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Loo, Shane Zhi Yuan

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APPLICATION OF CARBON NANOTUBES (CNTS) IN COPPER/LOW K INTERCONNECTS DESIGN

Loo Zhi Yuan Shane

School of Mechanical and Aerospace Engineering

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2. Shane Loo, Sridhar Idapalapati, Jijie Zhou, Subodh Mhaisalkar, Shanzhong Wang, Nosik Valery, Xueren Zhang, Tong Yan Tee, “**Enhancing Copper/low- k Interconnects Reliability with Carbon Nanotubes**”, ThinFilms 2006 oral presentation.

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ABSTRACT

With continuing device scaling from a 90nm to a 65nm node, wiring interconnect becomes increasingly crucial due to the effects on electrical resistance and wiring capacitance. The electrical resistance and parasitic capacitance associated with these metal interconnections has become a major factor that limits the circuit speed of such high performance IC's. This limitation is one of the motivating factor for microelectronics industry's move away from aluminium/silicon dioxide interconnects to Cu and low-k dielectrics material systems.

However, copper (*Cu*)/low-*k* interconnect structures suffer from backend manufacturing problems particularly, flip chip packaging and wirebonding. In this project, a novel solution is proposed to eliminate the problem by reinforcing carbon nanotubes (CNTs) in the interconnect structure. CNTs with their extraordinary strength and modulus are dispersed into the dielectric matrix to act as nano-springs to provide a cushioning effect to absorb the impact by wirebonding and the shear stress caused during flip-chip packaging.

The effect of various surfactants in the effective dispersion of CNTs in sol-gel silica is investigated experimentally through microstructural studies as well as mechanical and thermal characterization. Commercially available surfactants used are Hexa Cetyltrimethylammonium Bromide (CTAB) N Dimethyl Formaldehyde (DMF) NanoAQ Poly(4-vinylpyridine) (PVP-4). The CNT composite obtained using PVP-4 gave the best mechanical properties with a weight fraction of CNTs of 0.01%.

Increasing the CNTs weight fraction for physically dispersed composites gave rise to a degradation in properties.

Additional studies are carried out by reinforcing functionalized CNTs (using silane coupling agents) in sol-gel silica matrix. Functionalized CNT composites showed the best efficiency in that with increasing CNTs content, the modulus and hardness also increased. Chemical and thermal characterizations of the CNT composites suggest that CNTs impregnated into the sol-gel matrix did not compromise or affect the properties of the inherent xerogel structure. The experimental results show that the proposed solution is a viable technique that can be integrated into the semiconductor manufacturing process.

1 INTRODUCTION

1.1 Background and Motivation

In modern integrated circuits (ICs) design several active elements need high levels of signal integration with as many as eight to nine layers of high density interconnects. The continued miniaturization in transistor size has led to improvements in circuit speed and device density due to a reduction in gate length. The speed of an electrical signal in an IC is governed by two components – the switching time of an individual transistor (known as transistor gate delay) and the signal propagation time between transistors (known as RC delay, where R is metal line resistance, C is interlevel dielectric capacitance). With continuing shrinkage in device dimension, wiring interconnect becomes increasingly crucial due to the effects of resistance and capacitance. Figure 1-1 shows that RC delay becomes increasingly dominant as compared with the delay caused by the gate length with the reduction in device size.

For classical transistor scaling, performance of the device is purely associated with scaling in gate length, gate dielectric thickness and junction depth. On the other hand, the RC delay in interconnects experiences increased resistance and capacitance due to a decrease in metal line cross sectional area [1]. A model to calculate RC delay is illustrated in Figure 1-2 [2].

Figure 1-1: The gate delay, interconnect delay and sum of delays for Al/SiO₂ and Cu/low-*k* interconnect systems. The gate delay decreases while the interconnect delay increases with shrinkage in feature size [3].

Figure 1-2: Interconnect system with parasitic capacitance

For a given metal line of length L , resistivity ρ , width W , thickness T and pitch P , which is defined as $W + S$, where S is spacing between the metal lines, the total resistance of the metal line R , is

$$R = \frac{2\rho L}{TP} \quad \text{-----} \quad (1.1)$$

The total capacitance associated with both the lateral line to line capacitance, C_{LL} , and the vertical layer to layer capacitance, C_v , is

$$C = 2(C_{LL} + C_v) = \frac{4k\varepsilon_o LT}{P} + \frac{LP}{2T} \quad \text{-----} \quad (1.2)$$

where k is the dielectric constant of the inter layer dielectric material and ε_o is the permittivity of free space. After combining equations (1.1) and (1.2) the RC delay is expressed as:

$$RC = 2k\rho\varepsilon_o \frac{4L^2}{P^2} + \rho \frac{L^2}{T^2} \quad \text{-----} \quad (1.3)$$

As the RC delay is inversely proportional to the square of the metal line pitch and thickness, the transistor scaling will result in notable increase in RC delay. For simplicity, this equation excluded the effects of fringing fields and finite electrode thickness. The RC constant is dependent upon the resistivity of the metal line and the dielectric constant of the dielectric material. Hence, RC delay can be minimized either by decreasing the resistivity of the metal or decreasing the dielectric constant of the dielectric material.

Similarly, Bothra et. al [4] have derived an analytical expression for the dependence of signal rise based on their typical ceramic metal oxide semiconductor (CMOS) inverter circuit design. They conclude that a higher performance of the interconnect (also a decrease in switching delay) can be achieved by the introduction of materials

that has greater resistance to electromigration and also the application of low k dielectric materials as the insulation layer.

To address this problem, solutions have been proposed. These include the design of hierarchical multilevel interconnects, addition of repeaters and cascaded drivers and three-dimensional integration of integrated circuits (ICs) [1]. However, the most popular and sustainable approach is based on a materials solution to substitute the interconnect metal lines and dielectric with alternative materials.

A significant improvement in RC delay can be achieved by replacing the Al interconnects with Cu, which has a 30% lower resistivity than that of Al [5, 6]. This results in a decrease in metallization resistance. A further reduction in the signal delay (RC) can only be achieved by replacing existing dielectric silicon dioxide (SiO_2) with an alternative low- k dielectric material as the interlevel dielectric (ILD) material. It is to be noted that SiO_2 is mechanically strong and has good adhesion with other materials in the silicon wafer level interconnects. Therefore mechanical collapse (fracture) and interfacial delamination (adhesion problems) do not exist for SiO_2 structures.

