Properties of Nanomaterials

Introduction

Nanoscience and nanotechnology include the areas of synthesis, characterization, exploration, and application of nanostructured and nanosize materials. The application of nanomaterials can be historically traced back to even before the generation of modern science and technology. Nanoparticles were used as dye materials in ceramics by ancient people [1]; Colloidal gold was used in medical treatment for cure of dipsomania, arthritis etc, as early as from 19 countries; Systemic experiments conduced on nanomaterials had also been started from the known Faraday experiments [2] in the 1857. In 1959, Richard Feynman gave a lecture titled "There's Plenty of Room at the Bottom", suggesting the possibility of manipulating things at atomic level [3]. This is generally considered to be the foreseeing of nanotechnology. However, the real burst of nanotechnology didn't come until the early 1990s. In the past decades, sophisticated instruments for characterization and manipulation such as scanning electron microscopy, transmission electron microscopy and scanning probe microscopy became more available for researchers to approach the nanoworld. Device miniaturization in semiconductor industrial is also a significant factor for the development of nanotechnology. The Moore law stated that transistor performance and density double every 24 months as shown in Figure 6.1[4]. As the device dimension continues to shrink following this trend, there will be certain limitations due to both the intrinsic materials physics and the technological difficulties, which will remarkably raise the production costs. For example, the quantum effects will become more apparent as the device dimension decrease [5]; The high dopant concentration needed for smaller devices will exceed the solid solubility limit, which will not form stable and uniform doping propile [6]; The high power density and the subsequent device overheating will cause serious problems in the scaling of devices; Lithographic technique for

smaller critical dimension (CD) in the range of tens of nanometers for mass production posses technical difficulties[7]. To this point, nanotechnology may offer an alternative approach for continuing device scaling. Nanoelectronic devices based on new nanomaterials systems and new device structures will contribute to the development of next generation of microelectronics. For example, single electron transistor[8] [9] and field effect transistor [10-12] based on single wall carbon nanotubes are already on the way. Proto type simple logic circuits of carbon nanotubes have already been demonstrated [13-16].
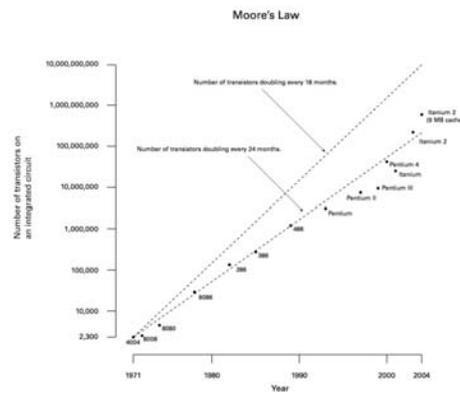

Figure 6.1 Moore law shows that the transistor performance and density double

every 24 months.

Further, nanotechnology was also expanded extensively to other fields of interest due to the novel properties of nanomaterials discovered and to be discovered. For example, nanowires can be potentially used in nanophotonics, laser, nanoelectronics, solar cells, resonators and high sensitivity sensors. Nanoparticles can be potentially used in catalysts, functional coatings, nanoelectronics, energy storage, drug delivery and biomedicines. Nanostructured thin films can be used in light emitting devices, displays and high efficiency photovoltaics. These are only a limited part of the fasting developing nanotechnology, yet numerous of other potential applications of nanomaterials have already been or will be discovered. During the real bursting of nanotechnology in the past decade, nanotechnology has become a real interdisciplinary research field in which many physicists,

chemists, biologists, materials science and other specialists are involved. Nanoinvestigations, being widely interdisciplinary by their very nature, promote the joining and merging of the various science and technology fields such as powder technology, colloid chemistry, surface chemistry and physics, clusters and aerosols, tribology, catalysis, simulation and modeling, computer technique, etc [17].

Table 1 Typical nanomaterials

	Size (approx.)	Materials
(a) Nanocrystals and clusters (quantum dots)	diameter 1–10 nm	Metals, semiconductors, magnetic materials
Other nanoparticles	diameter 1–100 nm	Ceramic oxides
(b) Nanowires	diameter 1–100 nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	diameter 1–100 nm	Carbon, layered metal chalcogenides
(c) 2-Dimensional arrays (of nano particles)	several nm^2–μm^2	Metals, semiconductors, magnetic materials
Surfaces and thin films	thickness 1–1000 nm	Various materials
(d) 3-Dimensional structures (superlattices)	Several nm in all three dimensions	Metals, semiconductors, magnetic materials

Table1.1 Typical nanomaterials [18]

The term of nanomaterials covers various types of nanosturctured materials which posses at least one dimension in the nanometer range. Table 1.1 summerized the typical nanomaterials, which include zero dimension nanostructures such as metallic, semiconducting and ceramic nanoparticles; one dimension nanostructures such nanowires, nanotubes and nanorods; two dimension nanostructures such as thin films. Besides this individual nanostructures, ensembles of these nanostructures form high dimension arrays, assemblies, and superlattices. Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk mateials [19]. Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large fraction of atoms of the materials

to be the surface or interfacial atoms, resulting in more "surface" dependent material properties. Especially when the sizes of nanomaterials are comparable to Debye length, the entire material will be affected by the surface properties of nanomaterials [20, 21]. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials, which bring the quantum effects. Nanoparticles can be viewed as a zero dimension quantum dot while various nanowires and nanotubes can be viewed as quantum wires. The quantum confinement of nanomaterials has profound effects on the properties of nanomaterials. The energy band structure and charge carrier density in the materials can be modified quite differently form their bulk count part and in turn will modify the electronic and optical properties of the materials. For example, lasers and light emitting diodes (LED) from both of the quantum dots and quantum wires are very promising in the future optoelections. High density information storage using quantum dot devices is also a fast developing area. Reduced imperfections are also an important factor in determination of the properties of the nanomaterials. Nanosturctures and nanomaterials favors of a self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced, the mechanical properties of nanomaterials will be better than the bulk materials. The superior mechanical properties of carbon nanotubes are well known.

