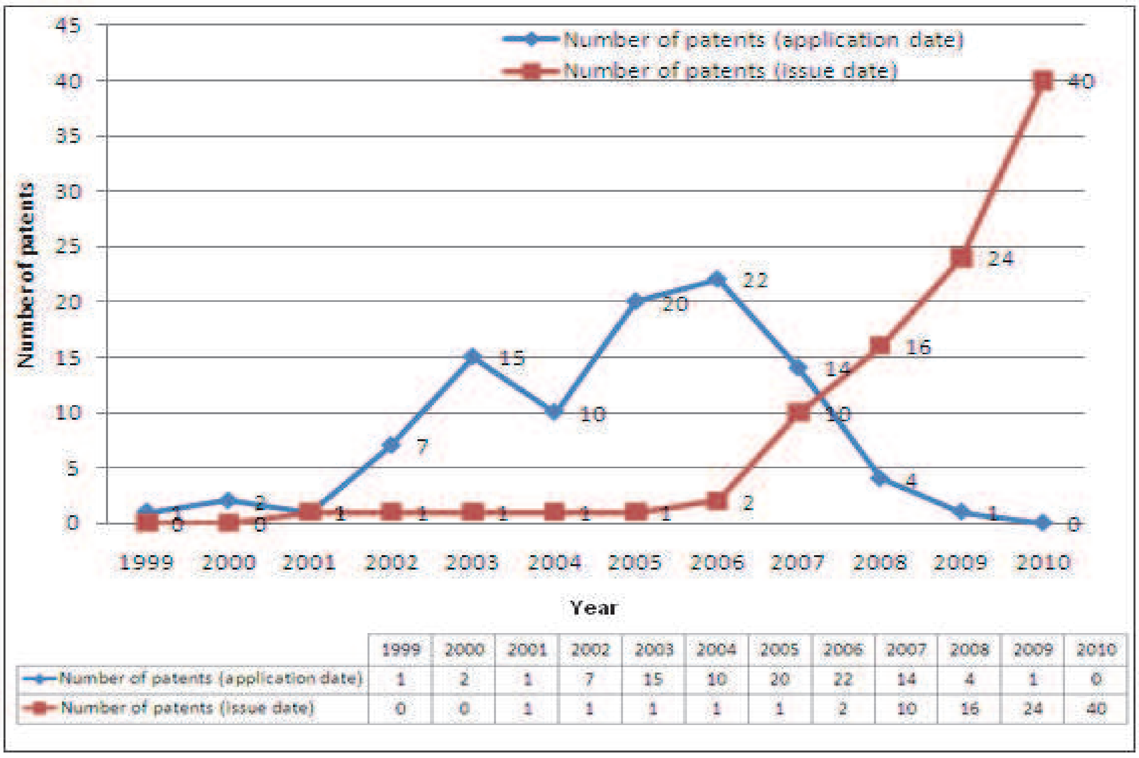
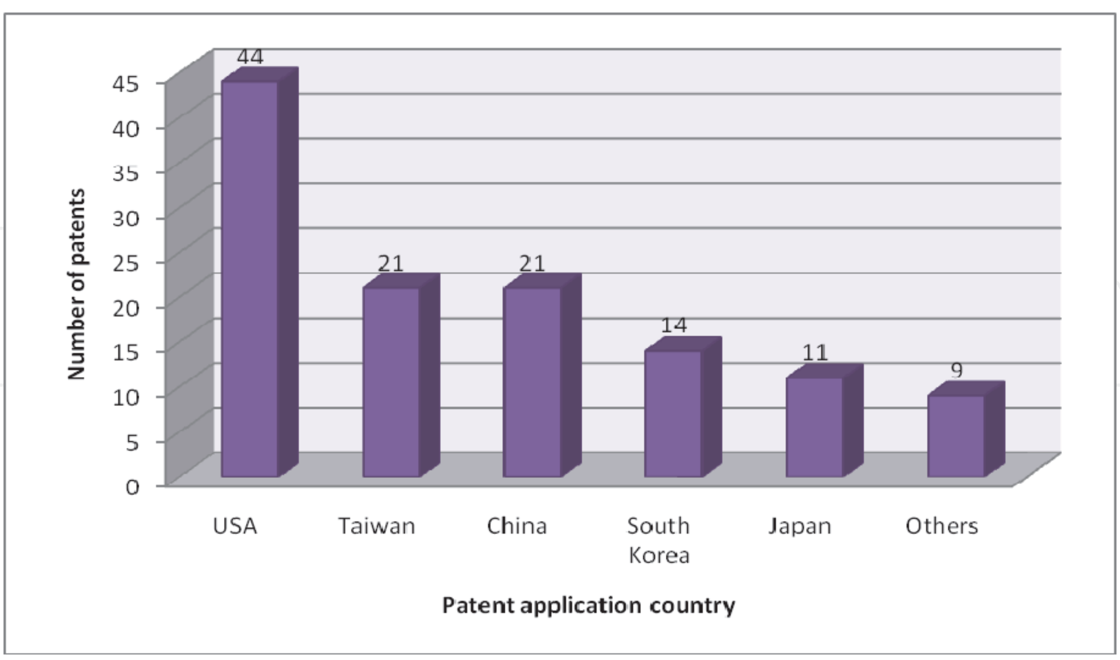


Fig. 1. Growth in patents

3.2 Country analysis

Figure 2 shows the distribution of patenting activity in different countries. USA is the most active in patents for the field of CNT fabrication. This result confirms the fact that USA owns



Note: There is discrepancy between "total number of all patents of all countries" and "total number of all patents" because 23 patents were filed by two countries at the same time.