However, with the replacement of Al/ SiO_2 by Cu/low- k , mechanical reliability has become a critical problem for the multilevel stacked interconnect structures. The low- k dielectrics such as SiLK (from Dow Chemicals) and polyimide are weaker and softer compared to SiO_2 and have poor adhesion to other materials. The presence of Cu lines in the new technology do not pose severe problems as compared to the aluminum interconnects. Unfortunately, compared with SiO_2 , most low- k materials have caused the industry to experience significant integration challenges for Cu/low-

k structures and packaging of $Cu/low-k$ chips. The improvement in electrical performance is nullified by the poor thermo-mechanical reliability of $Cu/low-k$ structures. Thus, it is critical to the mechanical properties of the interconnect structure to provide possible solutions to improve the mechanical properties of the interconnect structures. A possible solution is the reinforcement of $low-k$ interconnects with carbon Nanotubes (CNTs).

The interconnects often experience stresses when the integrated circuits undergo further processing. For example, the interconnects may experience compressive force during a subsequent ball bond process or shear stress during bumping in a flip chip process. These stresses could cause damage or destruction of the interconnects, such as by causing the dielectric material to collapse or by causing interfacial delamination of the copper and the dielectric material. Also, similar delamination can occur during chemical mechanical polishing (CMP) too. The protection layer includes dispersed carbon nanotubes in a sol-gel silica matrix. The carbon nanotubes help to reduce or prevent damage to the interconnect structure, such as by reducing or preventing collapse of the low- k dielectric material or delamination of the metal and the low- k dielectric material through improved adhesion.

1.2 Objectives

The objectives of this project are:

1. Synthesize multi-walled CNT/sol-gel silica dielectric composite films with 0.01, 0.02 and 0.04 wt. % of reinforcement through various dispersion techniques (random and non-aligned CNTs in matrix) by spin-coating.

2. Develop a chemical functionalization technique for the homogenous dispersion and possible chemical cross-links of CNT fillers with the sol-gel matrix.
3. Mechanical characterization of CNT/sol-gel silica hybrid dielectrics, especially the hardness, Young's modulus and adhesive strength.
4. Microscopy characterization of the CNT sol-gel hybrid dielectrics to determine the distribution of CNTs and the dispersion extent.
5. Investigate the chemical and thermal stability of the various composite films fabricated.

1.3 Scope of the Project

A synthesis route for sol-gel silica dielectric with a silane precursor and a chemical functionalization technique for multi-walled carbon nanotubes (MWCNTs) were established. The thin films and MWCNTs were subsequently characterized to determine the physical and chemical properties of the products obtained. The subsequent phase after initial characterizations was the inclusion of MWCNTs into the sol-gel silica matrix via two routes: (1) Physical dispersion of pristine MWCNTs with various solvents and surfactants and (2) chemically functionalized MWCNTs. The nanomechanical properties (modulus and hardness), thermal properties (thermal stability and exothermic heat of reaction) and chemical properties (covalent bonds formed) of the final sol-gel/CNTs composite thin films would be evaluated. In addition, field emission scanning electron microscope (FESEM) would be performed to examine the fabricated films for a detailed study of the effect CNTs have on the mechanical reinforcements of the thin films. Transmission electron microscope

(TEM) studies will also be performed to observe the CNTs in the sol gel dielectric in order to gain some insights into their dispersion, alignment and influence on the mechanical properties.

1.4 Organization of the Report

The report is organized into five chapters. Chapter 1 provides an introduction to the project along with motivation, objectives and scope. Chapter 2 reviews the relevant literature in the field of low-k dielectric materials and also includes interconnect integration challenges prevalent in the industry today. A brief summary of carbon nanotubes (CNTs) structure and their application as fillers for mechanical enhancement in the composite dielectric were also evaluated. Chapter 3 introduces the materials, equipment and experimental procedure adopted in the project execution portion. Next, Chapter 4 presents the preparation of sol-gel silica and chemical synthesis of functionalized MWCNTs. Physical characterizations were performed to analyze the final products obtained. The measured nanomechanical properties such as hardness, modulus and adhesion were discussed with reference to the obtained microstructures of the CNT/sol-gel composite. A section was also devoted to thermal stability studies of CNT/sol-gel composites. Major conclusions of the experimental research carried and recommendations for future work in this area of research is summarized in Chapter 5.

2 LITERATURE REVIEW

In this review, the requirements for the low-k dielectric materials are listed and a survey of the possible low dielectric constant materials is carried out. In addition, the currently used low k dielectric materials are also reviewed together with the present state of research in the field of low k dielectrics. However, the introduction of low k dielectrics into actual production has been stagnated by various difficulties that need to be resolved for successful integration in the Cu damascene structure. To exacerbate the situation, the transition to and implementation of porous low k dielectrics beyond the 65 nm node will introduce new integration problems that affect the mechanical reliability of low-k interconnect structures. The review concludes with the use of Carbon nanotubes (CNTs) , due to their excellent mechanical strength as possible choice fillers to reinforce the dielectric materials.

2.1 The Origin of Dielectric Constant of Materials

Dielectric materials are a class of insulating materials. Under the influence of an external field, bonds of a dielectric material are polarized in a direction opposite that of an external electric field. The dielectric properties of a material are defined by an electric permittivity ϵ , which is the equivalence of the constant k in the microelectronics terminology. When the dielectric material is subjected to an external homogenous electric field, a dipole moment per unit volume is induced as shown in Figure 2-1 [7]. In order to reduce the k value (which is also the dielectric constant), there is a necessity to include bonds that have a lower polarizability.

Figure 2-1: Schematic cross section of two parallel capacitor plates with surface charge density σ (signs indicate positive or negativity) and a dielectric polarized by an electric field E . Each Circle denotes a polarization moment.

The polarizability of selected atomic bonds and their bond energies are listed in Table 2-1 [8]. There are four main contributions to total polarization: electronic polarization, ionic polarization, orientation polarization and interfacial polarization which will ultimately contribute to the dielectric constant of the material. Polarizability will determine the ease and extent of the bonds being influence in the presence of an electric field.

Table 2-1: Electronic polarizability and bond enthalpies

Bond	Polarizability (A)	Average bond energy (Kcal/mole)
C-C	0.531	83
C-F	0.555	116
C-O	0.584	84
C-H	0.652	99
O-H	0.706	102
C=O	1.020	176
C=C	1.643	146
C $\equiv$ C	2.036	200
C $\equiv$ N	2.239	213

From the data shown in Table 2-1, it can be deduced that single C-C and C-F bonds rank among those with relatively low polarizability bonds. Hence, fluorinated and non fluorinated aliphatic hydrocarbons are potential candidates for low k dielectric materials. The incorporation of fluorine atoms into the dielectric material is extremely effective in lowering the polarizability [8]. This is due to the high electronegativity that results in tightly bound electrons to the nucleus of the fluorine atoms. On the other hand, in materials with high polarizability, the electrons are less tightly bound to the nucleus of the atoms. Materials containing a large number of double and triple bonds have large polarization due to an increased mobility of their π electrons. Conjugated carbon double bonds are a common source of extensive electron delocalization with the atoms of the material surrounded by a ‘sea of electrons’, leading to high electronic polarizability. Nevertheless, there is a tradeoff involved in achieving low dielectric constant and high bond strength, as the low polarizability single bonds are among the weakest in strength, whereas the double and triple bonding configurations have much higher bond enthalpies which translates to an increase in bond strength.