Due to their nanometer size, nanomaterials are already known to have many novel properties. Many novel applications of the nanomaterials rose from these novel properties have also been proposed. In this chapter, the properties of nanomaterials including the mechanical, thermal,

biological, optical and chemical properties of nanomaterials will be addressed together with the possible applications of nanomaterials. However, due to broad coverage of the nanomaterials and related applications, it is nearly impossible to cover all the aspects of the nanomaterials properties in one chapter. Readers are suggested to read references [19, 22-24].

Mechanical properties of nanomaterials

Due to the nanometer size, many of the mechanical properties of the nanomaterials are modified to be different from the bulk materials including the hardness, elastic modulus, fracture toughness, scratch resistance and fatigue strength etc. An enhancement of mechanical properties of nanomaterials can result due to this modification, which are generally resultant from structural perfection of the materials [19, 25]. The small size either renders them free of internal structural imperfections such as dislocations, micro twins, and impurity precipitates or the few defects or impurities present can not multiply sufficiently to cause mechanical failure. The imperfections within the nano dimension are highly energetic and will migrate to the surface to relax themselves under annealing, purifying the material and leaving perfect material structures inside the nanomaterials. Moreover, the external surfaces of nanomaterials also have less or free of defects compared to bulk materials, serving to enhance the mechanical properties of nanomaterials [19].The enhanced mechanical properties of the nanomaterials could have many potential applications both in nano scale such as mechanical nano resonators, mass sensors, microscope probe tips and nano tweezers for nano scale object manipulation, and in macro scale applications structural reinforcement of polymer materials, light weight high strength materials, flexible conductive coatings, wear resistance coatings, tougher and harder cutting tools etc.

Among many of the novel mechanical properties of nanomaterials, high hardness has been discovered from many nanomaterials system. A variety of superhard nanocomposites can be made

of nitrides, borides and carbides by plasma-induced chemical and physical vapor deposition [26]. In the appropriately synthesized binary systems, the hardness of the nanocomposite exceeds significantly that given by the rule of mixtures in bulk. For example, the hardness of nc-M_nN/a–Si_3N_4 (M=Ti, W, V,…) nano-composites with the optimum content of Si_3N_4 close to the percolation threshold reaches 50 GPa [27-29] although that of the individual nitrides does not exceed 21 GPa. These superhard nanocomposites will have promising potential in hard protective coatings. Superhardness also comes from pure nanoparticles. For example, Gerbericha report the superhardness from the nearly spherical, defect-free silicon nanospheres with diameters from 20 to 50 nm of up to 50 GPa, fully four times greater than the bulk silicon [30].

Since their discovery [31, 32], carbon nanotubes have stimulated intensive research interests. As the smallest carbon fibers discovered, carbon nanotubes have been found to have excellent mechanical properties. The strength of the carbon fibers would increases with graphitization along the fiber axis. Carbon nanotubes, which are formed of seamless cylindrical graphene layers, represent the ideal carbon fiber and should presumably have the best mechanical properties in the carbon fibers species, showing a high Young's modulus and high tensile strength [33]. Theoretical research has predicted the high modulus of carbon nanotubes aside from the direct experimental measurement, which calculated the Young's moduli Y of single wall carbon nanotubes to be from 0.5-5.5TPa, much higher than high-strength steel of ~200 GPa [34, 35]. The Young's moduli and the tensile strength have also been measured experimentally [33, 36-39]. The first experimental measurement of Young's modulus of Multiwall carbon nanotubes was obtained by measuring thermal vibrations of carbon nanotubes using transmission electron microscopy (TEM), yielding the Young's modulus of 1.8+/-0.9 TPa [38]. In this method, the amplitude of the thermal vibrations of the free ends as a function of temperatures of anchored nanotuebes was correlated with the young's modulous. Figure

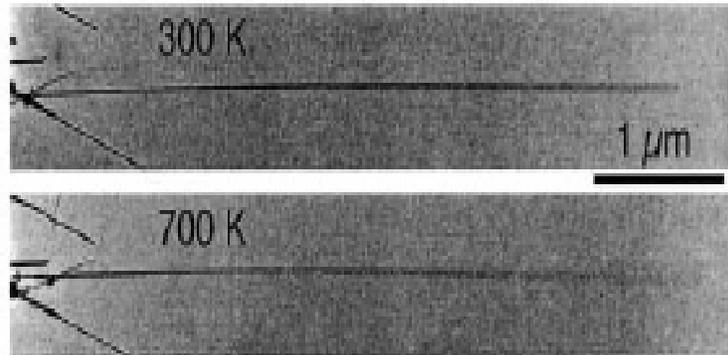1.2 shows the free standing multi wall carbon nanotubes with tip blurring due to thermal vibration.

