



CHALMERS

Chalmers Publication Library

Examining Carbon Nanofibers: Properties, growth, and applications.

This document has been downloaded from Chalmers Publication Library (CPL). It is the author's version of a work that was accepted for publication in:

IEEE Nanotechnology Magazine (ISSN: 1932-4510)

Citation for the published paper:

Desmaris, V. ; Saleem, A. ; Shafiee, S. (2015) "Examining Carbon Nanofibers: Properties, growth, and applications.". IEEE Nanotechnology Magazine, vol. 9(2), pp. 33-38.

<http://dx.doi.org/10.1109/MNANO.2015.2409394>

Downloaded from: <http://publications.lib.chalmers.se/publication/221549>

Notice: Changes introduced as a result of publishing processes such as copy-editing and formatting may not be reflected in this document. For a definitive version of this work, please refer to the published source. Please note that access to the published version might require a subscription.

Chalmers Publication Library (CPL) offers the possibility of retrieving research publications produced at Chalmers University of Technology. It covers all types of publications: articles, dissertations, licentiate theses, masters theses, conference papers, reports etc. Since 2006 it is the official tool for Chalmers official publication statistics. To ensure that Chalmers research results are disseminated as widely as possible, an Open Access Policy has been adopted. The CPL service is administrated and maintained by Chalmers Library.

(article starts on next page)

Carbon NanoFibers (CNF) properties, growth and applications.

V. Desmaris, A. M. Saleem, S. Shafiee

Smoltek AB, Regnbagsgatan 3, 417 55 Gothenburg, Sweden

One dimensional carbon nanostructures have been known and fabricated for more than a hundred years [01] and were originally referred to as "filamentous carbon", "carbon filaments" or "carbon whiskers" [02]. However, it is only during the 1990s and 2000s with the demonstration of carbon nanotubes [03-04] and the introduction of catalytic plasma enhanced chemical vapor deposition [05-06], that one dimensional carbon nanostructures emerged as promising for a large variety of applications. In this paper, Carbon NanoFibers (CNFs), a particular type of one dimensional carbon with unique properties are first described, before their growth is discussed and finally their main applications are presented.

CNF

CNFs are allotropes of carbon having a diameter size of about 50 to 100 nm with length ranging from one to hundreds of micrometers (Fig 1). Unlike carbon nanotubes (CNTs), which is a hollow cylindrical structure made of one or several concentric graphene rolls (single wall carbon nanotube and multiwall carbon nanotube respectively), CNFs consist of a stack of graphene cones. CNFs and CNTs are distinguished by measuring the angle (α) between the one dimensional carbon

nanostructure axis and the graphene layers forming it. Single or multi-wall CNTs exhibit an angle of 0, whereas CNF reveal a nonzero angle (Fig. 2).

The electronic bindings between carbon atoms in a CNF are twofold: in-plane covalent bonds within each cone of graphene and inter-plane Van der Waals bindings between the cones. As a result, the α angle does not only determine the nature of the carbon nanostructures, but also its electrical and mechanical properties.

Unlike CNT, whose conductivity depends on its chirality and usually present a ratio of metallic/semiconducting CNT of 1/3 [07], CNFs have the advantageous properties of being 100% metallic and possibly grown individually at low temperatures.

The typical properties of CNF are summarized in the table below, the variations depends on their processing conditions and hence their structural configuration, diameter, length, interface, contacting schemes... etc...

Table I: Typical properties of CNFs

Parameter	Typical values
Diameter	1-100 nm
Length	0.1-100 μm
Fill factor when grown as films	5-80 %
Density	$<2 \text{ g/cm}^3$
Thermal expansion coefficient (CTE)	$\sim 10^{-6}/\text{K}-10^{-7}/\text{K}$
Young Modulus	80-800 GPa
Poisson's Ration	0,2-0,25
Tensile strength	30 GPa
Electrical resistivity	$0.1 \mu\Omega\cdot\text{m} - 2\text{m}\Omega\cdot\text{m}$
Thermal conductivity	20-3000 W/m·K
Temperature tolerance	$>1000 \text{ C}$ without oxygen, $>400 \text{ C}$ with oxygen
Vertical pressure strength as grown	$>50 \text{ Bar}$
Horizon shear strength as grown	Weak
Shear strength of bonded nanostructures	1.5x-3x MIL

Growth

The properties of CNFs are largely depending of the growth conditions. Arc discharge and its modern variant electro spinning can provide very pure material, however the control and reproducibility of the length, shape and alignment of CNF produced using these techniques are inherently limited and consequently restrain their applications fields.