Fig. 2. Country analysis

the leading status in material science of nanotechnology. In fact, the systematic study of carbon filaments of very small diameters came from the discovery of fullerenes (C_{60}) by Harold Kroto, Richard Smalley, Robert Curl, and coworkers at Rice University, USA before 1991. Of course, a great deal of progress has been made in characterizing and understanding the unique properties of CNT in USA since the Iijima's discovery in 1991. In addition, the other countries in figure 2 are Taiwan, China, South Korea and Japan according to the number of patents. This phenomenon means that these Asian countries attach great importance to CNT fabrication research.

3.3 Assignee analysis

Figure 3 provides the patenting activity of assignees ranging from corporations, academic institutes, R&D institutes, government institutes, consortiums of corporations and academic institutes, and individual. The data indicate that corporations are the most active assignees which own 51 patents and occupy 52.58%; the second are consortiums of corporations and academic institutes which own 19 patents and occupy 19.59%; the third are academic institutes which own 17 patents and occupy 17.53%. In fact, CNTs arouse great interest in the research community because of their strange electronic properties, and this interest continues as other remarkable properties are discovered and promised for practical applications develop by industrials. Because the CNT fabrication belongs to the highly interesting material, not only corporations but also academic institutes play important role in assignee for CNT related basic research.

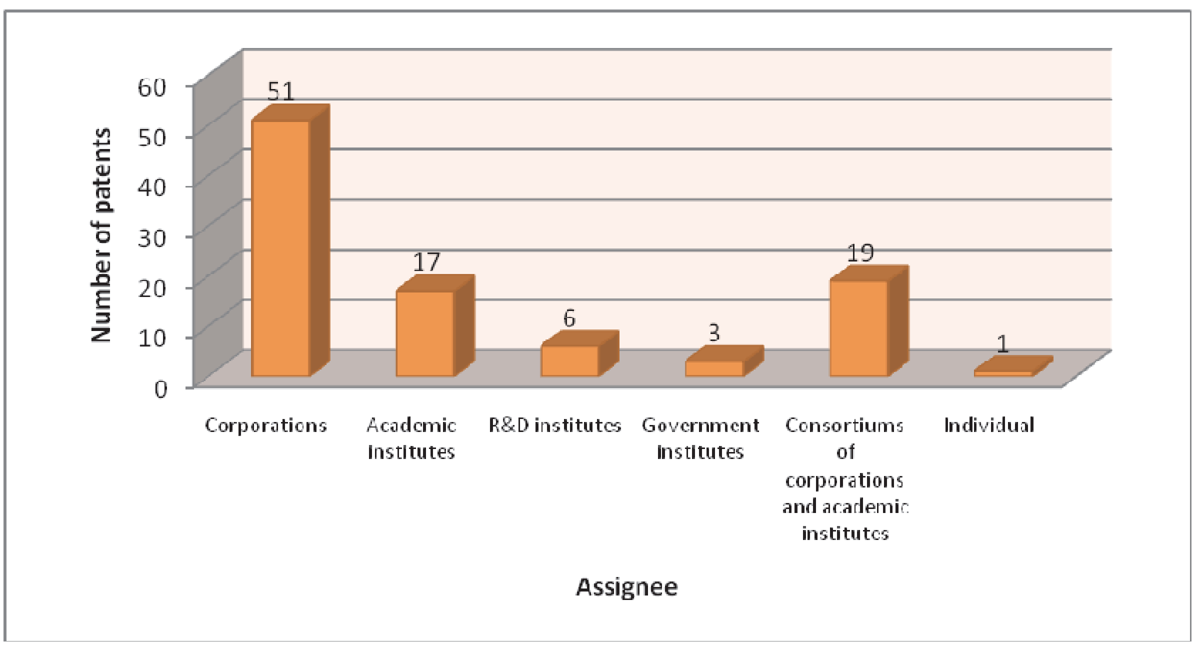


Fig. 3. Assignee analysis

This study further analyzes each assignee to find out the active assignees in CNT fabrication. In the corporate assignees, Samsung from South Korea is the most active company in the field of CNT fabrication. The second active corporations are Intel and IBM from USA as well as NEC from Japan. In fact, these companies possess the important status in the field of nanotechnology, and all of them take CNT fabrication seriously at this moment. In the academic institutes, most of patents were applied from several universities