Figure 1.2: the free standing multi wall carbon nanotubes with tip blurring due to thermal vibration. By using a similar technology, Krishnan measured the young's modulous of single wall carbon nanotubes, resulting in average value of Y=1.25 -0.35/+0.45 TPa [33]. Atomic force microscope (AFM) has also been employed to measured the young's modulus of the carbon nanotubes [39]. This is realized by bending the anchored carbon nanotubes with AFM tip wihle simultaneously recording the force by the tube as a function of the displacement from its equilibrium position. The resultant Young's modulous was 1.28+/- 0.5 TPa. The values of Young's moduli measured from different ways were all in the range in theorical prediction, proving the existence the high elastic modulus of the carbon nanotubes. The tensile strength of carbon nanotubes has also been measured [36, 37].
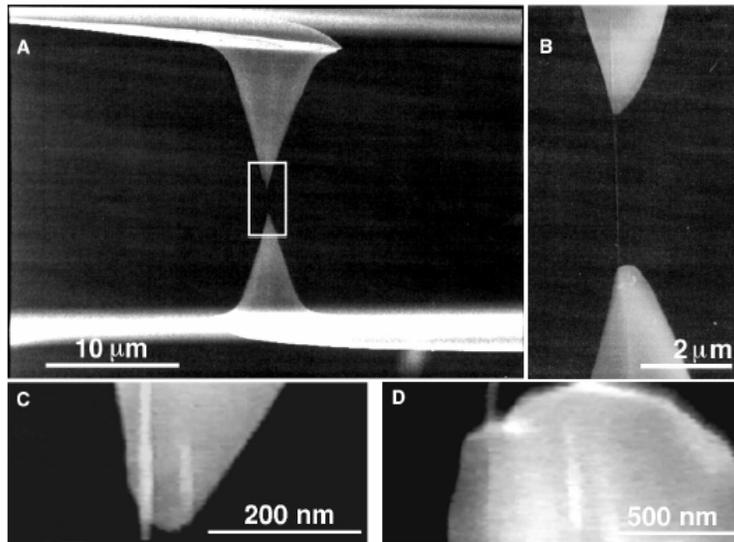
Figure 1.3: A multi wall carbon nanotube was aligned between two AFM tips. The lower AFM tip is on a soft cantilever whose deflection is recorded to determine the force applied on the carbon nanotube.

An individual multi wall carbon nanotube was mounted between two AFM tips, one on rigid cantilever and the other on soft cantilever (Figure 1.3). By recording the whole tensile loading experiment, both the deflection of the soft cantilever from which the force applied on the nanotube and the length change of the nanotube were simultaneously obtained. The carbon nanotubes broke in the outermost layer ("sword-in-sheath" failure), and the tensile strength of this layer ranged from 11 to 63 GPa and the measured strain at failure can be as high as 12%. For comparison, the tensile strength of high-strength steel is 1-2 GPa [36, 37].

The excellent mechanical properties of nanomaterials could lead to many potential applications in all the nano, micro and macro scales. High frequency electro-mechanical resonators have been made from carbon nanotubes and nanowires.
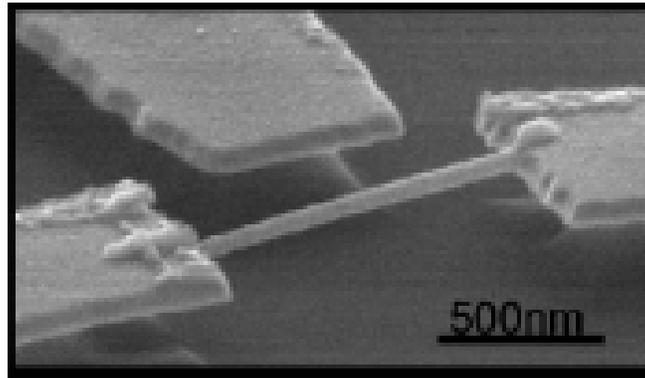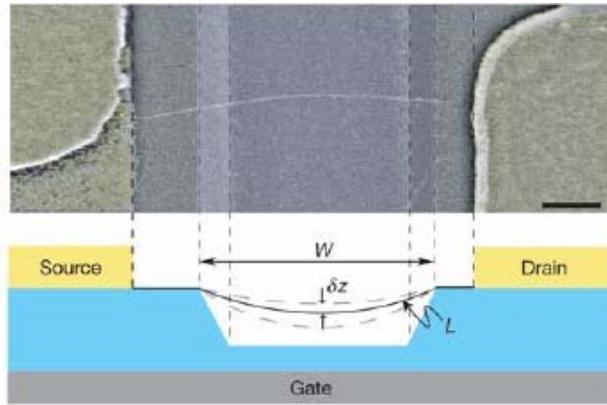
Figure 1.4 (a) SEM image showing the carbon nanotubes suspended between two electrodes (top). The schematic de vice geometry is shown at the bottom. Scale bar: 300 nm [40]. (b) SEM image of the resonator with a suspended nanowire.

An individual carbon nanotube was contacted with two metal electrodes and was doubly clamped and suspended across a trench, which was realized by conventional lithography technique (Figure 1.4). The nanotube resonator was actuated and detected through electrostatic interaction using back side gate electrode underneath the tube in a vacuum. The guitar-string-like oscillation modes of doubly clamped nanotube was discoved from the resonator with the resonant frequency as high as 55 MHz. A similar nanoelectromechanical resonator can also be fabricated from platinum nanowires [41]. The nanowire resonator bear a similar but a with side gate electrode to detect the actuation [40], which gave a resonant frequency of 105MHz. These NEMS oscillators could potentially useed in ultrasensitive mass detection1, radio-frequency signal processing, and as a

model system for exploring quantum phenomena in macroscopic systems.