It is the development of catalytic PECVD during the late 1990s [05] that made possible a more deterministic method to produce CNF on substrates. The positioning of the fibers on a substrate would depend on the presence of a catalyst, the CNF alignment is controlled by the electric field generated by the plasma, whereas the length of the CNF is simply determined by the growth time.

Even though the full growth process of CNF is not completely understood, it is generally accepted [08] that the perpendicular alignment of the CNF to the substrate results from uniform stress at the catalyst/CNF interface due to electrostatic forces, which compensate for any non-verticality during the growth process.

In addition, many PECVD systems using different RF and microwave sources developed [09- 11]. However, DC-PECVD produced so far the best results for the fabrication of CNF at low CMOS compatible temperature using different pre and post processing techniques to cope with the inherent discharge problems, which may rise when using insulating substrates [12].

The most accepted description of the growth mechanism of CNF originates from the pioneer work of Baker et al in the 1970s. It decomposes the growth process into four steps described in Fig 3. First, A molecule of gas precursor is adsorbed at the surface of the catalyst. Second, the gas molecule is dissociated at the surface of the catalyst. Third, the dissociated carbon atoms diffuse through [01]or at the surface [13] of the catalyst towards the CNF, depending on the propensity of the catalyst to form carbide or enable low-energy diffusion of carbon at its surface. Fourth, the carbon atoms are incorporated into the CNF.

As a result, the PECVD growth of CNF requires three components: gases, an underlayer and a catalyst.

The catalytic PECVD growth process involves generally two gases. The first one acts as a carbon precursor (usually acetylene or methane) and reacting with the catalyst, building the CNF. The second being a carbon etchant (often Ammonia or hydrogen) prevents parasitic growth [14].

The role of the underlayer, located between the catalyst and the substrate, acts as a diffusion barrier between the catalyst and the substrates, in order to avoid poisoning of the catalyst through a reaction with the substrate or diffusion in the substrate as a result of the elevated temperature during the growth process. Various metal underlayer based on refractory metals or alloy have been used depending on the choice of substrates of catalyst and a comprehensive review can be found in [15].

The activity of the catalyst particle is crucial for the growth process [16]. It can consist of consists of one or few elements [15], however vast majority of the reports regarding the growth of CNF deals with catalyst made of transitions metals: Fe, Co, Ni [15]. In addition, it is currently believed that the catalyst should form nanoparticles of a favorable size in order to initiate the growth of a CNF. Therefore the catalyst can be deposited as a film using Physical vapor deposition techniques, or directly as nanoparticles using spray coated [17] or spinning [18], providing that the growth temperature will lead to a dissociation of the film into droplet/nanoparticles of appropriate size.

Applications

Their remarkable properties, combined with the unique low temperature deterministic growth (Fig. 4) process makes CNFs very suitable for semiconductor packaging applications as well as building advanced capacitors.

CNF as interconnects

Since the CNFs grown by catalytic PECVD are vertical dimensional material with large aspect ratio and are inherently rooted and attached to the underlying substrates which can be grown individually (Fig. 4) with controllable pitch down to down to single digit microns on substrates, CNF have been first thought as alternative to micro-and nano copper pillars for packaging chips with high density of IOs [19]. In fact their resilience to electrical [20] and chemical corrosion makes them highly relevant when electromigration is limiting the reliability of copper interconnects for small pitch applications.

Clusters of thousands of CNFs result in the form of a “forest”, which as such have been considered as interconnects. Such bump interconnects (Fig 5), made solely of CNF rooted on the underlying bonding pads, used as flip chip or integrated, have been demonstrated to form robust interconnects supporting current densities of several tens of MA/cm². In addition, such bumps made solely out of CNFs have been demonstrated to provide a microwave link suitable for high frequency operations to about 20 GHz [21] and would be perfectly suited for the packaging of high power microwave devices such as GaN FETs or SiC transistors or diodes.

