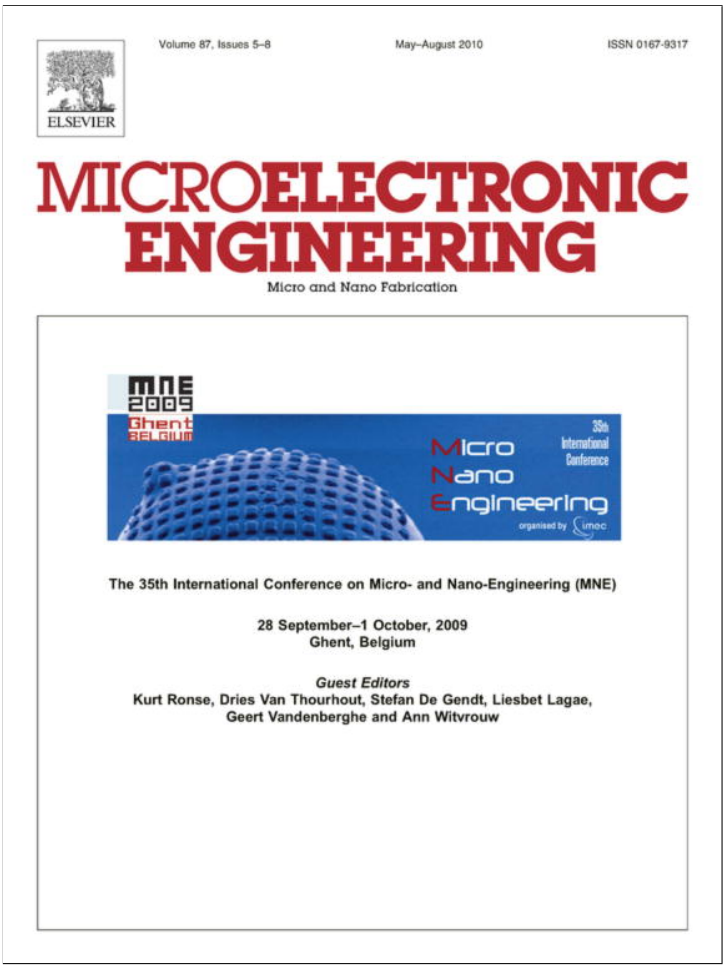

Microelectronic Engineering 87 (2010) 1491–1493

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Controlling the growth of carbon nanotubes for electronic devices

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ARTICLE INFO

Article history:
Received 2 October 2009
Received in revised form 11 November 2009
Accepted 13 November 2009
Available online 1 December 2009

Keywords:
Carbon nanotubes
Electronic devices
Field emission

ABSTRACT

This paper acts as an introduction to carbon nanotubes (CNTs). Chemical vapour deposition (CVD) is detailed together with a summary of their applications in electronics. Among the most promising applications is in field emission. The morphology can be controlled to produce high-brightness field emission sources for SEMs, microwave amplifiers and X-ray sources.

1. Introduction

Carbon nanotubes (CNTs) are a unique form of carbon which can be described as graphene sheets rolled up to form tubes with a fullerene cap. The CNTs can exhibit either metallic-like or semiconductor-like properties, which depends on their chirality – or the way in which the graphene sheet is rolled up. Two thirds of single-walled CNTs are semiconducting, whilst the rest are metallic. The band gap of semiconducting single-walled CNTs decreases with increasing diameter. Multi-walled CNTs, which tend to be of larger diameter, exhibit "semi-metallic" behaviour. They have been investigated for their application to devices throughout nanotechnology because of their high aspect ratio, large surface area, electrical conductivity, stability and strength [1]. CNTs can be grown by either arc discharge, laser ablation or by chemical vapour deposition (CVD). The latter process has advantages over the others in that the position, from which the CNTs grow, together with their dimensionality, can be controlled. In contrast, the others cannot, with the resultant CNTs entangled and embedded within soot.