Nano structured materials can also be used as nanoprobes or nanotwizzers to probe and manipulate nanomatierals in a nanometer range [42-46]. Due to their high aspect ratio and small dimensions, one-dimension nano structures such as carbon nanotubes can also be used as nano probe tips. Dai attached multi wall carbon nanotube to conventional pyramidal tip of a silicon cantilever for scanning force microscopy [43].
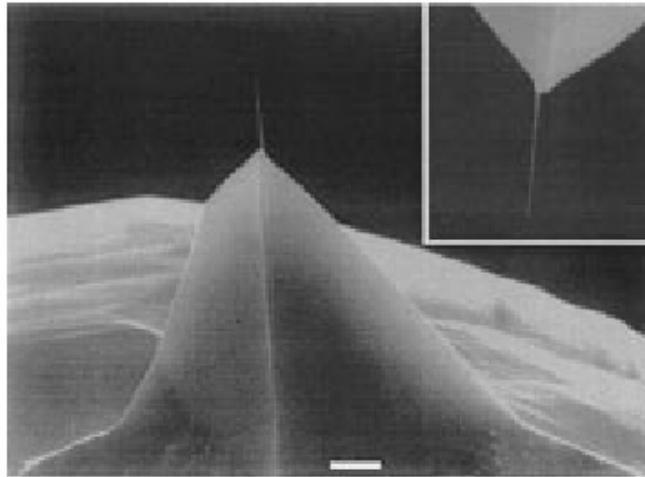

Figure 1.5: SEM image of a MWNT attached on the silicon cantilever tip [44].

sample	tip	width at half-maximum (nm)^a	depth between subunits (nm)^b	tip radius (nm)^c
type-1 fibril	MWNT	18.6 ± 2.2	3.2 ± 0.4	9.3
	SWNT	11.9 ± 0.7	2.7 ± 0.4	2.6
	Si-TESP	26.0 ± 0.9	2.7 ± 0.3	19.7
	Si-FESP	21.5 ± 1.8	2.5 ± 0.3	12.9
protofibril	MWNT	11.4 ± 0.4	1.1 ± 0.1	9.7
	Si-TESP	14.4 ± 0.3	0.6 ± 0.1	15.9
	Si-FESP	14.8 ± 1.7	0.7 ± 0.2	16.9

Table 1.2 The comparasion of the Resolution Obtained with Nanotube and Silicon Tips on A, 40 Fibrils and Protofibrils [44].

Stanislaus S. Wong acquired high resolution AFM image for biological systems by using carbon nanotubes tips[42, 44]. Figure 1.5 shows a typical nanoprobe tip made from carbon nanotube. While most conventional tips suffer from "tip crash", posse significant constraints on potential lateral resolution, and furthermore, the large probe size restricts the ability of these tips to access narrow

and deep features. Probe tips from carbon nanotubes could offer several advantages: the flexibility of carbon nanotubes makes the tip more resistant to damage from tip crashes; the high aspect ration of carbon nanotubes makes them suitable to image sharp recesses in surface topography; Tips from carbon nanotubes could significantly improved lateral resolution; carbon nanotubes tips are more robust and less prone to contamination. By investigating the amyloid-β1-40 (Aβ40) fibrils under AFM, Stanislaus compared the performance of nanotubes tips and the single crystal silicon tips (Table 1.2) An improvement of the image resolution (smaller fibrils and protofibrils with were imaged using carbon nanotube tips) due to a reduction of the effective tip radii when imaging with nanotube tips was acquired [44].

Similar to the carbon nanotube nanoprobe fabrication, if on the supporting micro structure, two individual carbon nanotubes are attached instead of only one nanotube in case of nanoprobe, then a nanotube nano tweezers would result. Phillip Kim showed such a nanotube tweezers by attaching two carbon nanotubes on glass micropipettes [45]
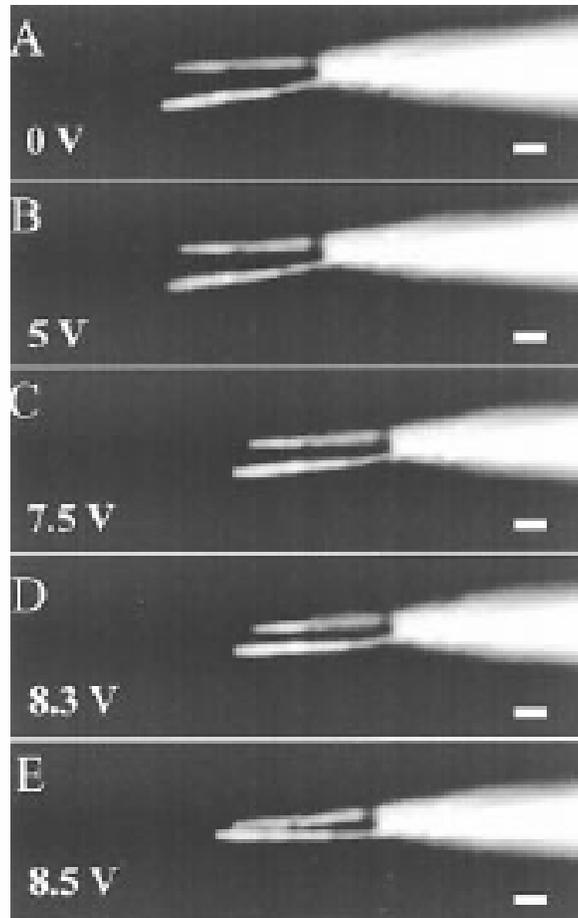
Figure 1.6 Dark field optical images of the electro-actuated nanotube nanotwizzers.

This nano tweezers operated under electrical stimulus and was used to probe the electrical characteristics of nanostructures. It could be useful both in the nanostructure characterization and the manipulation. The nanotweezers could be used as a novel electromechanical sensor that can detect pressure or viscosity of media by measuring the change in resonance frequency and Q-factor of the device. They can also be explored into manipulation and modification of biological systems such as structures within a cell.