The dielectric constant is determined not only by the type of atoms and bonds, but also by their bond densities. The dielectric constant of any material can be reduced by decreasing the dielectric film density. The density can be lowered by using low molecular weight atoms and/or by incorporating more free space around the atoms by increasing the amount of free volume to the structure i.e. addition of non-polar groups: methyl, ethyl and phenyl. For example, the lower dielectric constant of organic polymers relative to silica is partly due to the lighter C and H atoms versus Si and O, and due to low-packing factor [9]

2.2 Copper/Low-k Interconnects

The adverse effects of the dominance of RC delay for lower technological nodes have raised concerns on the practicality of incessant transistor scaling. The technological solution endorsed by the microelectronics industry has led to the substituituon of traditional interconnect materials, aluminum metal line/silicon dioxide dielectric with copper metal lines/low k dielectric materials. Figure 2-2 shows the variation of clock frequency with device feature size for various metal (Cu or Al) and dielectric systems (SiO₂ or low-*k*): it is clear that Cu/low-*k* is the best one.

Figure 2-2: Microprocessor performance as a function of feature size and interconnect technology [10]

In addition, Murarka [11] and Ting and Seidel [12] predicted that low dielectric materials are needed because should traditional dielectrics like silicon dioxide be used in extremely small interconnect dimensions, cross talk and power consumption will increase but degradation of signal speed would occur and hence result in an increase in RC delay.

The introduction of Cu metallization enables aggressive interconnect scaling due to its lower resistivity ($1.6 \mu\Omega\text{cm}$) as compared to Al metallization ($3.3 \mu\Omega\text{cm}$) which amounts to a more than 30% reduction in resistivity [6]. Hence RC delay can be reduced, other additional benefits include less power consumption and reduced joule heating. The lower resistivity of Cu implies a thinner metal could be used for a fixed resistance per unit length, which reduces sidewall capacitance responsible for crosstalk as the thickness of the adjacent dielectric material is also reduced (since crosstalk is proportional to sidewall capacitance and total capacitance ratio [13])

In addition to its electrical property benefits, Cu is also mechanically reliable owing to its higher stiffness (130 GPa vs 70 GPa) [13-15] and is a better heat conductor as compared to Al ($24.440 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ vs $24.200 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) [16], allowing better heat dissipation. It is also established that the self diffusivity of Cu is lower than that of Al, making Cu more electromigration-robust than Al [11] and Cu wires can withstand approximately five times more current density than Al wires while assuming similar reliability requirements. This is mainly due to the higher electromigration activation energy levels of copper caused by its superior electrical and thermal conductivity as well as its higher melting point (1357K for Cu and 933K for Al). These properties are highly desirable as the electronic industry trend drives integration enhancement which requires higher current densities to be used in design.

2.3 Candidate Low-k Materials

For 2 to 0.25 micron CMOS technology nodes, SiO_2 has been the standard dielectric material used with a dielectric constant of 4.0. However, this is set to change for lower technology nodes (less than 0.18 micron). The low- k candidates can be divided into two main categories, silicon based low k and carbon based *low-k* which can be deposited on the silicon wafer in two ways: by the spin on method or chemical vapor deposition (CVD) method. Figure 2-3 provides a schematic outline of the two deposition processes [17].

Figure 2-3: Process flow outline of low k deposition techniques Chemical Vapour Deposition and spin on[17].

Basically, the processes can be described as follows: The spin on technique drips the low k material on to the silicon wafer. A spin coater is then used to provide a revolving action that spreads out the low-k material homogenously over the entire surface and is finally allowed to cure. On the other hand, the CVD technique begins with a gas and precursor molecules. Heat is supplied to the gas mixtures in a controlled vacuum environment. The heat causes decomposition of the gas mixtures and the low k material that forms is deposited on to the silicon substrate. Numerous low k organic and inorganic materials have been explored for applications in interconnects. Table 2-2 lists various dielectric candidate materials in general decreasing k value.

Table 2-2: Low-k Candidate materials [1]

Low-k Materials	Dielectric constant	Deposition Method
Fluorosilicate glass (FSG)	3.2-3.6	CVD
Polyimides	3-3.5	Spin on
Hydrogen Silsesquioxanes (HSQ)	2.8-3.0	Spin on
Methyl Silsequioxanes (MSQ)	~2.7	Spin on
Methylated Silica	2.7-3.0	CVD
Flourinated Polyimides	2.5-3.0	Spin on
PAE[Poly(arylene ethers)]	2.7-2.9	Spin on
Thermoset polymers	~2.6	Spin on
Parylenes	2.2-2.6	CVD
Flourinated amorphous carbon	2.1-2.5	CVD
Teflon – PTFE	~1.9	Spin-on
Porous Inorganics (Xerogels, Templated Silica)	1.8-2.2	Spin-on
Porous Organics	<2.2	Spin-on

The first generation low- k dielectrics are those with k value between 2.8 and 3.5, which include hydrogen silsesquioxanes (HSQ - $\text{HSiO}_{1.5}$), methyl silsesquioxanes (MSQ- $\text{CH}_3\text{SiO}_{1.5}$) and Fluorinated Silicate Glass (FSG - F_xSiO_y). The second generation low k dielectrics candidate are those with k values between 2.5 and 2.8. The promising candidates are (spin on organic low- k) fluorinated polyimides and poly (aryl ethers) (PAE) and (CVD dielectrics) Organosilane glass (OSG -carbon doped) and Parylene F.

For industry, FSG has been recognized as a promising inter-metal dielectric (IMD) material for both the 180 and the 130nm technology nodes [18-20]. In addition, high gap-filling ability has also been demonstrated for a feature with aspect ratio, AR, of metal line height to metal line separation up to 1.35:1. FSG has been regarded as the quick fix approach to the reduction of the dielectric constant.

In a typical FSG structure a number of the Si-O bonds are substituted with F atoms producing Si-F bonds and hence fluorinated silicate glasses (FSG) (see Figure 2-4 for SiO_2 structure). This aids in the decrease of polarization of the bond and correspondingly a lower dielectric constant. In order to successfully integrate this FSG film into the manufacturing processes for sub 180nm technology, chemical vapor deposition (CVD) was widely employed [18].