2. Growth of CNTs by CVD

There now follows a typical CVD CNT growth process. Catalyst is deposited onto a substrate, often by evaporation or by sputtering. Ferromagnetic metals have proven to be the most successful catalysts. In the case of a silicon substrate, a diffusion barrier layer 10–20 nm thick is deposited first. These tend to be silicon dioxide, titanium nitride, alumina or indium tin oxide. The barrier prevents the catalyst particles diffusing into the substrate during the growth process. Upon heating, the film dewets to form balls (as can be seen in Fig. 1a and b). The catalyst particles are annealed at temperature with a flow of either ammonia or hydrogen and in the case of plasma-enhanced CVD (PECVD), with a plasma. After the annealing step, the carbon feedstock (usually a short-chain hydrocarbon or alcohol) is leaked into the chamber. The diameter of the CNT is controlled by the catalyst particle size, the length by the growth time. In CVD, the energy required to break down the reactant deposition gases into graphene comes solely from the heat supplied to the catalyst particle and its immediate environs. Usually, there is no alignment of CNTs from the CVD process. The grown CNTs are often randomly orientated and resemble spaghetti. However, under certain reaction conditions, even in the absence of plasma, closely spaced nanotubes will maintain a vertical growth direction resulting in a dense array of tubes resembling a carpet or forest. Such growth is being investigated for CNT vias, because a dense forest of CNTs is required to give the maximum current density. In PECVD, the applied plasma creates a sheath above the substrate in which an electric field perpendicular to the substrate is induced. This field breaks down some of the deposition gases and vertically aligns the CNTs as they follow the induced field. This is shown in Fig. 1c.

CNTs can have a Young's Modulus ~10 times that of steel [2] and an electrical conductivity up to 1000 times that of copper [3]. A summary of the optimum properties of CNTs are listed in Table 1 [4].

Many devices and technologies have the potential to be enhanced by incorporating CNTs. For instance, CNTs can be used

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doi:10.1016/j.mee.2009.11.072

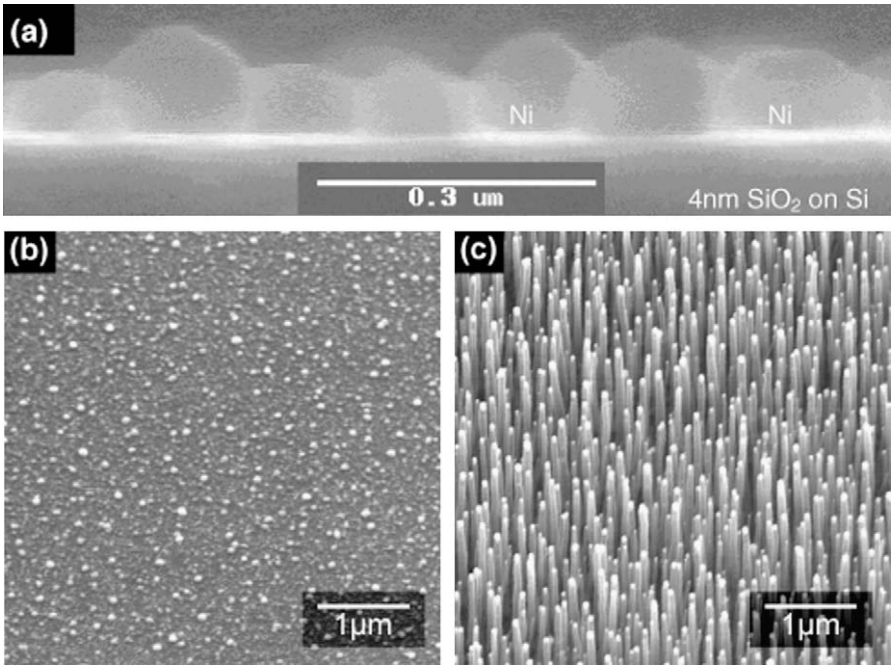

Fig. 1. When Ni nanoclusters (a) and (b) are on a 4 nm layer of SiO_2 deposited onto a Si substrate, they exhibit weak interactions (c.f. 'hydrophobic') with their supports hence favouring tip growth (the Ni is the high contrast dot seen at the tip of the nanotube as in (c)).