The enhancements of mechanical properties of polymeric materials by nanofillers are also very active applications of nanomaterials. Micrometer size fillers were used in traditional polymer composites and showed improvements in their mechanical properties such as the modulous, yield strength and glass transition temperature [47, 48]. However, these performacen enhancements will

sacrifice the ductility and toughness of the materials and large amounts of filler were needed to achieve the desired properties. Comparably, polymer nanocomposites from nano size fillers could result in unique mechanical properties at very low filler weight fractions [49]. Sumita found dramatic improvements in the yield stress (30%) and Young's modulus (170%) in polypropylene filled with with ultrafine SiO_2, compared to micrometer-filled polypropylene [50].Ou et al. filled nylon-6 with 50 nm silica particles using in situ polymerization method. They reported increases in tensile strength (15%), strain-to-failure (150%), Young's modulus (23%), and impact strength (78%) with only 5 wt % nanoparticles content [51]. Petrovic found a 6 times increase in the elongation-at-break and a 3 times increase in the modulus in a rubbery polyurethane elastomer filled with 40 wt % 12 nm silica, compared to a micrometer-sized filler reinforced polymer [52]. Vinylacetate, acrylic ester, synthetic rubber, and other polymer latexes have been used in coatings and adhesives; colloidal silica is used with these polymer emulsions in order to improve adhesion, durability, and abrasion resistance. The silica also serves to prevent stickiness and improves the washing resistance of the coatings [53]. Besides nanoparticles, One-dimension nanostructures such as carbon nanotubes are also superior candidates for nano fillers because of their high aspect ratio and excellent mechanical properties. Nanocomposite materials from carbon nanotubes are expected to exhibit outstanding mechanical properties, such as high Young's modulus, stiffness and flexibility.

Polymer	E' (40°C, 1 Hz) (matrix) (MPa)	E' (40°C) CNTs composite (MPa)	CNTs (wt%)	% Increase E'
PMMA	≅800	≅1600	26	100
PS	≅2400	≅3500	5	44
PSBA	≅0.681	≅1.584	7	132
PVA	≅5000	≅11200	60	124
MEMA	708	2340	1	230

Table 1.3 Comparative results (E′, % increase E′) of CNTs composites obtained in different polymer matrices at 40°C 1Hz of frequency [54].

Table 1.3 summarized some results from several research groups of the enhancement of mechanical properties of polymers nanocomposites containing carbon nanotubes fillers [54-59]. Without the use of additives, generally more than 100% in "E′" was acquired. Besides the improvement of mechanical properties in carbon nanotube- polymer nanocomposites, they can further be employed as multifunctional materials providing light weight, strong and tough structural materials as well as excellent electrical conducting and thermal conducting properties.

Thermal properties of nanomaterials

The recent advances of nanotechnologies in the past decades have resulted in the burst of promising synthesis, processing and characterization technologies, which enables the routine production of a variety of nanomaterials with highly controlled structures and related properties. By controlling the structures of nanomaterials at nano scale dimensions, the properties of the nanostructures can be controlled and tailored in a very predictable manner to meet the needs for a variety of applications. Examples of the engineered nanostructures include metallic and non-metallic nanoparticles, nanotubes, quantum dots and superlattices, thin films, nano composites and nanoelectronic and optoelectronic devices which utilize the superior properties of the nanomaterials to fulfill the applications.

Many properties of the nanoscale materials have been well studied, including the optical electrical, magnetic and mechanical properties. However, the thermal properties of nanomaterials have only seen slower progresses. This is partially due to the difficulties of experimentally measuring and controlling the thermal transport in nano scale dimensions. Atomic force microscope (AFM) has

been introduced to measure the thermal transport of nanostructures with nanometer-scale high spatial resolution, providing a promising way to probe the thermal properties with nanostructures [60]. Moreover, the theoretical simulations and analysis and of thermal transport in nanostructures are still in infancy. Available approaches including numerical solutions of Fourier's law, computational calculation based on Boltzmann transport equation and Molecular-dynamics (MD) simulation, all have their limitations [60]. More importantly, as the dimensions go down into nanoscale, the availability of the definition of temperature is in question. In non-metallic material system, the thermal energy is mainly carried by phonos, which have a wide variation in frequency and the mean free paths (mfp). The heat carrying photons often have large wave vectors and mfp in the order of nanometer range at room temperature, so that the dimensions of the nanostructures are comparable to the mfp and wavelengths of photons. However the general definition of temperature is based on the average energy of a material system in equilibrium. For macroscopic systems, the dimension is large enough to define a local temperature in each region within the materials and this local temperature will vary from region to region, so that one can study the thermal transport properties of the materials based on certain temperature distributions of the materials. But for nanomaterial systems, the dimensions may be too small to define a local temperature. Moreover, it is also problematic to use the concept of temperature which is defined in equilibrium conditions, for the nonequilibrium processes of thermal transport in nanomaterials, posing difficulties for theoretical analysis of thermal transport in nano scales [60].

In spite of all the difficulties in both experimental and theoretical characterization the thermal properties of nanomaterials. Recent advances in experiments have showed that certain nanomaterials have extraordinarily thermal properties compared to their macroscopic counterparts, as will be explained in detail in this section. In nanomaterials systems, several factors such as the

small size, the special shape, the large interfaces modified the thermal properties of the nanomaterials, rendering them the quite different behavior as compared to the macroscopic materials. As mentioned above, as the dimension goes down to nano scales, the size of the nanomaterials is comparable to the wavelength and the mean free path of the photons, so that the photon transport within the materials will be changed significantly due the photon confinement and quantization of photon transport, resulting in modified thermal propeties. For example, nanowires from silicon have a much smaller thermal conductivities compared to bulk silicon [61]. The special structure of nanomaterials also affects the thermal properties. For example, because of it tubular structures of carbon nanotubes, they have extreme high thermal conductivity in axial directions, leaving high anisotropy in the heat transport in the materials [62]. The in interfaces are also very important factor for determine the thermal properties of nanomaterials. Generally, the internal interfaces impede the flow of heat due to photon scattering. At interface or grain boundary between similar materials, the interface disorder scatters phonons, while as the differences in elastic properties and densities of vibrational states affect the transfer of vibrational energy across interfaces between dissimilar materials. As a result, the nanomaterials structures with high interfaces densities would reduce the thermal conductivity of the materials [63]. These interconnected factors joined together to determine the special thermal properties of the nanomaterials. Thermal properties of several nanomaterials systems and their possible applications will be discussed below.