CNF as solder joint enhancers

A number of studies find that CNF's can reduce the Coefficient of Thermal Expansion (CTE) of solder when embedded in the solder [22-25]. Commonly used SAC solders can have CTEs ranging from 16.7 to 26 ppm/°C , whereas the CTE of the adjoining silicon can range from 3 ppm/°C to 8 ppm/°C creating a mismatch which can cause solder joint cracking over time and thermal cycling. The effect of this mismatch as the solder volume is reduced raises the probability of joint failure significantly. CNFs have the ability to bond with solder while still remaining rooted on the IC pads enabling them build composite materials, which take advantage of their high (TPa) young modulus to provide robust joints between two chips or chips to package [25-26]. Studies show that CNFs, using flash metal layers, wet many of the commonly used IC assembly solders, such as Indium IN 290, In-Sn [19]or SAC305 [4], remarkably well leaving hardly any voids at the fiber/CNF interface and forming a

composite joint with lower CTE than the solder itself, since VACNF have hardly any CTE. Further, the wettability of the CNF to the solder could prevent the solder from wicking out and away from the pads, thus reducing the number of solder shorts that occur as the solder pad-pad pitch gets smaller. The length of the rooted CNF is solely determined by the CVD growth process. Such length makes it possible to enhance the reliability of the fiber to solder joint, since fibers could be longer than the intermetallic region on the solder to pad interface. All the above features of the CNF/ solder composites make them very promising for Nano-scale interconnect with improved reliability. The thermal fatigue life was demonstrated to increase by 87 % by creating a 29% by volume mixture of CNFs and solder [22].

The considerable Young Modulus of the CNFs along their growth axis confers them remarkable piercing properties, e.g. for nano-imprinting [27]. Therefore, besides the rebar of the IMC layer in the bump formation, the CNF remarkable compressive strength would imply that they could provide considerable reinforcement of a solder bump, preventing it to deform and dimple during testing [28].

CNF-based adhesive interconnects

CNF films can also be used as performance enhancers of flip-chip bonding when soldering is not possible. Using standard thermal compression flip-chip technique, composites made of CNF grown directly on chips such as SiC power transistors or Si LDMOS and embedded into a polymer have shown to be able to provide good ohmic contacts (specific contact in the order of $105 \Omega \cdot \text{cm}^2$) on direct-copper-bonding or leadframes [19]. The embedding of CNF in polymers forms, after assembly, a type of Anisotropic Conducting Film (ACF), where the polymer provides the necessary sufficient adhesion and compensates the relatively weak shear stress resilience of the CNF. Such adhesive interconnects meet the MILx1 to MILx3 standards.

CNF as electrode material for capacitors

Due to their metallic nature CNF, when grown on metallic surfaces, provide a large increase in effective surface area per footprint. As a result, CNF have also been implemented as electrode material for two types of capacitors, namely decoupling capacitors and super-capacitors.

CNF-based capacitor electrode can be used in two relatively large decoupling capacitors directly on-chip, having a large advantage over the embedded film capacitors [29-30] surface mount and land side decoupling capacitor can be realized by growing directly the CNF of the connecting pads of an IC chip, provided that the growth process is compatible with the IC's technological node [31]. Different prototypes of CNF-based decoupling capacitors have shown an enhancement by a factor of 10 to 100 in capacitance density compared to current technology [31].

Supercapacitors are electrochemical capacitors [32] with high power density. Their life time is 100 times larger than Lithium batteries and their performance is largely dictated by the effective area of the electrode materials, its structure. Historically active carbon has been used as electrode material, however more recently flexible sheets of electrospun CNFs are considered prospective electrodes materials for supercapacitors because of their well interconnected pores, high mechanical and electrochemical stability [33-34]. Their main drawback of low specific surface area has nowadays been circumvented by their nitrogen doping and functionalization with CNTs, resulting in 3D CNT/CNF composites suitable for supercapacitors with high power density and long life-cycle performance [35] for next generations supercapacitors.

CNF as Thermal Interface Material.

CNF exhibit very large thermal conductivity but mainly in the direction of its growth axis. As a result, early studies [36] have emphasized the need to combine CNFs as a filler into in a matrix of another material such as solders [37] or Copper[36]. This intrinsic isotropic heat conduction in the CNF, limited the tentative of using them in a TIM material. In fact, much focus on the packaging industry has been heat spreading using various materials such as graphite. Despite the successful

implementation of heat spreaders, removing heat from the chips to the package and CNF is expected to play a key role in the vertical extraction of heat from the chip to the package [38],

CNF for Nanoelectromechanical systems.

Vertically aligned carbon nanofibers have also great potential in nanoelectromechanical system because a single carbon nanofiber can be grown upto a few micron long, standing alone vertically aligned at controlled position which can be addressed easily. The long single CNF can be bent easily by applying low electric field. The NEMs based on CNF grown using PECVD technique at CMOS compatible temperature can be embedded in CMOS chips. [39] made the nanoelectromechanical switch by bending vertically aligned carbon nanofiber using electric field and actuated the fiber by applying 10V potential across a 5 microns distance. The fiber could bear the 90° bend and came back to original position on switching electric field off.