in USA. This confirms that academic institutes in USA play the important roles in CNT basic research. In the R&D institutes, the Industrial Technology Research Institute (ITRI) from Taiwan is the most active assignee. ITRI is the main R&D institutes in Taiwan, and the manufacturing technology of CNT is one of their developmental directions in applications of field emission displays (FEDs). In the government institutes, the three assignees are from USA, and all these patents are produced from USA government subsidy plan.
Among all consortiums of corporations and academic institutes, there are 18 patents were filed jointly by Hon Hai Precision Company in Taiwan and Tsinghua University in China. This cooperation shows that the two assignees have grasped the critical technologies in CNT fabrication and these technologies were expected to create the marketable product in the future. For the individual, the only one patent was filed by inventor Cheol-Jin Lee.

3.4 Co-inventors analysis

Figure 4 shows the pattern of co-inventorship in the field of CNT fabrication. Among all 97 patents, only 15 patents are from single inventors, and the other 82 patents are from co-inventors. More than half of all patents are from two or three inventors. The remaining patents come from four or more inventors. The highest number of inventors for one patent is 9 persons. Thus, it is clear that research in CNT related project is most frequently done by teamwork.

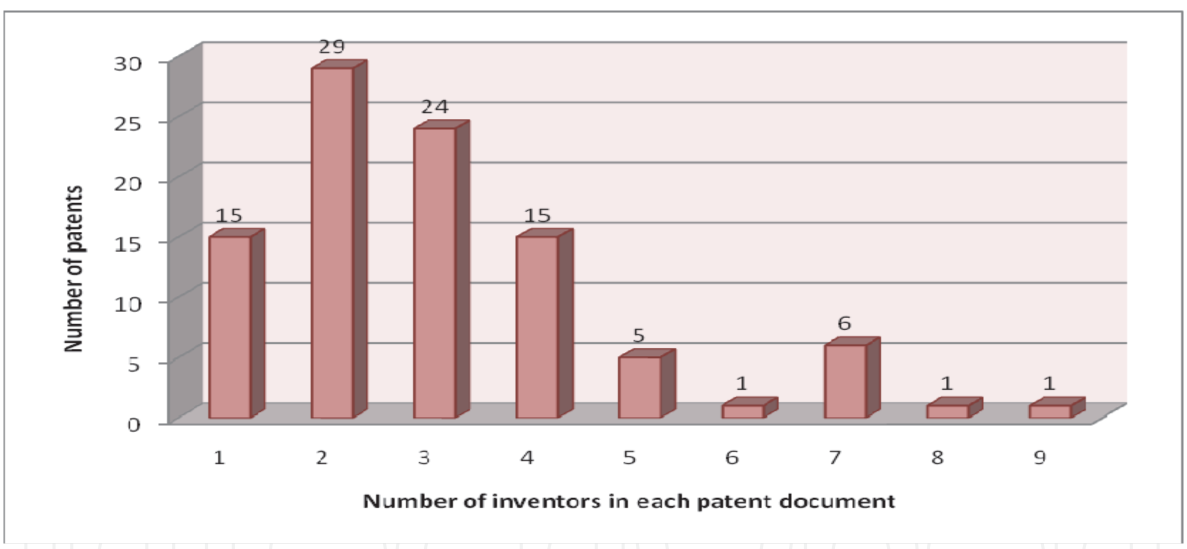


Fig. 4. Co-inventors analysis

3.5 Productivity of inventors

This section further analyzes the total number of patents owned by each inventor. In other words, the productivity of inventors in the patents of CNT fabrication was evaluated. Figure 5 demonstrates the information on the productivity of inventors. There are totally 210 inventors in all collected patents. Among these inventors, 174 inventors produced only one patent each. The inventors owning only one patent consist of 82.86% of all inventors. Only 14 inventors produced more than two patents each, and they occupy 6.67% of all inventors. Further, the most productive inventor produced a maximum number of seventeen patents, and the inventor is Shou-Shan Fan from Tsinghua University in China. The second most productive inventor is Liang Liu from Tsinghua

University in China, who produced eleven patents. The analytical result means that the high productivity of inventors is concentrated on a few inventors although there are many inventors in the field of CNT fabrication.