Figure 2-4: Silicon Dioxide Structure

Lower dielectric constants were also achieved for silsesquioxane based materials and these are inorganic hybrid materials (Si-H and Si-CH₃ bonds), which have better mechanical and thermal stability as compared to purely organic ones such as polyimide. The better strength behind these silica based materials is that the SiO₂ network structure is more rigid in nature due to the higher bond strength.

Low dielectric constant can be achieved by the incorporation of chemical substitutions that tend to introduce voids into the solid film structure. Silsesquioxanes belong to a class called spin on glasses [21]. For silsesquioxanes, each Si atom is bonded to a terminating group such as hydrogen (HSQ), or methyl (MSQ) which results in the formula – SiO_{1.5}R_{0.5}. The HSQ and MSQ chemical structures are illustrated in Figure 2-5.

(a) Hydrogen Silsesquioxane (HSQ)

(b) Methyl Silsesquioxane (MSQ)

Figure 2-5: Chemical Structures of (a) HSQ and (b) MSQ [8]

The decrease in dielectric constant of MSQ and HSQ is a result of a corresponding reduction in density. Note that the density of HSQ is one third less than that of SiO₂ [22]. Also, the usage of HSQ and MSQ stems from their good mechanical stability and thermal stability due to their rigid crosslinking network [23-27]. Possession of such desirable properties clearly fit in the criteria of candidate *low-k* materials for technology nodes beyond 130nm.

Despite this, current trends point to CVD OSGs as the main *low-k* candidates for the 90nm node [28-31]. The most common CVD OSG materials in the market are Black Diamond™ (k<3: Applied Materials), Coral™ (k=2.85: Novellus), and Aurora™ (k=2.9: ASM).

OSG films are relatively hard materials as compared to other low k films. Nanoindentation experiments found their hardness to be 1.5GPa [32]. The low k field has narrowed considerably over the past few years and now only a handful of strong candidates remain (See Table 2-3).

Table 2-3: The Narrowed Dielectric Material Choices [21]

IMD material	k-value	Deposition Method
Silicon Dioxide (SiO ₂ or TEOS)	4.0-4.5	CVD
Fluorinated Silicate Glass (FSG or SiOF)	3.2-3.6	CVD
Hydrogen Silsesquioxanes (HSQ)	2.8-3.0	Spin-on
Methyl Silsequioxanes (MSQ)	~2.7	Spin-on
Organosilicate Glass (OSG or SiOC(H))	2.8-3.0	CVD
Organic aromatic polymers	2.6-2.9	Spin-on

However, in the same generation, another class of organic carbon based aromatic polymers exists. The best known is Dow Chemicals’ SiLK (k -2.65) of P-SiLK [33]. Unfortunately, their use is limited as the chemical bonds tend to be weaker leading to weaker mechanical reliability and substrate adhesion problems.

2.4 Requirements for Low-k Dielectric Materials

In order for low-k dielectric materials to be introduced for production and successful integration into the conventional or copper damascene structures, the low k dielectric materials must meet stringent material property requirements. Among the material requirements for low-k, the most obvious one is for the material to have a low dielectric constant. SiO₂, with the dielectric constant of about 4.0 implies that for materials to qualify as low k, the dielectric constant is defined to be less than 3.9.

However, having a low dielectric constant alone does not make a particular dielectric suitable for interlayer dielectric. There are many parameters for consideration, among which the compatibility with the processing steps is that has to be investigated before device applications are implemented. Table 2-3 shows some of the desirable properties that low k dielectric materials should possess.

Table 2-4: Ideal Properties of low k materials [34]

Electrical Isotropic k < 3 @ 1 MHz	Chemical No material change when exposed to acids, bases and strippers	Mechanical Thickness uniformity <10% within and <5% wafer to wafer for 8" wafer at 3σ	Thermal T _g > 400°C
Low Dissipation	Etch rate and selectivity better than oxide	Good adhesion to metal and other dielectrics	coefficient of thermal expansion <50ppm/°C
Low leakage current	<1% moisture absorption at 100% relative humidity	Residual stress <(+)100MPa	Low thermal shrinkage
Low charge trapping	Low solubility in H ₂ O	High hardness	< 1% weight loss
High electric field strength	Low gas permeability	Low shrinkage	High thermal conductivity
High reliability	High purity	Crack resistance	
High dielectric breakdown voltage > 2-3 MV/cm	No metal corrosion	Tensile modulus >1GPa	
	Long shelf life	Elongation at break >5%	
	Low cost of ownership	Compatible with CMP	
	Commercially available		
	Environmentally safe		

The mechanical and thermal stability of low k dielectric materials must be sufficient in order to withstand the elevated processing temperatures and warping stress effects that can occur and critically affect the interconnect structure. Resistance to thermal degradation is an important material property requirement for a dielectric because at high temperatures, many of the dielectric's material properties are severely degraded. Moreover, the presence of outgassing at elevated temperatures can cause film delamination, blistering, and via poisoning.

Failure of the dielectric material can be attributed to the weakening of intermolecular interactions at elevated temperatures. The bond stiffness and strength are inversely proportional to temperature. Figure 2-6 shows typical variation of modulus with temperature obtained using Dynamic Mechanical Analyzer (DMA).

Figure 2-6: A Typical DMA storage modulus curve

As temperature is increased, there is an analogous *decrease* in the storage and loss modulus, accompanied by a corresponding loss in thermal stability. In order to improve the stability of temperature degradation, *low-k* dielectrics should possess desirable features such as strong individual chemical bonds, high number of crosslinking, and networked/intertwined structures. The multiple bonds in the network structure have to be broken for thermal decomposition to occur. Thermal stability with regard to decomposition is often determined using isothermal thermogravimetric analysis (TGA), which measures weight loss as a function of time at a given temperature.

Backend of the Line (BEOL) process temperatures ranging from 400–450°C dictate the thermal stability requirements of the low *k* dielectric materials used for subtractive Al processes [8, 11]. As these materials are mostly organic, they cannot withstand the elevated temperatures. This largely eliminates a large majority of organic polymers which do not display good thermal stability within this temperature range.

The difficulty of this situation is somewhat resolved as the BEOL process temperature becomes lower. The Cu Damascene process offers the possibility of reducing the maximum BEOL processing temperature to 350°C, thus increasing the processing window temperature for candidate low *k* materials. Thermal degradation for inorganic silica-based materials is a less severe problem. However, Si-H and Si-C bonds in some of these materials are vulnerable to decomposition at 400–450°C, especially in an oxygen-rich environment [21, 35-38].