Summary

Even though CNF do not fully meet electrical and thermal performance of CNTs, the reliability, and deterministic nature of their low temperature growth and properties makes them extremely attractive for various applications. They have been shown to provide alternative and potentially disruptive solution for high reliability low-pitch interconnects or flip-chip and die-attach when employed intrinsically (I.e. as grown) or in combination with solders and polymers, respectively. Additionally their thermal properties and possibility to grow them on chip can provide new thermal managements solutions for packaged components. Furthermore CNF-based materials for the enhancement of supercapacitors as replacement for Lithium battery or on-chip decoupling capacitors widen the prospective application area of CNFs.

References

- [01] R.T.K Baker "Catalytic Growth of Carbon Filaments", Carbon, 27, pp. 315-323, 1989.
- [02] A. V. Melechko, R. Desikan, T. E. McKnight, K. L. Klein, and P. D. Rack, "Synthesis of vertically aligned carbon nanofibres for interfacing with live systems", Journal of Physics D: Applied Physics, 42, pp.193001, 2009
- [03] S. Iijima, "Helical Microtubules of Graphitic Carbon", Nature, 354, pp. 56-58, 1991.
- [04] S. Iijima and T. Ichihashi, "Single-shell carbon nanotubes of 1-nm diameter", Nature, 363, pp. 603-605, 1993.
- [05] Y. Chen, Z. L. Wang, J. S. Yin, D. J. Johnson, and R. H. Prince, "Well-aligned graphitic nanofibers synthesized by plasma-assisted chemical vapor deposition", Chemical Physics Letters, 272, pp. 178-182, 1997.
- [06] Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. "Provencio, Synthesis of Large Arrays of Well-Aligned Carbon Nanotubes on Glass", Science, 282, pp. 1105, 1998.
- [07] G.D. Nessim, " Properties, synthesis, and growth mechanisms of carbon nanotubes with special focus on thermal chemical vapor deposition". Nanoscale, 2, pp. 1306, 2010.
- [08] V. I. Merkulov, A. V. Melechko, M. A. Guillorn, D. H. Lowndes, and M. L. Simpson, "Alignment mechanism of carbon nanofibers produced by plasma- enhanced chemical-vapor deposition", Applied Physics Letters, 79, pp. 2970, 2001

- [09] H. Le Poche, J. Dijon, and T. Goislard de Monsabert, "Radio-frequency plasma system to selectively grow vertical field-aligned carbon nanofibers from a solid carbon source", *Carbon*, 45, pp. 2904-2916, 2007.
- [10] L. Delzeit, I. McAninch, B. A. Cruden, D. Hash, B. Chen, J. Han, and M. Meyyappan, "Growth of multiwall carbon nanotubes in an inductively coupled plasma reactor", *Journal of Applied Physics*, 91, pp. 6027-6033, 2002
- [11] C. Bower, O. Zhou, W. Zhu, D. J. Werder, and S. H. Jin, Nucleation and growth of carbon nanotubes by microwave plasma chemical vapor deposition, *Applied Physics Letters*, 77, 2767-2769, 2000.
- [12] M. A. Guillorn, T. E. McKnight, A. Melechko, V. I. Merkulov, P. F. Britt, D. W. Austin, D. H. Lowndes, and M. L. Simpson, "Individually addressable vertically aligned carbon nanofiber-based electrochemical probes", *Journal of Applied Physics*, 91, pp. 3824, 2002.
- [13] S. Hofmann, G. Csanyi, A. C. Ferrari, M. C. Payne, and J. Robertson, "Surface diffusion: The low activation energy path for nanotube growth", *Physical Review Letters*, 95, pp. 036101, 2005.
- [14] M. Kabir, R. Morjan, O. Nerushev, P. Lundgren, S. Bengtsson, P. Enoksson, and E. Campbell, "Plasma-enhanced chemical vapour deposition growth of carbon nanotubes on different metal underlayers", *Nanotechnology*, 16, p. 458-466, 2005.
- [15] A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes, and M. L. Simpson, "Vertically aligned carbon nanofibers and related