as electrodes in many devices. The advantage they have is structural, in that their large surface area enables a high degree of efficiency. For instance, higher charge storage capabilities result, which is suitable for electrochemical supercapacitors [5]. Their high electrical conductivity and relative inertness also make CNTs potential candidates as electrodes for use in electrochemical reactions [6]. There has also been research into using CNTs to store hydrogen [7] though the amount stored less than was originally anticipated [8]. CNTs mechanically deflect upon electric stimulation which opens up the possibility of their application in cantilevers and actuators. There has also been extensive work on their application in composites which utilize their physical strength and small size. These composites are already available on the market. For instance, Easton-Bell Sports and Zyvex use CNTs in bicycle components. Here single-walled CNTs are favoured as they are more flexible whilst still very strong [9].

Table 1
Properties of CNTs.

Mechanical properties	
Young's modulus of multi-walled CNTs	~1–1.2 TPa
Young's modulus of single-walled CNT ropes	~1 TPa
Tensile strength of single-walled nanotube ropes	~60 GPa
Thermal properties at room temperature	
Thermal conductivity of single-walled CNTs	1750–5800 W mK
Thermal conductivity of multi-walled CNTs	>3000 W mK
Electrical properties	
Typical resistivity of single- and multi-walled CNTs	$10^{-6}\ \Omega$ m
Typical maximum current density	$10^7 - 10^9$ A cm^2
Quantized conductance, theoretical/measured	$(6.5\ k\Omega)^{-1}/(12.9\ k\Omega)^{-1}$
Electronic properties	
Single-walled CNT band gap	
Whose $n - m$ is divisible by 3	0 eV (metallic)
Whose $n - m$ is non-divisible by 3	0.4–0.7 eV (semiconducting)
Multi-walled CNT band gap	~0 eV (non-semiconducting)

Semiconducting single-walled CNTs have been investigated for their use as a channel material in transistors and in logic elements [10–13] to take advantage of their high mobility. Contact resistance, however, remains a significant problem as does obtaining 100% semiconducting CNTs; ideally, the CNTs employed in this situation will all be of the same chirality. Nevertheless, the electronic properties of a single CNT in these devices varies greatly with adsorbed chemical species, which means they can be used as sensors [14,15].In a highly crystallized CNT, the coherent nature of electron transport can be employed in spin-electronic devices [16]. Because the electrical characteristics of CNTs change upon structural mechanical deformation, they can also be used as electromechanical sensors [17].

It is clear that the integration of CNTs as the active part in electronics is, as yet, a long way away. Whilst the devices and structures proposed above have a realistic chance of success eventually, the most success will result from a device in which its structure is the most important aspect, rather than its electronic properties. In the near term, the CNT applications most likely to come to market first are their employment in various electron sources. Much research has been focused on the application of CNTs to field emission sources because they have several advantages over other field-emitting materials.

3. Field emission devices with CNTs

Electron microscopy demands a bright, stable, low-noise electron source with a low kinetic energy spread to maximise spatial resolution and contrast. Detailed analysis was carried out by De Jonge and co-workers and the field emission properties of CNTs

Table 2
Properties of CNT emitters for microscopy.

Short-term stability (peak to peak)%	0.2
Virtual source size/nm	0.2
Reduced brightness/(Asr^{-1} m^{-2} V^{-1})	~10^9
Energy spread/eV	0.25–0.50

collated from all of De Jonge's papers[18] for their use in SEM/TEM sources are summarized in Table 2 below.

The CNTs act as a cold cathode source (running at a temperature of 400–500 °C). The standard manufacturing procedure is to add them to the tip of a standard tungsten emitter by carbon glue or by electrophoresis. Of all the methods explored so far, in situ PECVD growth, rather than attachment is felt to be a better process. This is because the CNT can be aligned with the applied field and because the contact with the tungsten is reproducible. Mann et al. [19] used PECVD to grow a single CNT on each W tip as shown in Fig. 2. The method uses geometry rather than lithography for growth control. In this case, ITO is used as the diffusion barrier, which is deposited on the tip by sputtering, followed by nickel catalyst. This is a process which can be scaled up to mass production. Conditioned CNTs [20], which have undergone a rapid thermal anneal to 1100 °C to complete the graphene cap structure at the tip of the tubes, are seen as a possible solution to the increasingly high-brightness requirements for TEMs whilst being able to combine this with a low energy spread.