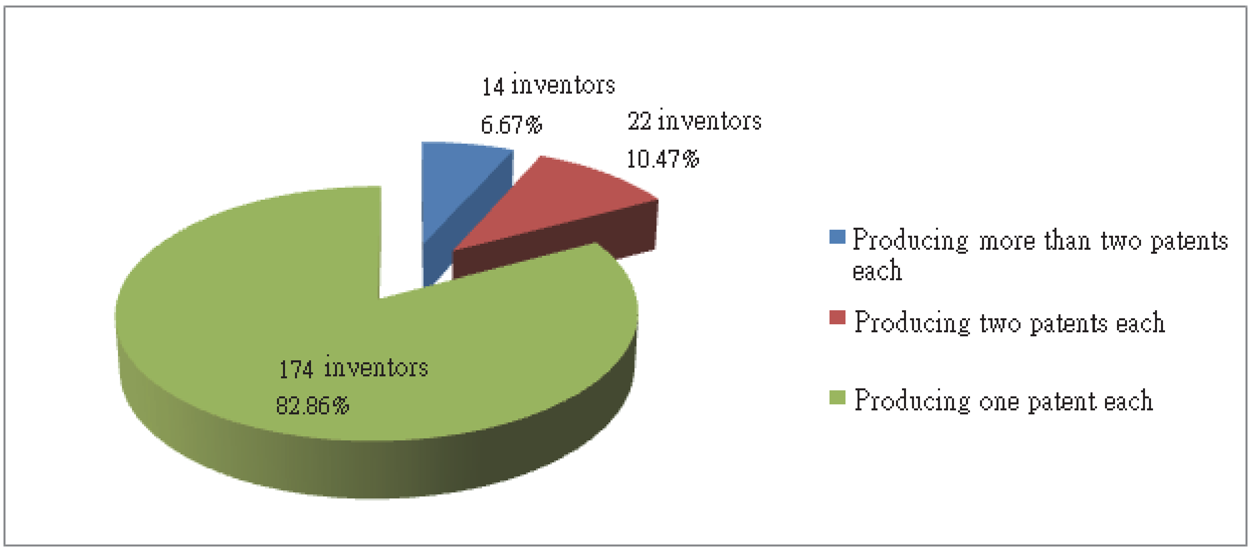


Fig. 5. Productivity of inventors

4. Results of patent network analysis

In order to obtain more information from patent documents, patent network analysis was used to further analyze the overall structures among the 97 patents regarding CNT fabrication. On the basis of five steps in the section of methodology, the representative patent keywords with important technical feature were adopted for producing the patent network. A total of 17 keywords were selected in step 1, including "chemical vapor deposition", "arc discharge", "laser", "catalyst", "substrate", "array", "evaporation", "pattern", "purification", "amorphous", "voltage", "derivatized", "helium", "crystalline", "gas", "current" and "modified", and the cut-off value p=0.18 was chosen in step 5. In the following section, the structural features of patent network were described and discussed in depth.

Figure 6 demonstrates the overall patent network in terms of connectivity. This network analysis divides all the 97 patents into two sets, an interconnected set and an isolated set. The interconnected set represents the critical key point of overall patent network, including 85 patents and the relationship among these patents. It provides much information in the fabrication and application of CNT based materials. From these inventions, the processes for CNT fabrication can be classified according to their manufacturing technologies, such as arc-discharge, laser ablation, chemical vapor deposition, and novel synthesis for functional CNTs. Nevertheless, there are still 12 patents in the isolated set. Among these patent documents, their main inventions are also claim for controlling CNT growth through the unique apparatus, system, method or process. However, these progresses don't meet the recent mainstream tendency, their originality is not ready to establish in present production level. Moreover, their improvements don't well fit the major technological trends and recent industry requirements in CNT applications, so they are excluded from the network through this patent network analysis.