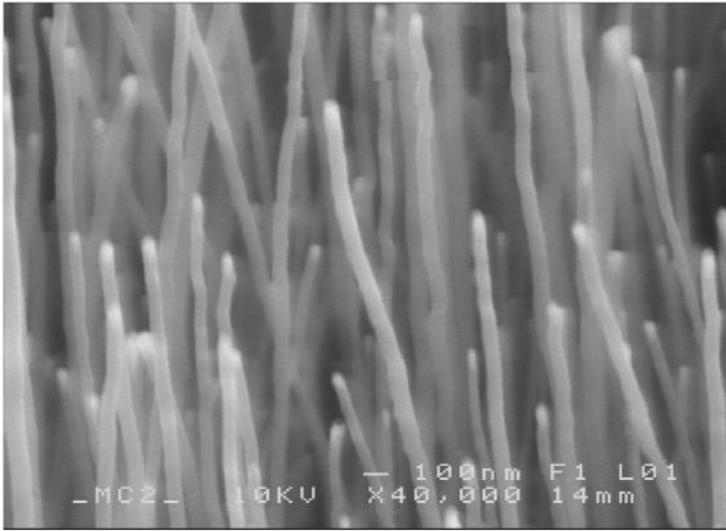
structures: Controlled synthesis and directed assembly”, *Journal of Applied Physics*, 97, pp. 041301, 2005.

- [16] V. I. Merkulov, D. K. Hensley, A. V. Melechko, M. A. Guillorn, D. H. Lowndes, and M. L. Simpson, “Control mechanisms for the growth of isolated vertically aligned carbon nanofibers, *Journal of Physical Chemistry B*, 106, pp. 10570, 2002.
- [17] Gohier A, Kim KH, Norman ED, Gorintin L, Bondavalli P and Cojocaru CS, “Spray-gun deposition of catalyst for large area and versatile synthesis of carbon nanotubes”, *Appl. Surf. Sci.* 258 pp. 6024-28. 2012.
- [18] A. M Saleem, S. Shafiee, T. Krasia-Christoforou, I. Savva, G. Göransson, V. Desmaris and Peter Enoksson, “Low temperature and cost-effective growth of vertically aligned carbon nanofibers using spin-coated polymer-stabilized palladium nanocatalysts”, *Science and Technology of Advanced materials*, 2015.
- [19] Desmaris V, Saleem AM, Shafiee S, Berg J, Kabir MS and Johansson A, “Carbon Nanofibers (CNF) for Enhanced Solder-based Nano-Scale Integration and on-chip Interconnect Solutions”, in *Proc. Electronics Components and Technology conf.* 2014, 2014 p.1071-76.
- [20] Q. Ngo, T. Yamada, M. Suzuki, Y. Ominami, A.M. Cassel, L. Jun, M. Meyappan and C. Y. Yang, “Structural and Electrical Characterisation of Carbon Nanofibers for Interconnects Via Applications”, *IEEE. Trans. Nanotechnol*, vol 6, no 6, pp. 688-695, 2007.
- [21] Desmaris V, Saleem AM, Berg J, Enoksson P, Kabir MS, Huss L-G, Jonsson R, Rudner S, Höijer M, Tamburrano A and Sarto MS, “A Test Vehicle For RF/DC Evaluation and Destructive Testing of Vertically Grown Nanostructures (VGCNS)” presented at *NT11, Int. Conf. on the Science and Application of Nanotubes*. Cambridge, UK. 2011

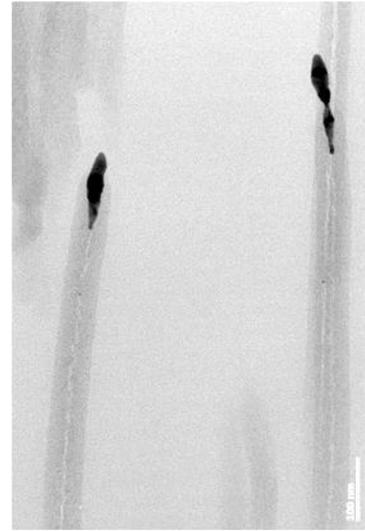
- [22] C. Ho, D.Chung, " Carbon fiber reinforced tin-lead alloy as a low thermal expansion solder preform", Journal of Materials Research, Vol. 5 (6), p 1266-1270, 1990.
- [23] J. Wasniewski,D. Altman, S. Hodson, T. Fisher, A. Bulusu, S. Graham,B. Cola, " Characterization of Metallically Bonded Carbon Nanotube-Based Thermal Interface Materials Using a High Accuracy 1D Steady-State Technique", J. Electron. Package 134(2), pp. 020901, 2012.
- [24] Poveda, Achar, Gupta, " Thermal Expansion of Carbon Nanofiber-Reinforced Multiscale Polymer Composites", JOM, vol64 (10), p1148-1157, 2012.
- [25] X.D. Liu, Y.D. Han, H.Y. Jing, J. Wei, L.Y. Xu," Effect of graphene nanosheets reinforcement on the performance of Sn-Ag-Cu lead-free solder", Materials Science and Engineering: A, Vol. 562, pp. 25-32, 2013.
- [26] S. Chen," Ultra-short vertically aligned carbon nanofibers transfer and application as bonding material", Soldering & Surface Mount Technology, vol 25(4), p242-250, 2013.
- [27] Saleem AM, Berg J, Desmaris V and Kabir MS, "Nanoimprint lithography using vertically aligned carbon nanostructures as stamps". Nanotechnology, 20, pp. 375302-06, 2009.
- [28] K.Smith, "Probing 25 μ m-diameter micro-bumps for Wide-I/O 3D SICs", Chipscale Review, Vol 18. No. 1, pp20-23, 2014.
- [29] H. Kim, B-K Sun, J. Kim, "Suppression of GHz range power/ground inductive impedance and simultaneous switching noise using embedded film capacitors in multilayer packages and PCBs", IEEE Microwave Wireless Compon Lett, 14 pp.2, 2004.