As the first example, carbon nanotubes are carbon nanostructures relating to diamond and graphite, which are well known for their high thermal conductivities. The stiff sp^3 bonds in diamond structure result in high phonon speed and consequently high thermal conductivities of the material. In carbon nanotubes, the carbon atoms are held together by the even stronger sp^2 bonds, so that the

nanotube structures, consisting of seamlessly joined graphitic cylinders are expected to have extraordinarily high thermal conductivities. The rigidity of the these nanotubes, combined with virtual absence of atomic defects or coupling to soft photon modes of the embedding medium, should make isolated nanotubes very good candidates for efficient thermal conductors [64]. The high thermal conductivity of carbon nanotubes were first proved by some theoretical calculations [64, 65]. Savas Berber et al combined the equilibrium and nonequilibrium molecular dynamics simulations with Tersoff potential to determine the thermal conductivity of carbon nanotubes and its dependence on temperature.
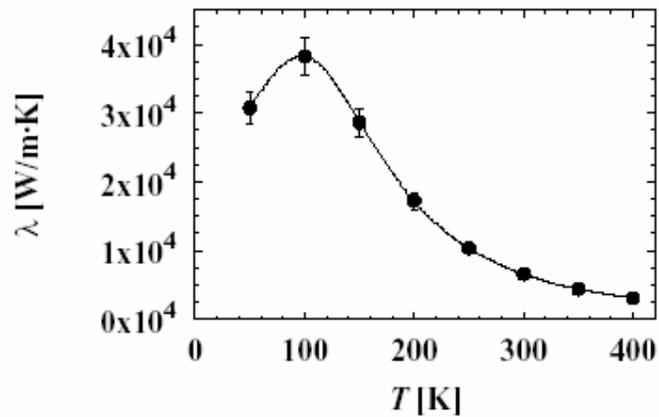

Figure1.7 Temperature dependence of the thermal conductivity for a (10, 10) carbon nanotube

for temperatures below 400 K [64].

They concluded that the thermal conductivity of an isolated (10, 10) nanotubes was dependent on the temperature and an extraordinarily high value of ~6600W/mK was resultant at room temperature, shown in Figure 1.7. This is comparable to the thermal conductivity of a hypothetical isolated graphene monolayer or diamond. From the thermal conductivity of bulk carbon nanotube samples, J. Hone, et al estimated the thermal for a single tube to be 1800 - 6000 W/mK at room temperature [66]. Che et al also used equilibrium molecular dynamics simulations to calculate carbon nanotubes' thermal conductivities and gave a thermal conductivity of ~ 2980 W/mK along

the tube axis for a (10, 10) nanotube [67]. In spit of the discrepancies of the values from these theoretic works, nonetheless, it showed that carbon nanotubes have high thermal conductivities. Experimental work has also been performed to measure the thermal conductivities of single carbon nanotubes or small nanotube bundles [68, 69].
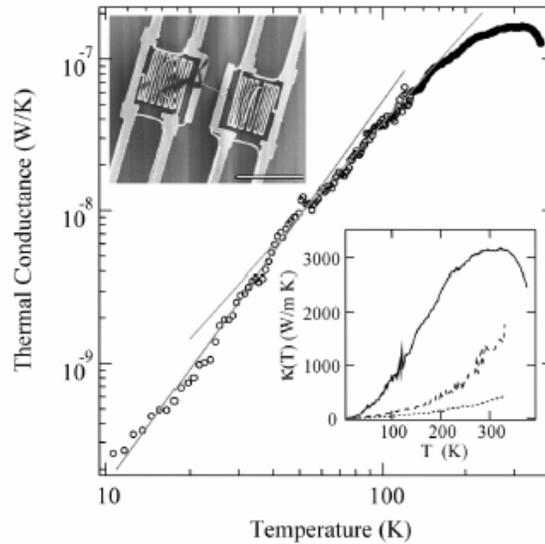

Figure 1.8: the thermal conductance of an individual MWNT (d=14 nm). Lower inset: Solid line represents thermal conductivity of an individual MWNT (d=14 nm). Broken and dotted lines represent small (d=80 nm) and large bundles (d=200 nm) of MWNTs, respectively. Upper inset: SEM image of the suspended islands with the individual MWNT. The scale bar represents 10 mm [68].

P. Kim et al measured the thermal conductivity of an individual carbon nanotube by attaching single nanotube or small bundles to the microfabricated suspended devices as shown in Figure 1.8, and reported the thermal conductivity of above 3000W/mK for a single nanotube at room temperature. Recently Motoo Fujii et al measured the thermal conductivity of single carbon nanotube using a suspended sample-attached T-type nanosensor [69], and reported values exceeding 2000W/mK for a carbon nanotube of 9.8nm diameter. These experimental values were in the range of the

theoretical calculations, proved the high thermal conductivity of the carbon nanotubes experimentally. Due to their high thermal conductivities, carbon nanotubes or nanotubes based nanocomposite could be promising candidates for heat transport management in many applications such as in the integrated circuits, optoelectronic devices and MEMS structures.