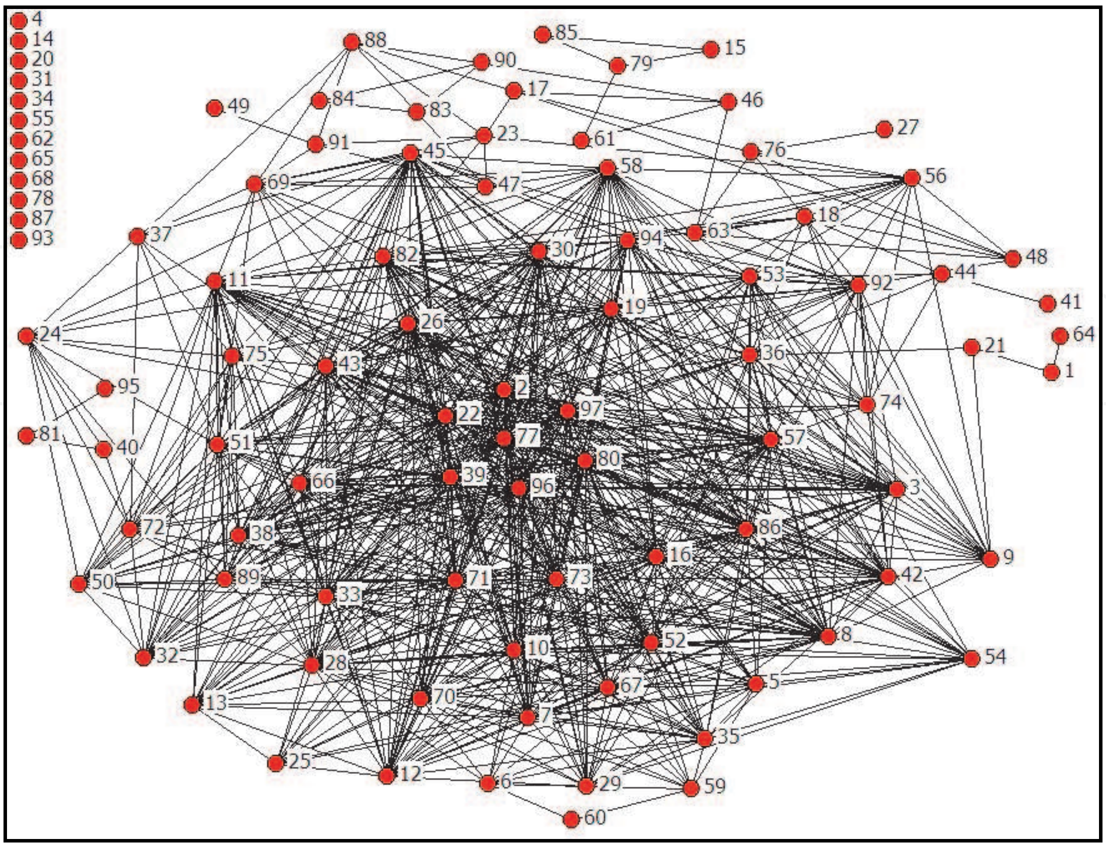


Fig. 6. Patent network of CNT fabrication

4.1 Quantitative analysis of patent network: TCI method

From this patent network, it can be observed that several patents close mutual linkages intuitively. As intuitive identification in the visual network, these patents are located in the central area of the patent network and possessed close relationship. They may represent the core technology in the field of CNT fabrication and application. Furthermore, the TCI method is used to identify the relatively important patent in this patent network. There are seven patents with higher TCI values above 0.42, including patent numbered 77, 97, 96, 2, 39, 80 and 22. Table 1 shows these relatively important patents in the patent network with higher TCI values, and far ahead of other patents. Through the visual patent network and TCI values, we can find out the relatively important patents. These patents represent the core technologies and the developing trends in CNT fabrication and application. We discuss the detailed meanings further as follows.

Patent number (real patent number)	TCI value
77 (U.S. Patent No. 7,744,843)	0.4896
97 (U.S. Patent No. 7,854,991)	0.4688
96 (U.S. Patent No. 7,851,064)	0.4479
2 (U.S. Patent No. 6,401,526)	0.4479
39 (U.S. Patent No. 7,514,116)	0.4375
80 (U.S. Patent No. 7,763,230)	0.4375
22 (U.S. Patent No. 7,374,793)	0.4271

Table 1. TCI values of the relatively important patents

From the above table, these seven patents with higher TCI values are further classified according to their titles, abstracts and claims of the patent documents. A reasonable explanation is expanded as below. The patent numbered 77 is the most important patent with a highest TCI value. This invention is to provide a method for synthesizing SWNTs which comprise extracting metals from carbide by halogen treatment at ambient or low pressure. Accordingly, this novel technology provides a method for the bulk synthesis of carbon nanotubes from metal carbides. The nanotube nucleation and growth occur upon the conversion of carbides into carbon without any catalyst. Thus, bulk nanotube powders, free-standing nanotube films, and thin layers of carbon nanotubes can be easily grown on SiC single crystals, polycrystalline carbide ceramics and particulate substrates. This convenient method is significant and useful for the further applications.

Furthermore, the patent with second order of TCI value is numbered 97. This invention has an object to provide carbon nanotubes and aligned single-walled carbon nanotube bulk structures with high purity and high specific surface area from CVD production process. In previous experience, the growth of the carbon nanotubes by the existent CVD method involved a problem that the activity lifetime of the metal catalyst was short, the activity was degraded in several seconds, and the growth rate of the carbon nanotube was not under best condition, which hindered the productivity. Thus, this patent has been proposed a method of controlling the activity of the iron catalyst and the growth of the carbon nanotube by a novel production process and apparatus. Based on this technique, various application uses can be attained such as for heat dissipation materials, heat conductors, electric conductors, optical devices, reinforcing materials, electrode materials, batteries, capacitors or super capacitors, electron emission devices, adsorbents, gas storages and so on. Accordingly, the CVD based production process for the growth of MWNTs is also important. The patent numbered 80 on the sixth order of TCI value reveals a useful process for the formation of all types of fullerenes, and in particular yields MWNTs with low defect density and controllable weight percent of metal impurity atoms. The advance in a wide range of nanotechnology applications depend critically on the availability of suitable starting materials, fabricating methods, or producing apparatus. In the case of applications and products using CNTs, the critical issues are freedom from defects and attaining low levels of impurities. Both problems are related to growth conditions and parameters, they have been virtually impossible to control the defect densities and impurity levels of fullerenes in previous research.