Mechanical reliability or strength is another important requirement because if the low k dielectric materials cannot withstand stresses subjected to during processing, then the structural integrity of the entire interconnect can be compromised [39-45]. Moreover, in CMP process, the downward mechanical force as shown in Figure 2-7 can severely damage the low k layers that do not have sufficient mechanical strength [46-49]. The mechanical stability for low- k candidate materials is measured by the Young's modulus (E). The Young's modulus of most organic and inorganic low- k candidate materials are found to be at least an order of magnitude lower than that of the standard SiO_2 dielectric material which constitutes a serious concern [50].

In addition to the modulus, the film's coefficient of thermal expansion (CTE) is also of importance as most of the stresses that occur in the interconnect are thermally induced due to CTE mismatch between various material layers in the interconnect structure. It would be desirable to minimize the thermal mismatch, especially for dielectrics with a low modulus and a relatively low CTE dielectric.

Moisture absorption is a primary concern because a small amount of moisture presence can have a large impact on the dielectric constant. The introduction of water occurs during chemical mechanical polishing (CMP) as it involves a wet chemistry process. A schematic representation of the CMP process is shown in Figure 2-7.

Figure 2-7: *Mechanics of CMP process*

Water is known to have an extremely large dielectric constant of 83 [11]. To complicate the situation, most low- k films are hydrophilic in nature. This causes the overall dielectric constant of the low- k to be raised tremendously which erases any benefits of introducing low- k in the first place. Low- k dielectric materials are also required to have good chemical stability to the solvents and etchants (i.e. HF) commonly used during IC fabrication.

In addition, the corrosion of the Cu metal lines also may result in metallic ions that will diffuse into the inter-dielectric layer (IDL) and cause contamination. Metal contaminants can lead to compromises in device functions and provide a leakage path between lines. This is often a problem for polymers (which are especially what most low k dielectric materials are made of) synthesized using metal catalysts. Other chemical processing requirements include the ability to pattern and etch the film, etch selectivity to resist, good thickness uniformity, gap-fill in submicron trenches, and planarization.

2.5 Integration issues for Cu/Low-k Interconnects

2.5.1 Process Integration Issues

The delay in the introduction of many low k dielectric materials [51-53] into the copper dual damascene structures is due to a range of difficulties associated with copper/low k integration as illustrated in Figure 2-8.

Figure 2-8: Schematic Illustration of the Integration Challenges [21]

The thermal conductivity for low k materials is often poor and is less than one third of silicon dioxide [54]. The result is that the temperatures of the interconnect will rise by Joule heating [55-57]. This is undesirable as Joule heating accelerates the electromigration in metal lines and thus affect the reliability of the interconnects because electromigration (and its close association stress voiding) are primary failure mechanisms in Integrated Circuits (ICs) [58].

Carbon depletion due to oxygen plasma damage on silsesquioxanes [59] is also a deleterious process as it leads to deterioration of material properties as observed from the increase in k values and leakage current with a corresponding decrease in strength. The presence of oxygen radicals have an effect of oxidizing the methyl and hydrogen groups and convert them to a Si-OH group. Since the SiOH is hydrophilic in nature, it will stimulate water absorption leading to increments of k value. The overall electrical performance is much affected and is especially pronounced as the dielectric spaces between metal lines/wiring shrink [60].

A particularly difficult challenge in material development is to obtain a combination of low dielectric constant coupled with good thermal and mechanical reliability. It has been observed that chemical structures that impart the mechanical stability have strong bonds that lead to large atomic polarizability. This situation is exacerbated with the introduction of porosity into the dielectric films which ultimately results in inferior mechanical stability because films with voids will undoubtedly be weaker than similar fully dense materials. As a result, elastic modulus of the low k film is decreased and this affects the survivability of the fragile low k material during integration process like CMP [61-63]. For reliable low- k materials, the size, and distribution of porosity these parameters have to be carefully controlled. It is to be noted that for porous solids the mechanical properties such as modulus, strength etc. scale with the relative density [8].

Because it is difficult to reduce the dielectric constant below 2.5 (ITRS requirement for the 45nm node and beyond), by using fully dense material, it may become necessary to introduce additional porosity into the ‘dense’ low-k materials to get to ultra-low-k values (2.0) (Figure 2-9). However, there is a need to balance the introduced porosity with the maintenance of a rigid matrix structure in order not to compromise the mechanical properties.

Figure 2-9: Schematic Representation of porous dielectric

The main purpose for the decrease in dielectric constant is due to the lowering of material density. Hence, by varying and modifying the amount of porosity introduced, the density and dielectric constant can be changed. The introduction of voids is a natural strategy to increase the free space and decrease the material density. The relationship between the porosity and the dielectric constant can be described using Bruggeman effective medium approximation [64] (see Figure 2-10).

Figure 2-10: Result of Bruggeman's Effective Medium Approximation

Most of the above mentioned materials are not as fully developed as dense dielectrics. Research is however being done in this area [42]. Porosity can also be introduced in the material either through a sol-gel process [65, 66] and includes the aerogel and xerogel porous silica films or by inclusion of sacrificial nanoparticles (i.e. “porogens”). For example, one can use a surfactant [67] or dendritic structure [68, 69] as a template, build what will become the porous film around this template, and then remove the template, leaving voids. Sol-gel chemistry is briefly discussed in section 2.5.2.

2.5.2 Sol-gel chemistry

Sol-gel processing is an ambient temperature means of synthesizing dielectric materials. It is particularly attractive as it offers an alternative approach to the synthesis of materials where using molecular precursors undergoing polymerization reactions to obtain an oxide network that is compact, adheres well to the substrate and is uniform. The uniformity of thin film is an important property for interlayer dielectric applications.

Sol-gel porous silica is prepared using tetrafunctional silicon alkoxides such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). As TMOS fumes cause blindness when eyes are exposed to it and it is expensive, hence TEOS is a preferred precursor [70]. The typical sol-gel process using these silane precursors undergo two types of reactions, hydrolysis and condensation, in the presence of catalyst(s) (which may be an acid, base or both). Sol-gel silica is formed through the following reactions:

The sol-gel porous silica films are produced by the hydrolysis and condensation of TEOS, water, and ethanol in a two step acid and base procedure. In acid catalysis (where $\text{pH} < 2.5$), rate of hydrolysis is fast, there is a tendency toward linear and randomly branched chains as shown in Figure 2-11 to form a dense silica film [71]. On the other hand, in base catalysis (where $\text{pH} > 7.5$), the condensation rate is rapid and the growth forms highly branched clusters. Eventually, these spherical clusters would form a highly porous film but with low mechanical strength. Therefore a combination of a two step acid base catalyst film would produce a porous film with good mechanical strength[71].

Figure 2-11: (a) Acid catalyzed and (b) base catalyzed nature of silica xerogel films.