- [30] G.-W. Kim, M. Min, M. Yang, A. Gundurao, E. You, H. Gill, et al. "Package embedded decoupling capacitor impact on core power delivery network for ARM SoC application", *Electron Compon Technol Conf*, pp. 354–359, 2014.
- [31] A.M. Saleem, G. Göransson, V. Desmaris, P. Enoksson, "CMOS compatible on-chip decoupling capacitor based on vertically aligned carbon nanofibers", *Solid-State Electronics*, 107, pp. 15–19, 2015
- [32] J.B. E. Conway, *Electrochem. Supercapacit, Sci. Fundam. Technol. Appl.* 1999
- [33] K. Gao, Z. Shao, J. Li, X. Wang, X. Peng, W. Wang and F. Wang. "Cellulose nanofiber-graphene all solid-state flexible supercapacitors", *Journal of Materials Chemistry A*, 1, pp. 63-67, 2013.
- [34] J. Fang, H. T. Niu, T. Lin and X. G. Wang, "Applications of electrospun nanofibers. *Chinese Science Bulletin*", 53(15), pp. 2265-2286, 2008.
- [35] V. Kuzmenko, A. M. Saleem, O. Naboka, H. Staaf, G. Göransson, M. Haquea, V. Desmaris, P. Gatenholm, P. Enoksson, "Carbon nanotubes/nanofibers composites from cellulose for supercapacitors", In . *Proc. ECCM16*, 2014.
- [36] Q. Ngo, B. Cruden , A. Cassell , G. Sims , J. Li, M. Meyyappan , and C. Y. Yang, "nano-engineering carbon nanofiber-copper composite thermal interface material for efficient heat conduction", *Surface Engineering in Material Science III*, 2005.
- [37] M. Murugesan, C. Zandén, X. Luo, L. Ye, V. Jokubavicius, M. Syväjärvi , J. Liu, " Carbon fiber solder matrix composite for thermal management of high power electronics", *Journal of Materials Chemistry*. ,2 (35), p. 7184-7187. 2014

- [38] S. Snyder, J. Thompson, A. King, E. Walters, P. Tyler, M. Weatherspoon, " Thermally enhanced 3 dimensional integrated circuit (TE3DIC) packaging", in Proc. Electronics Components and Technology conf. 2014, 2014 p.601-608.
- [39] B A. Cruden and Alan M. Cassell, " Vertically Oriented Carbon Nanofiber Based Nanoelectromechanical Switch", IEEE trans. Nanitech. Vol 5 (4), pp.350-355, 2006.