On the other hand, one-dimensional nanowires may offer ultra low thermal conductivities, quite different from that of carbon nanotubes. In nanowires, phonons behave differently from those in the corresponding bulk materials due to the quantum confinement in the one dimension structures. The nanowire surface can introduce surface phonon modes, resulting in many different phonon polarizations other than the two transverse and one longitudinal acoustic branches found in bulk semiconductors. Those changes in the dispersion relation can modify the group velocity and the density of states of each branch. The phonon lifetime also changes due to the strong phonon–phonon interactions and the boundary scattering within the nanostructures [60]. Thus the phonon transports and the thermal properties of the nanowires will be significantly different from that of the bulk materials. The phonon transport of semiconducting nanowires have been studied experimentally [61, 70] and theoretically [71-73]. Deyu et al measured the thermal conductivity of silicon nanowires using a microfabricated suspended device over a temperature range of 20–320K [61, 70]. The device structure is shown in Figure 1.9 (left). Also shown in Figure 1.9 (right) is the measurement results for silicon nanowires with different diameters. Although the nanowires had well-defined crystalline order as in bulk materials, the observed thermal conductivity was more than two orders of magnitude smaller than that of bulk silicon, which also showed a strong dependence on the nanowires size. For a silicon nanowire with 22nm diameter, the thermal conductivity was reduced to be in the sub 10 W/m range. The appreciable change of the thermal conductivity compared to the bulk materials was ascribed to phonon–boundary scattering and the possible

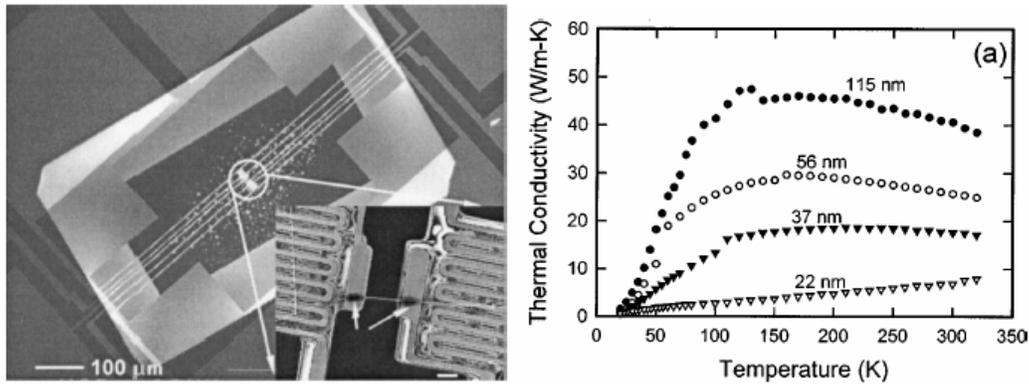change in phonon dispersion due to confinement within the nanostructures.

Figure 1.9 Left: SEM image of the suspended heater. The lower inset shows a 100 nm Si nanowire bridging the two heater pads. The scale bar in the inset represents 2 mm. Right: Measured thermal conductivity of different diameter Si nanowires. The number beside each curve denotes the corresponding wire diameter.

The same research group also measured the thermal conductivity on Si/SiGe superlattice nanowires [70], with even smaller thermal conductivity reported on the superlattice nanowires compared to pure silicon nanowires. These experimental results agreed fairly well with the theoretical calculations based on phonon dispersions approach [71, 72]. The low thermal conductivity in these one dimensional semiconducting nanowires will find applications in thermoelectric power generation and the thermoelectric refrigeration. However, they are not desired in for thermal management in electronics, which generally need much higher thermal transport capabilities.

Besides the one dimensional nanowires, multilayer and superlattices are another type of nanostructures offering low thermal conductance. David G. Cahilla et al wrote an excellent review about the thermal transport of the nanomaterials and elaborated the thermal transport in multilayer and superlattices [60]. Multilayers and superlattices are thin film structures that contain alternating layers of two different materials stacked upon each other. In multilayers structure the films can be either amorphous or polycrystalline while in superlattices the films are single crystal. There are

many effects in the multilayers or superlattices structures that affect the phonon transport properties of the materials. When alternating layers of materials are stacked together, many collective mode of phonon transport may appear besides the phonon modes in each single layer. This stacking effect will be more apparent when the coherence phonon length scales are much larger than that of a single layer. It is also a coupled behavior resulting from interference of phonon waves reflected from multiple interfaces. When the mean free path of phonons span multiple interfaces, the phonon dispersion relation is modified and zone folding occurs, even resulting in multiple phonon band gaps [74]. Moreover, due to the modification of the phonon dispersion, the phonon group velocities will be reduced significantly and the scattering rate will also be increased. The interfaces is also an important factor in determine the phonon transport properties due to the high density of interfaces in the multilayers or superlattices structures. For example, if the two materials in the superlattice have large mismatch in the phonon dispersion relations, phonons in certain frequency range cannot propagate to the neighboring layer unless there are mode conversions at the interface; The interfaces between two different materials with different lattice constants can contain dislocations and defects, which can also scatter phonons and reduce thermal conductivity; physical roughness and alloying will also exist at the interface depending on the processing, and affect the phonon transport. The over all effect in of these factors on the phonon transport in the multilayer and superlattice structures is a general decrease of thermal conductivities.
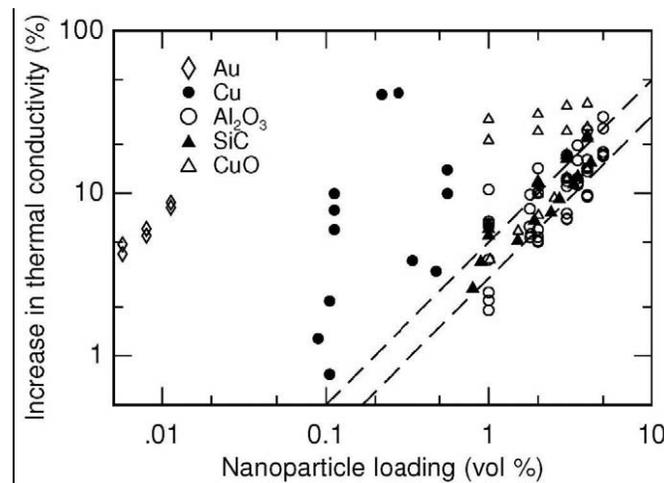
Materials	Effects considered	Temperature behavior	Period behavior	Lowest thermal conductivity
GaAs/AlAs	not applicable	not applicable	in-plane: max at 200 Å	in-plane: 12 W m^{-1} K^{-1}
GaAs/AlAs	interface roughness	in-plane: decrease 190−450 K	(700 Å/700 Å only)	in-plane: ≈ 40
GaAs/AlAs	AM, band gaps, roughness	decrease 100−400 K	increase 10−400 Å	4
Si/Ge	dislocations	increase to ≈ 150 K	maximum at 70 Å	≈ 1.6
Si/Si$_{0.71}$Ge$_{0.29}$	AM	not applicable	50 Å/50 Å only)	22, in-plane: 54
Si/Ge	doping, period, dislocations	increase 80−150 K, constant to 330 K	decrease $b = 40-90$ Å	1.2
Si/Si$_{0.7}$Ge$_{0.3}$	AM	increase 100−300 K	slight decrease to $b = 140$ Å increase for $b = 45-300$ Å in-plane: max shifts with period	10
Si$_{0.84}$Ge$_{0.16}$/Si$_{0.76}$Ge$_{0.24}$	AM	increase 50−180 K, constant to 300 K	constant for $b = 67$, 100, 133 Å	8.4
InAs/AlSb	growth temp, annealing	maximum at 150 K	not applicable	2.5
InP/InGaAs	thickness ratio	increase 50−100 K	not applicable	7
Bi$_2$Te$_3$/Sb$_2$Te$_3$	doping, tunneling, localization	not applicable	lattice: minimum at 40 Å	0.2
PbTe/PbSe	not applicable	decrease 200−400 K	40 Å only	1.6