During the condensation reaction, the release of an alcohol or water molecule results in the formation of Si-O-Si. As the reaction continues to proceed in the forward direction, the polymerization reaction results in a growing siloxane chains of Si-O. Due to the tetrafunctional nature of the alkoxide precursor [72], the chains of molecules crosslink to form a three dimensional network structure. The silica xerogel films can then be obtained after spin-on deposition and drying, where the solvents are evaporated from the sol-gel.

2.5.3 Packaging Effects on Cu/Low- k Structures

The inherent mechanical properties of low k materials are particularly poor. The low- k materials have low modulus, low fracture toughness, and poor adhesion with the Cu film compared to other dielectric materials. The low- k films generally have moduli less than 10 GPa, compared with 70 GPa for SiO₂. As such only a limited number of low k dielectrics have been introduced into microelectronics industry.

Table 2-5: Low-*k* dielectrics for Cu/low-*k* structures [73]

Material	Organic-O Inorganic-I	Modulus (GPa) 25°C	Hardness (GPa)	Fracture- Tough (MPa-m ^{1/2})	CTE (10 ⁻⁶ /°C)
DVS-BCB	O	2.9	0.37	0.37	52
SILK-H	O	2.45	0.31	0.60	62
Black Diamond (SiO ₂ + C)	I/ O (the class of OSGs)	7.76	0.13-3.6	0.2-0.3	23
HSG-R25	O	2.5	-	-	-
FLARE	O	2.5	0.35	-	60
HOSP	O-I	6	0.4	-	17
HSQ	I	4.9	0.85	0.27-0.44	14
TEOS (SiO ₂)	I	72-100	9.5	0.46	1-2
Nanoglass silica (gels) pores<5nm	I	0.5-2.3	0.03-0.1	<0.04 to 0.14	4up (varies)
Parylene AF- 4	O	2.28	-	-	30-80
Speedfilm BX	O + 5% I	1.66	-	-	55

Another important consideration for low *k* dielectrics is its compatibility with the packaging environment. Flip chip packaging stresses the copper low *k* interconnect structure through the process of bumping. The shear stresses experienced by the thin films stack is a critical concern particularly because low *k* materials have low adhesion strength, which can result in interfacial crack initiation and propagation. Mercado et al [74] made a study of flip chip packaging challenges on copper low *k* interconnects. They found that when low-*k* material was placed at the last layer, the possibility of fracture increases. Also, when the number of metal layers increases, they are more prone to fracture. This is undesirable within the context where the high density connects compose of as many as 8-10 layers.

During the process of wire bonding of low k materials, the bond yield and reliability of the chips are affected because of bond pad cupping and delamination of the low k dielectric [73]. The reason for this is due to the fact that the low modulus for low k dielectric material below the bond pad does not provide a rigidly stable platform for bonding. This results in cupping of the dielectric material. As most of the common low k dielectric materials have a low modulus, they tend to fracture easily and mechanically collapse. To address this issue, researchers have been designing support structures for enhancing the mechanical stability of the copper low k interconnect structures such as tungsten plug arrays [73, 75] and hybrid structures [76]. However, these hybrid structures are complex and costly for industrial scales up and thus, do not realize the full benefit of applying the low k dielectric materials to reduce RC delay.

In addition, the effect of packaging on the energy release rate driving interfacial delamination and the impact on the reliability of copper low k interconnects have been extensively studied by Wang et al [77, 78]. In their combinations of experimental and finite element analysis (FEA) work, they discovered that the packaging process can increase the driving force for delaminations along the interfaces of the copper/low k dielectrics. In particular, the interfaces parallel to the die surface were found to be more susceptible to delamination. In addition, the packaging effect was discovered to be generally more pronounced for lower modulus low- k material as compared to the one with a higher modulus. As such an effective solution to mechanically support the weak low k dielectrics should be considered. A

plausible method is the use of carbon nanotubes (CNTs) as reinforcement fillers for the weak dielectric matrix.

2.6 Carbon Nanotubes

Carbon Nanotubes (CNTs) were first discovered by Iijima in 1991 [79] in the soot of arc discharge apparatus. CNTs are basically made from the element of carbon and they belong to the same family group of materials such as diamond, fullerenes and graphite. The schematic structures are as shown below.

Figure 2-12: *Various types of carbon structures [80]*

There are two basic configurations of CNTs, namely, the single-walled carbon nanotube (SWCNT) which is composed of a graphene sheet rolled into a singular cylinder with one external wall and the multi-walled carbon nanotube (MWCNT) with multiple concentric coaxial cylinders. Compared with multiwalled nanotubes, single-walled nanotubes are expensive and difficult to obtain and clean, but they have been of great interest owing to their novel electronic, mechanical, and gas adsorption properties.

CNTs are cylindrical carbon molecules with novel properties. They exhibit extraordinary strength and unique electrical properties. Depending on the chirality they could be both efficient electrical conductors or semiconductors and channel the heat. These properties of CNTs could provide a wide variety of applications in electronics and materials engineering: for instance field emission devices, sensors, interconnects, composites with high strength, catalysis, nanocontainers for storage of hydrogen, lithium and other materials [81]. Some important properties of carbon nanotubes are listed in Table 2-6.

Table 2-5: Properties of single-walled carbon nanotubes (SWNTs) [82]

Attribute	Comment
Metallic to semiconductor electrical conductivity, depending on microstructure	No other known molecule has this property
Electrical conductivity: $10^8\Omega^{-1}\text{m}^{-1}$	Comparable to that of copper
Thermal conductivity: $10^4\text{Wm}^{-1}\text{K}^{-1}$	> that of diamond
Carrier mobility: $10^4\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	> that of GaAs
Supports a current density of 10^9Acm^{-2}	Due to very weak electromigration
Nanoscale heterojunctions	Common defect that can create an on-tube heterojunction
Young's modulus: 1TPa	Stiffer than any known material
Tensile strength: 150GPa	600 times the strength/weight ratio of steel

While the attributes in Table 2-5 refer to high quality single-walled carbon nanotubes (SWNTs), Mutli-walled carbon nanotubes (MWCNTs) also exhibit comparable properties. While the electrical properties of CNTs offer immense potential for nanoelectronics, the mechanical and thermal properties of CNTs are also of great importance. As such, the physics, properties and potential applications of CNTs [82] have been well documented by researchers. Characterization of CNTs by various methods have also gained importance and was reviewed by Belin and Epron [83].

CNTs can be synthesized by various techniques. Currently, the three main techniques are arc discharge [84-87], laser ablation [88-90] and chemical vapour deposition (CVD) [91-95]. A summary of the major production methods is given in Table 2-6 with their advantages and disadvantages.