a



b

Fig 1. a.SEM picture of CNFs, b. TEM picture of CNFs

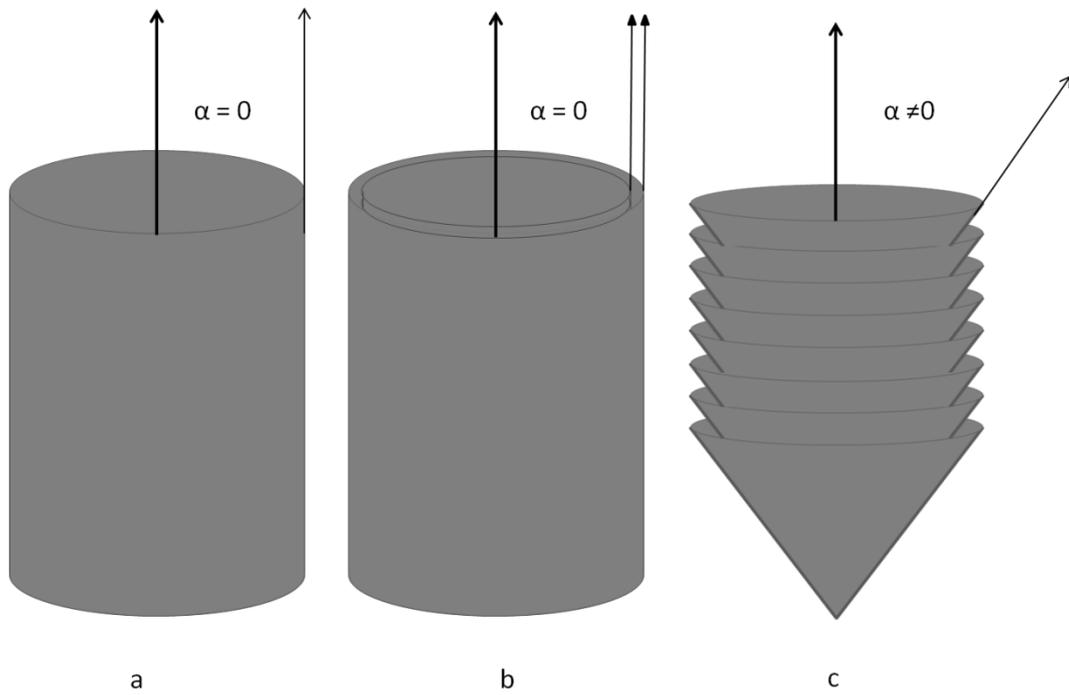


Fig 2. Schematic of the internal structure. a. a single wall CNT b. multiwall CNT. C. CNF