From the viewpoint of commercial applications, the semiconductor devices and the microelectronic elements are both the integral parts in global high-tech industries. The patents with the order of third, fifth and seventh are numbered 96, 39 and 22, they are all related to apply CNTs as role materials in semiconductor and microelectronic devices. According to recent results of scientific researches, CNTs are nanoscale high-aspect-ratio cylinders consisting of hexagonal rings of carbon atoms that may assume either a semiconducting electronic state or a conducting electronic state. The availability of CNTs and the cost of their synthesis is a primary issue hindering their introduction in various potential mass-produced end products, especially in IC industrials. Therefore, the conventional method for synthesizing carbon nanotubes is to deposit a layer of catalyst material on a substrate, which may be patterned to form an array of small dots that operate as seed areas for CVD growth using a carbonaceous precursor in FET device applications. Otherwise, the CNTs produced from CVD processes can be also applied to conductive patterns in microelectronic fields using CNT pastes to reinforce printed and applied paste-based metal wires. Such printed wires may be used in a wide range of electric circuits or metallic interconnections and the CNTs provide superior electrical and thermal conductivities, higher current densities, and remarkably improved strength compared to metal wires printed without CNT reinforcement.

Finally, the last patent within above table 1 is numbered 2. Unlike the previous six patents, its application date is earlier than the year of 2000. This reveals that this patent plays an important role in the early stage of CNT based research, and it still has influences in recent years. This invention relates generally to SWNT probe-tips for the atomic probe microscopy by direct synthesis method. The growth of SWNT tips involves dip coating silicon pyramids with a liquid phase catalyst followed by CVD using methane. The interactions between the silicon pyramidal surface and the nanotube ensure proper SWNT orientation. Production of large scale arrays of nanotube probe-tips using contact printing and controllably shortening nanotubes in an inert discharge are also mentioned.

From this patent network analysis, TCI can help us to realize the technological trends in the field of CNT fabrication and application. The full potential of CNTs for applications will be realized until the growth of nanotubes can be optimized and well-controlled. Real-world applications of CNTs require either large quantities of bulk materials or device integration in scaled-up fashions. Therefore, the front seven patents in TCI analysis reveal that fabrication and application of CNTs have the same importance in the future. The researchers work for different goals should pay the same attention in these two areas. For materials such as composites and hydrogen storage, it is desired to obtain high quality CNTs at the kilogram or ton level using growth methods that are simple, efficient and inexpensive. For devices such as CNT based electronics, scale-up will unavoidably rely on self-assembly or controlled growth strategies on surfaces combined with microfabrication techniques. Significant work has been carried out in recent years to tackle these issues.

Nevertheless, many challenges remain in the nanotube growth area after TCI analysis. First, an efficient growth approach to structurally perfect nanotubes at large scales is still lacking. Second, growing defect-free nanotubes continuously to macroscopic lengths has been difficult. Third, control over nanotube growth on surfaces should be gained in order to obtain large-scale ordered nanowire structures. Finally, there is still a seemingly formidable task of controlling the chirality of single-walled CNTs by any existing growth method. In this way, development of functional devices based on CNTs will surely have a significant impact on present and future technology needs.

4.2 Quantitative analysis of patent network: TCT method

TCT index reflects the trends of technological progress. The short TCT represents faster technology progress, but long TCT has the opposite result. The changing trends of technological progress in CNT fabrication and application should be monitored by this analysis. In this study, we calculate the median of age gaps between each subject patent and other connected patents in the whole patent network. TCT value varies from 0.37 to 5.65 years in this patent network, which shows the different rates of technological innovation in the synthesis and use of CNTs. Table 2 shows the front eight patents which own the shorter TCT index values (less than 1 year) and lists the front ten patents with long TCT index values (more than 3 years).

Short TCT group		Long TCT group	
Patent number (real number)	index value	Patent number (real number)	index value
85 (U.S. Patent No. 7,781,017)	0.37	47 (U.S. Patent No. 7,585,584)	3.08
49 (U.S. Patent No. 7,597,869)	0.62	18 (U.S. Patent No. 7,338,648)	3.16
79 (U.S. Patent No. 7,744,958)	0.70	72 (U.S. Patent No. 7,728,947)	3.18
91 (U.S. Patent No. 7,820,245)	0.73	7 (U.S. Patent No. 7,160,530)	3.20
15 (U.S. Patent No. 7,291,319)	0.73	81 (U.S. Patent No. 7,767,275)	3.41
23 (U.S. Patent No. 7,394,192)	0.76	46 (U.S. Patent No. 7,582,507)	3.48
11 (U.S. Patent No. 7,268,077)	0.94	6 (U.S. Patent No. 7,078,007)	3.57
71 (U.S. Patent No. 7,728,497)	0.99	3 (U.S. Patent No. 6,743,408)	3.78
		40 (U.S. Patent No. 7,531,156)	5.19
		2 (U.S. Patent No. 6,401,526)	5.65

Table 2. Short and long TCT index values of some patents

4.2.1 Short TCT

From the result of TCT index, the patents which have short TCT are related to the fabrication and utilization of CNTs for further industrial applications, and this index can provide the speed of technological innovation in this patent network. The patents with short value are numbered 85, 49, 79, 91, 15, 23, 11 and 71 which can be divided into three groups including CNT production, CNT based devices, and CNT based emitters.