Table 2-6: A summary of the major production methods and their efficiency [96]

Method	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization)
Who	Ebbesen and Ajayan, NEC, Japan 1992	Endo, Shinshu University, Nagano, Japan	Smalley, Rice, 1995
How	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma.	Place substrate in oven, heat to 600 °C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90%	20 to 100 %	Up to 70%
SWNT	Short tubes with diameters of 0.6 - 1.4 nm	Long tubes with diameters ranging from 0.6-4 nm	Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm.
M-WNT	Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm	Long tubes with diameter ranging from 10-240 nm	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible.
Pro	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Con	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

In recent studies, CNTs were also produced by magnetron sputtering [97]. The most popular technique is the CVD technique which has the highest productivity on industrial scale and ability to control the carbon nanotube structures.

A variant of the CVD technique is the plasma enhanced chemical vapour deposition (PECVD). Application of plasma achieves the growth of CNTs at lower temperatures. The current status of carbon nanotube growth by PECVD was reviewed by Meyyappan et al. [98]. The paper reviewed important aspects of the technique and cited areas of research and directions for future work.

Briefly, the procedure for CNT growth by PECVD is as follows: A substrate is placed on the one electrode of the CVD chamber and the reaction gas such as C_2H_2 , CH_4 , C_2H_4 , C_2H_6 or CO is supplied from the opposite plate. First row transition element metals, such as Fe, Ni and Co are used on for example a Si, SiO_2 , or glass substrate using a variety of techniques such as magnetron sputtering, electron beam deposition or thermal CVD etc. After the fine metal catalyst particles are deposited, carbon nanotubes will be grown from the metal particles (root/tip growth) on the substrate by glow discharge generated from high frequency power.

While the electrical, optical and thermal properties have been clearly discussed in detailed, the focus of this review is on the mechanical properties possess by CNTs. As a result of their carbon-carbon sp^2 bonding, they have high stiffness and axial strength [99].

Despite the obvious difficulties in the manipulation of carbon nanotubes, advances have been made in the measurements of the Young's Modulus of CNTs experimentally. The first such study was undertaken by Treacy et al. [100] with an in-situ transmission electron microscope. On the other hand, the Young's Modulus of MWNTs was also measured by Wong et al.[101] through the use of the atomic force microscope (AFM). Their estimated Young's modulus was determined to be in the range of 1.26TPa and 1.8TPa respectively. By comparison, the Young's modulus of carbon fibres is only 680GPa [102]. The Young's modulli depends also on the degree of order within the tube walls and those with an increase in order reflect a correspondingly higher Young's modulus. This is illustrated in Figure 2-13 [103].

Figure 2-13: Modulus vs Disorder in MWNTs

It has been recognized that the outstanding mechanical properties of CNTs can be best exploited by reinforcing them into a soft and weak matrix. However, to benefit from the high Young's Modulus and strength of CNTs, some important criteria must be fulfilled.

Among the most crucial is the load transfer efficiency between the nanotube and the matrix. The three main load transfer mechanisms that control the stress transfer are micromechanical interlocking, chemical bonding (interaction) and a weak Van der Waals attractive force. The relatively smooth surface of the cylindrical nanotubes has been associated with a low coefficient of friction and will result in nanotube slippage within the matrix [104]. Should the adhesion between the matrix and CNTs be not strong enough to withstand the applied load then the CNT based composite cannot function as an effective structure.

Most of the earlier research work has focused on the development of nanotube reinforced polymer composites[105]. Subsequent research progress yield positive results in terms of electrical conductivity, mechanical improvements and enhanced performances for photovoltaic devices. In addition, carbon nanotube composites with ceramic [106-108] and metallic matrices [109, 110] have also been explored but to a smaller extent. All of them showed that CNTs do act as reinforcements to the subsequent composites obtained as there were improvements in strength, adhesion and fracture toughness. However, with the current experimental results, there is still a sizable gap between what has been achieved and what is theoretically possible.

The studies performed on CNT composites have so far been limited to polymers, metals and ceramics as mentioned above. In recent publications [111, 112], the application of CNTs into inorganic silica matrices have been proposed. SiO_2 is an excellent dielectric material with outstanding thermal properties and this enables one to overcome the obvious drawbacks of CNT based polymers such as ageing and limited operating temperature range. However, these CNT composites referred to bulk material applications. To date, only Gavalas et al. [113], Berguiga et al. [114] and Vincent et al. [115] published works with regards to the incorporation of CNTs into matrices with the sol gel technique. Most of these studies limited their investigations to the fabrication of thin films and no mechanical characterization of the films were carried out.

3 Materials and Experimental Methods

3.1 Proposed Protection Mechanism

An important aspect of low-*k* dielectrics application is the compatibility with the packaging environment. Figure 3-1 shows a design of an interconnect structure. In the ball bond stage of the wirebonding process the high compressive forces exerted on the low-*k* films can lead to their failure and hence collapse of Cu/low-*k* interconnects. Conversely, the bumping in flip chip process will induce high shear stresses to the multi layered Cu/dielectric stack which lead to the delamination of metal/dielectric interface [1]. The CNTs positioned at the etch-stop layer, will serve as a cushion or nano springs to absorb the impact energy caused to the structure due to their high modulus and strength. In this design, a xerogel/silica sol gel is synthesized and carbon nanotubes are dispersed into the matrix as reinforcing fillers. In the following sections, the manufacturing procedure adopted and other manufacturing protocols are explained.

Figure 3-1: Carbon Nanotubes on Cu/low-k structures

3.2 Sample Preparation Methodology

Thin film sol-gel/carbon nanotube composite on silicon substrates having a silicon nitride coating were prepared according to the procedure outlined in the flow chart in the flow-chart (see figure 3-2). The preparation of the sol-gel solution and addition of CNTs is the fundamental step in the work, followed by spincoating onto cleaned substrates and thermal curing. The following sections describe the fabrication of the film and the characterization techniques used for this study.

*No surfactant was used in the case of functionalized carbon nanotube reinforcement

Figure 3-2: Flow chart describing the fabrication of CNT reinforced low k dielectric material

3.2.1 Carbon Nanotubes (CNTs)

The CNTs used in this study were purchased from Shenzhen Nanotech Port Co. Ltd (China) and the MWCNTs-COOH were obtained from Nanocyl, Belgium (Europe). This CNTs powder was fabricated through catalytic pyrolysis of hydrocarbon. The detailed specifications of the procured CNTs are laid out in Table 3-1. The transmission electron micrographs (TEM) of the MWCNTs as supplied are shown in Figure 3 (a) and (b) respectively. The CNTs in Figure 3(a) are relatively well formed and contained some metal catalyst particles. The length of the CNTs causes some entanglement. The MWCNTs-COOH in Figure 3(b) showed that despite functionalization oxidative treatment, the structures of the CNTs have been largely preserved.