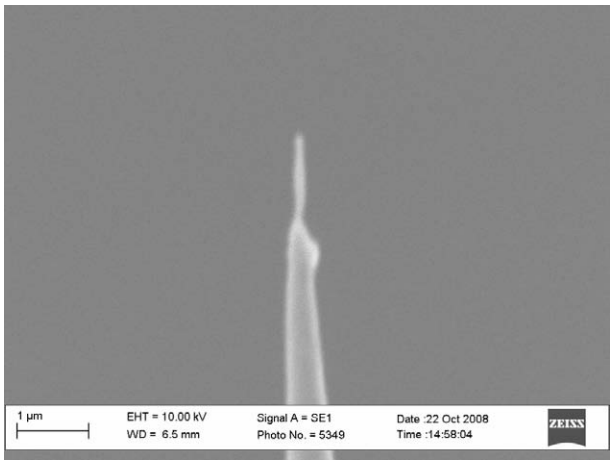

Fig. 2. On-axis grown CNT on etched tungsten. The scalebar is 1 µm.

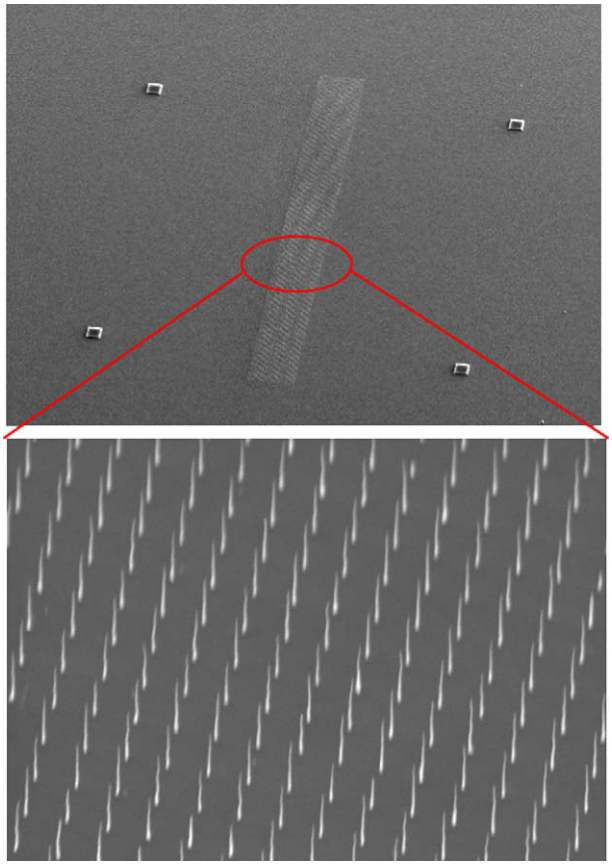

Fig. 3. 10,000 CNTs grown in 1000 × 100 µm array in which their separation is twice the height to optimize current density. The squares are alignment marks and do not contribute to the emission current.

Scaling the process up further still, lithography can be used to position catalyst particles so that CNTs grow from where desired. This process can be used to grow an array of vertically aligned CNTs. This can be used as high-current, cold field emission sources for microwave amplifiers [21] (which should significantly reduce the weight and operating power of satellites, for instance), or electron sources for high-powered X-ray tubes [22] (an example of which is shown in Fig. 3). In order to realize the maximum current density, each CNT needs to be individually ballasted. Small deviations in CNT geometry can significantly change the field amplification factor, and given that current increases roughly exponentially with field (assuming Fowler–Nordheim emission) current runaway and CNT loss can result.

Scaling up the process even further, CNTs have been investigated as possible sources for field emission displays and in backlighting. Unfortunately, the low vacuum requirement (less than 10^{-8} mbar) is preventing this for now.

4. Conclusion

Whilst the application of CNTs to integrated electronics is longer term, many near term applications which take advantage of CNT geometry have the potential to be widely available soon. There still seems to be an excellent outlook for CNT FE applications.

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