Table 1.4 Experimental results on thermal transport in semiconductor superlattices. Unless noted, the comments refer to cross-plane transport. AM stands for "acoustic mismatch". [60]

Table 1.4 listed several experimental results of thermal conductivities of some semiconducting superlattices of Si, Ge, and their alloys as well as those of III–V materials. Together shown in this table are the several effects being considered for the reduction of thermal conductivities: interfacial roughness, phonon band gaps, dispersion mismatch, doping, structural defects, processing conditions, etc, and also the observed dependence of thermal conductivity on temperature and superlattice period. All of these results showed a significant decrease in thermal conductivities in multilayer or superlattice structures as compared to their bulk materials. In a recent report by R. M. Costescu et al, atomic layer deposition and magnetron sputter deposition were used to synthesize thin-film multilayers of W/Al$_2$O$_3$. With individual layers only a few nanometers thick, the high interface density produced a strong impediment to heat transfer, giving rise to a ultra low thermal conductivity of 0.6 W/mK [63]. Mulitlayers and superlattice nanosturctures could have many potential applications. For example, multilayer thin films can be used as thermal barriers at high temperatures environments, such as in engines to improve their efficiencies; epitaxial superlattices of semiconductor films with low thermal conductivity can be used in thermoelectric power generation because of the ability to the control both electronic band structure and phonon transport

at the same time.

The use of nanofluid to enhance the thermal transport is another promising application of the thermal properties of nanomaterials. Nanofluids are generally referred to the solid-liquid composite materials, which consist of nanomaterials of size in the range 1-100nm suspended in a liquid. Nanofluids hold increasing attentions in both research and practical applications due to their greatly enhanced thermal properties compared to their base fluids. Many type of nanomaterials can be used in nanofluids including nanoparticles of oxides, nitrides, metals, metal carbides, and nanofibers such as single wall and multi wall carbon nanotubes, which can be dispersed in to a variety of base liquid depending on the possible applications, such as water, ethylene glycol, and oils [75]. The most important features of nanofluids are the significant increase of thermal conductivity compared with liquids without nanomaterials, which have been proved by many experimental works.

Figure1.10 Relative increase in the thermal conductivity as a function of the volume fraction of Nanoparticles [75].

Figure 1.10 summarized several reported experimental data for the increase of thermal conductivity of the nanofluids. Masuda et al. reported a 30% increase in the thermal conductivity of water when 4.3 vol.% Al_2O_3 nanoparticles was added into the nanofluid [76], while Xie et al reported a smaller value of increase in thermal conductivity ~20% by Al_2O_3 nanoparticle loading of 5 vol.% [77]. Xie

and coworkers also reported an increase of ~23% for the thermal conductivity of DI water with the addition of SiC at a volume fraction of 4% [78]. J. A. Eastmana et al reported that an addition of 0.3 vol% Cu nanoparticles of mean diameter~10 nm in ethylene glycol resulted in an increase of 40% in the effective thermal conductivity of the nanofluid [79]. Hrishikesh E. Patel et al reported a thermal conductivity enhancement of 5%–21% in the temperature range of 30–60 °C at an Au nanoparticle loading of 0.000 26 (by volume) [80]. On the other hand, carbon nanotubes have also been used in nanofluids. Choi et al. measured thermal conductivities of nanotube-in-oil suspensions which contains multi wall carbon nanotubes, showing an enhancement in thermal conductivity of ~160% for 1.0 vol% nanotubes in oil [81]. All of these experimental results showed a significant increase in of the thermal conductivity of the nanofluids. More over, recent experimental results reveal more thermal properties of the nanofluids, including a nonlinear relationship between thermal conductivity and concentration for nanofluids containing carbon nanotubes; strongly temperature-dependent thermal conductivity; and a significant increase in critical heat flux in boiling heat transfer. Combined with an acceptable viscosity, nanofluids with these merits would be a promising candidate for future thermal transport and management systems [75].

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