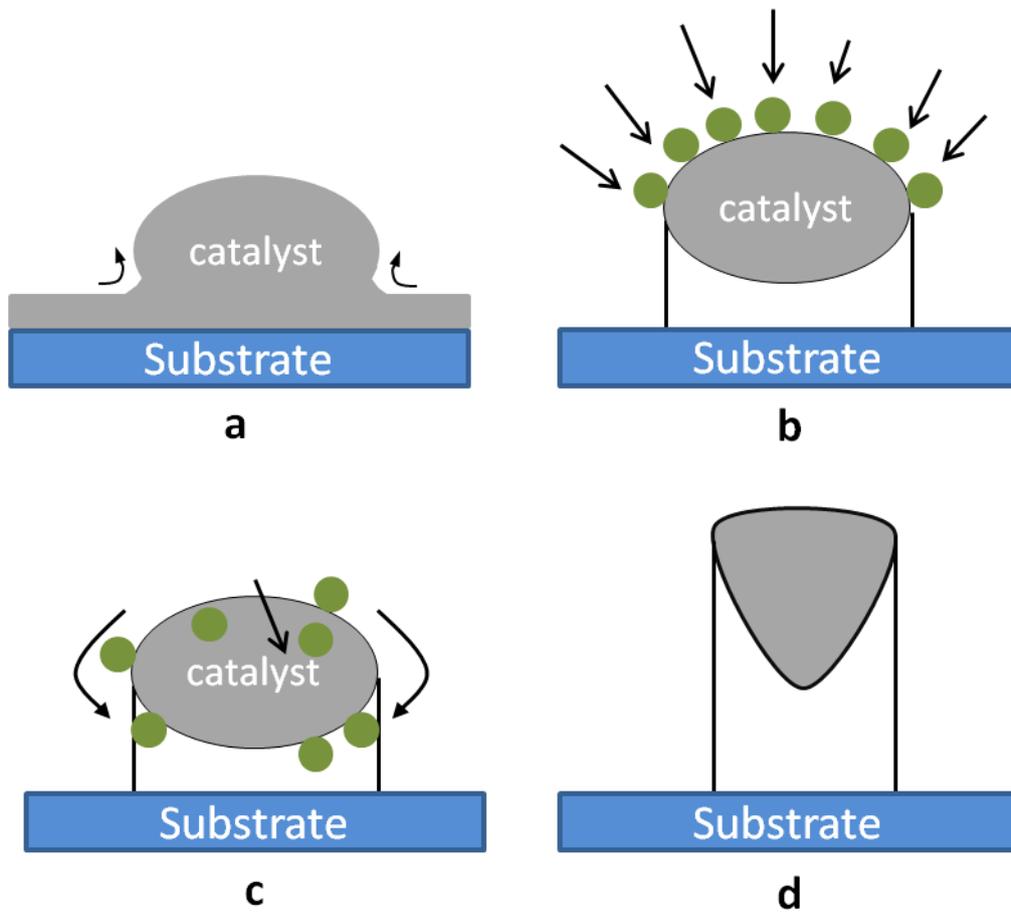


Fig 3. CNF Growth mechanism: a. catalyst nanoparticle formation. b. Carbon adsorption at the catalyst site. c. Carbon through the bulk and or surface diffusion of the catalyst. d. nucleation.

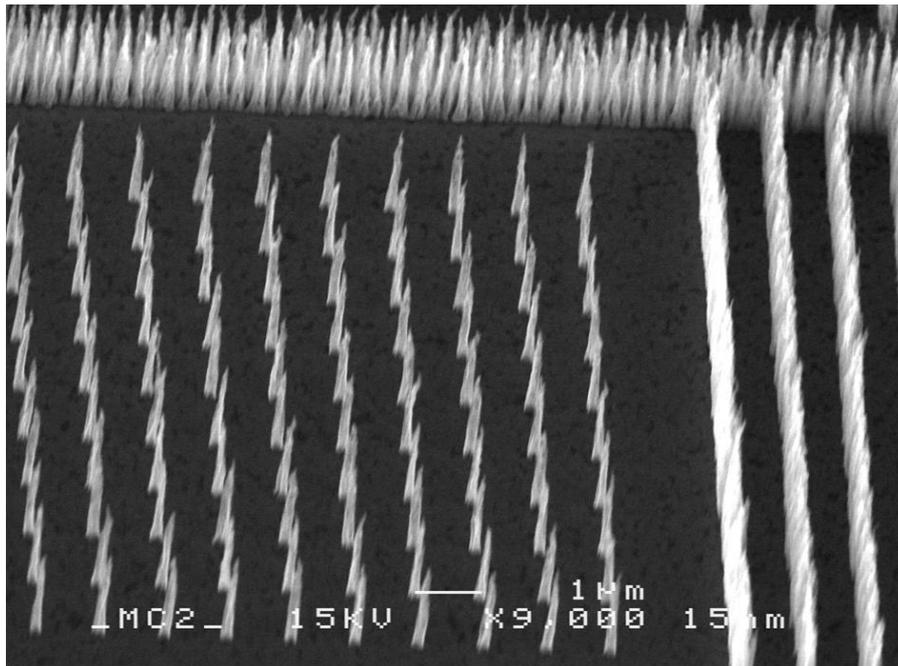
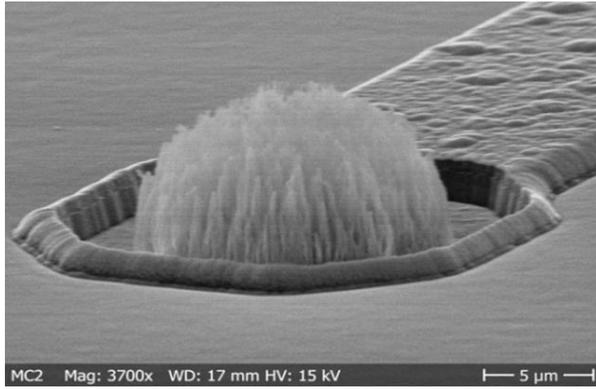
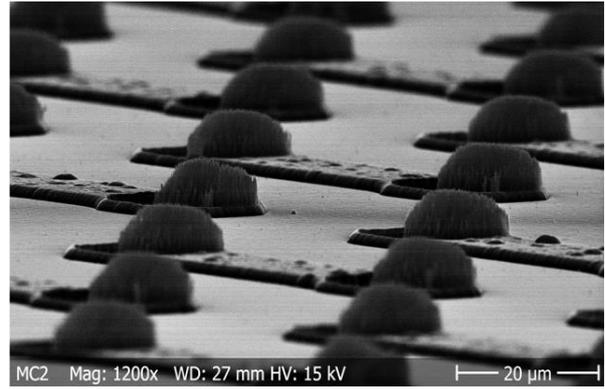


Fig 4. SEM picture of individual fibers.



a



b

Fig 5.a. SEM micrograph of Carbon bumps grown (hence rooted) on solder pads. B. array of Carbon bumps