The patents numbered 49 and 91 are classified into CNT production. From the discoveries of researches, the CNTs have excellent electrical, magnetic, nonlinear optical, thermal, and mechanical properties, such as possessing a high Young's modulus, a high elastic modulus, and a low density. Depending on their length, diameter, and mode of spiraling, the CNTs can exhibit metallic or semiconductor properties. They are widely used in a variety of diverse fields, such as nanometer-scale electronics, materials science, biological science, and chemistry. At present, methods for producing carbon nanotubes include an arc discharge method, a laser ablation method, and a CVD method. The CVD method generally uses transition metals or oxides as a catalyst to grow CNTs at high temperature by decomposition of carbon-containing reactive gas. Compared with the other two methods, the CVD method is superior in operational simplicity, low cost, and mass production, therefore the CVD method has become widely used. A typical CVD method for producing CNTs includes the steps of (1) providing a substrate coated with a catalyst layer on a surface; (2) putting the substrate in a reaction device; (3) heating the reaction device; (4) introducing a carbon-containing reactive gas and thereby growing CNTs on the substrate. However, when using a typical method to produce CNTs after about 5 to 30 minutes, the rate of precipitation of carbon is greater than that of diffusion of carbon. Thus, the catalyst particles become blocked by accumulation of the decomposed carbon of the carbon-containing reactive gas. Therefore, the CNTs stop growing at a short length.

In addition to above mention, another four patents regarding CNT based devices own the shorter TCT values (numbered 85, 79, 15 and 11). These inventions relate to methods for making devices from substrates by CVD processes. At present, the CNT based devices from CVD methods already have a wide range of applications, but the CNT based devices fabricated by arc discharge or laser ablation can not be directly use for applications. The process control is needed over the building and organization of nanotube-based architectures. Normally, the orientation of growing nanotubes is controlled for the purpose of achieving rectilinear and parallel CNTs with each other, and the CVD method can help to align along a

linear direction and extend perpendicularly from the substrates. Even though there are many devices prepared from CVD based methods, most of the synthesis methods suffer from a lack of control over the size and shape of the nanotubes. Some methods of CNT production lead to mixtures of SWNTs and MWNTs. Other methods result in production of nanotubes with variations in nanotube shape and size, leading to a lack of control over the properties of the resulting nanotubes. From above analysis, the scientists and researchers should pay their attention to this matter for improving the technology progress. This shows that a larger proportion of the CNT based subjects, which need to be promoted in both academia and industrial, is of immediate relevance for the inventive activity leading to patents in this field.
Finally, the other two patents with short TCT (numbered 23 and 71) are related with aligned CNTs as electrode emission source to improve applications. The electron emission devices are displays that create images by emitting light by having phosphors in a phosphor layer of an anode plate collide with electrons emitted from electron emission sources of a cathode under an electric field generated when a voltage is applied to the anode and the cathode. The CNTs with good electron conductivity have properties such as a good field enhancement effect, low work function, good field emission property, low driving voltage, and an ability to be fabricated over a large area. Therefore, CNTs are good electron emission sources for electron emission devices. Recent interests in these inventions provide CNTs which exhibit good characteristics due to small differences in CVD process and apparatus.
According to above mentions, the result of TCT index with lower value can effectively reflect the present technological trends, and the CNT production, CNT based devices, and CNT based emitters are really the most popular subjects in industrial applications of CNTs.

4.2.2 Long TCT

In addition to the patents with short TCT index value, the front ten patents with long TCT index value are also listed for further discussion. These ten patents are numbered 47, 18, 72, 7, 81, 46, 6, 3, 40 and 2. From the contents of these patents, they are still related to the CNT fabrication and application through CVD processes, but these inventions focus on the controlling synthesis of CNTs for the specific situations uses or applications. Since the first observation of CNTs, the subjects of patent documents can be classified according to their subjects, such as synthesis method, growth mechanism, chemical/physical property, theoretical prediction, and potential applications. Nevertheless, the patents with long cycle time indicate the subjects are not in popular demand or with narrow utility in this analysis. Their subjects are relative mature and useful without further progress, and this situation indicates these inventions could not be easily replaced and overtaken.
The patents numbered 18, 81, 6 and 40 describe the CNT synthesis through the different core techniques. The technological importance in CNT fabrication processes is including of low temperature synthesis, self vertical alignment, nanoparticle based synthesis, and organic liquid based catalysis growth. The technical advantages of these four patents are designed to produce CNTs with controlled shape, diameter, wall thickness, length, orientation, and location of growth. Although these patents are filed and applied for a period of time, their main invention is still the critical factor for the controlling synthesis of CNT on a substrate. For this reason, it is very reasonable for these four patents owning the long TCT index value. But there are still some problems needed to be solved in the future, the final goal of these inventions is applied for the industrial applications.
Furthermore, the patents numbered 47, 72, 7, 46, 3 and 2 also describe the CNT fabrication regarding the controlling synthesis of CNT onto various templates for applications, such as

fuel cell electrodes, LCD devices, hydrogen storage devices, electronic transistors, AFM tweezers and so on. Specifically, vertical alignment has been an important objective due to the technological requirements for applications in above fields. Until now, there is still no more effective solution which can manipulate CNTs for mass production. Because these techniques are still difficult to control and labor intensive, in situ aligning of nanotubes during growth onto the porous substrates including foam, felt, mesh and membrane have been attempted. However, the reactions and the synthesis of these materials in novel combinations with varying substrates or coatings cannot be easily achieved. Therefore, the techniques of making above structures are always disclosed as patents with longer TCT.

Even if it is important for creating a new fabrication process for CNT, a new method is very difficult to establish in recent years. All researchers are moving their resources to create the application of CNT related products. Therefore, TCT will become longer and longer for the fabrication process research. This phenomenon may further indicate that the TCT index can monitor the changing trends of technological advancement for fabrication and application of CNT. And the TCT index value can quickly point out that the object in mind for CNT materials is modified the CNT structure to improve the whole process of device production.

5. Conclusions

In this study, patent bibliometric analysis and patent network analysis were both used to monitor the states and the trends of CNT fabrication. These analyses not only can assist researchers in understanding the developmental states of CNT fabrication, but also can help them to quickly grasp the technological trends for CNT fabrication. Moreover, the results of this study fully demonstrate the critical technologies of CNTs and provide suggestions regarding future technological development.

For all the analytical results of this study, first, the main growth methods of producing CNT are classified for laser ablation, arc-discharge, and CVD methods. Although the CNT material was observed from the year of 1991, the fabrication process is still attracting much attention after 2000. The key technology of CNT fabrication is finding the way to produce CNTs in higher yields, high purity, well conformation, and better quality by CVD process, and the growth of nanotube materials in bulk was also mentioned.

Second, the patent network graph was obtained from the keywords of CNT related patents. A major portion of patents in the center of network graph can be obviously distinguished, and it seems to reflect the actually technological trends. It represents the truth that major purpose of CNT production is in the field of CNT fabrication and application. The similar result was found in TCI and TCT measurements. The CVD process plays an important role for manufacturing CNT based devices in industrial field. Therefore, it is without doubt that patent documents are a valuable resource of technical and commercial knowledge. The potential, market demand, and future direction of patent data can be easily realized from this analysis.

Third, this study reveals the critical technologies for growing the CNT materials generally fallen into two categories: (1) enhancing the characteristic of CNT with various methods, and (2) producing CNT by CVD method on various substrates for applications. Some of these inventions could become real marketable applications in the near future, but others need further modification and optimization. Moreover, there still remains a strong need for better control in purifying and manipulating CNTs, and the development of functional devices or structures based on CNTs will surely have a significant impact on future technology needs.

From this analysis result, the advantage of CNTs makes them of potential use in controlling synthesis of nanoscale structures, which play an important role in the field of nanotechnology engineering. Up to the present, it is not really possible yet to grow CNTs in an ambient condition for mass production. Even if there have been some successes in growing CNTs through tuning the conditions and apparatuses by trial and error, the general challenges for developing CNTs still focus on growing stable and functional materials. Furthermore, another challenge is in the manipulation of CNTs. The operational skill of CNT related materials is still in the infancy, and it relies strongly on the powerful tools of manipulating CNT structures at the atomic scale. This will become a major challenge in the near future, among several others.

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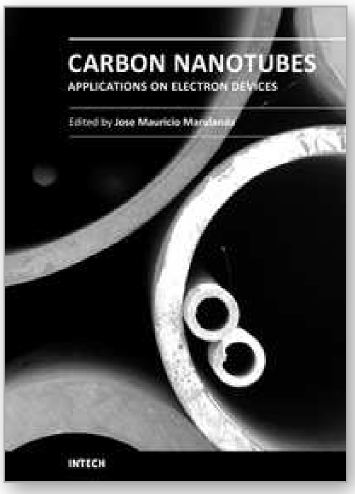

Carbon Nanotubes Applications on Electron Devices

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Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. In the past decades, although carbon nanotubes have undergone massive research, considering the success of silicon, it has, nonetheless, been difficult to appreciate the potential influence of carbon nanotubes in current technology. The main objective of this book is therefore to give a wide variety of possible applications of carbon nanotubes in many industries related to electron device technology. This should allow the user to better appreciate the potential of these innovating nanometer sized materials. Readers of this book should have a good background on electron devices and semiconductor device physics as this book presents excellent results on possible device applications of carbon nanotubes. This book begins with an analysis on fabrication techniques, followed by a study on current models, and it presents a significant amount of work on different devices and applications available to current technology.

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