Table 3-1: Specifications of the CNTs used in the experimental study

Properties	MWCNT	MWCNT-COOH
External Diameter	10~30nm	9.5nm
Purity of CNTs	≥95 %	≥95 %
Ash	≤ 0.2 wt %	NA
Length	5~15μm	<1μm
Special Surface Area	40~300 m ² /g	NA

Figure 3-3: (a) MWCNTs and (b) Functionalized COOH-MWCNTs used in sol-gel silica

3.2.2 Preparation of Silicon Nitride (Si_3N_4) wafer substrates

The silicon wafers substrates used in this experiment are 6" in diameter with a 160.5nm Si_3N_4 coating on a 100nm silica layer. To optimize the spin coated films planarity and facilitate the fabrication and characterization processes, the silicon nitride wafers were cut into $25.4 \times 25.4\text{mm}^2$ square wafers using a diamond tip scriber. The properties of the wafers used are as follows:

- Thickness : $500 \pm 25\mu\text{m}$
- Type/dopant : N/P
- Orientation : (100)
- Resistivity : 40-60 ohm-cm
- Flats : 2 semi-std
- Front side polished
- Back side etched

The Si_3N_4 coated wafer surfaces are cleaned using Piranha, Standard cleaning 2 (SC2) and Standard cleaning 1 (SC1) solutions respectively to create a hydrophilic surface to ensure a uniform thin film formation during the spincoating process. This process eliminates possible surface contamination.

Piranha solution comprises of sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) with a molar ratio of 2:1 (H_2SO_4 98% and H_2O_2 35% by weight) and it is used to remove organic residues from substrates. Piranha solutions are extremely corrosive and may result in explosion or skin burns if not handled with extreme caution. Standard Clean (SC) Solution #2; The SC-2 solution is best suited for removing metal contaminants from the wafer surfaces by continually oxidizing and then etching the surface of the wafer, thereby dissolving the contaminants into solution.

Standard Clean (SC) Solution #1; The SC-1 solution removes dust particles from the surface of the wafer. The SC-1 solution is also very effective at removing organic contaminants and some metallic contaminants from the surface of the wafer. It accomplishes this by continually oxidizing and then etching the surface of the wafer, thereby dissolving the contaminants into solution. The wafer substrates were carefully cleaned in the following procedure and the three main steps are highlighted in bold:

Immerse substrates in Piranha solution ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 2 : 1$)

- Wait for 5 minutes to allow the stabilization of the exothermic reaction
- Immerse substrate for 8 minutes
- Rinse with deionised (DI) water
- Dry using nitrogen gas

Clean with Standard Cleaning (SC) 2 solution ($\text{HCl} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 10$)

- Immerse substrate for 10 minutes
- Rinse with DI water
- Dry using nitrogen gas

Clean with Standard Cleaning (SC) 1 solution ($\text{NH}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 5$)

- Immerse substrate for 10 minutes
- Rinse with DI water
- Dry using nitrogen gas

3.2.3 Sol-gel Preparation

The manufacturing route to produce silica sol-gel is explained by means of a flow-chart in Figure 3-4. The SiO₂ sol was prepared by mixing tetra orthosilicate (TEOS) 99.999% with ethanol (absolute L260 denatured) for dilution. Hydrochloric acid (20% HCl solution in water PPB/PTFE grade), and ammonium hydroxide (28% NH₃ in water, Purity 99.99%) were used as catalyst. The chemical stoichiometry of the reactants were in the molar ratio of 1:10:0.003:3.5 respectively [116]. All the solutions were obtained from Sigma Aldrich and used without any further purification. The solution was then mixed with a magnetic stirrer for three to four days to allow sufficient time for ageing before the sol-gel solution is spin-coated.

Figure 3-4: Sol-gel silica synthesis route with TEOS precursor

3.2.4 Assisted Dispersion of Carbon Nanotubes

In order to improve the uniform dispersion of the CNTs in the silica sol-gel, the CNTs are initially dispersed using five different commercially available surfactants/solvents listed in Table 3-2. The resultant mixtures were sonicated for 2 hours followed by the continual magnetic stirring for 3 hours to promote even dispersion of the CNTs in the sol-gel mixtures. For the functionalized carbon nanotubes, no surfactant was used in that case as chemical surface modification. The procedure for preparation of such nanotubes are outlined in the following paragraph.

Table 3-2: The Surfactants and solvent used in the dispersion of the carbon nanotubes

Surfactant/Solvent	Type of dispersion
Hexa Cetyltrimethylammonium Bromide (CTAB)	Cationic surfactant; cationic/positive repulsion
N Dimethyl Formaldehyde (DMF)	Solvent assisted dispersion; wetting of nanotubes
NanoAQ	Nonionic and anionic surfactant. Negative steric repulsion
Poly(4-vinylpyridine) (PVP-4)	Polymer assisted dispersion by wrapping mechanism

COOH modified MWCNTs were procured from Nanocycl. Generally, the method to create such nanotubes are as follows: MWCNTs were dispersed in a mixture of concentrated sulphuric acid and nitric acid (3:1). The purpose of the oxidative process is to create active sites and carboxylic acid moieties on nanotubes and also to purify the MWCNTs of the metal catalyst particles residue.

In a typical reaction, 4mg of COOH modified CNT was added into a centrifuge tube with 0.8ml of N-(3-dimethylaminopropyl)-N-ethyl-carbodiimide (EDC) first and probe sonicate for 20 minutes. After sonicating, 3.2mg of N-hydroxy succinimide was added and the bath sonicated for 1 hr. The mixture is centrifuged for 15 minutes to remove the unwanted liquid. Next 3-4 drops of (3-Aminopropyl)tris(trimethyl siloxy) silane (silane coupling agent) were added and the water bath sonicated for 1½ hours. The mixture is then centrifuged to remove the supernatant. DI water was added and bath sonicated for 5-10 minutes to and centrifuged for 5 minutes to remove the supernatant with the unreacted silane agent. Washings with DI water was repeated for three times. Then the sample is freezed dry and stored.. Several days later, sample is ready in powder form.

3.2.5 Experimental Matrix for sol-gel CNT composites

In this study of sol-gel composites, different routes of dispersing the MWCNTs into sol-gel silica were taken as shown in Table 3-3 where $x = 0.3\text{mg}$, $y = 0.6\text{mg}$ and $z = 0.9\text{mg}$ weight of MWCNTs, i.e. three different weight fractions of CNT reinforced silica composites are fabricated.

Table 3-3: Composition of silica sol gel and CNTs chemistry

Sample	Composition of Mixtures		
	Sol gel (mg)	CNTs (mg)	Surfactant* (mg)
Silica sol-gel	2400	NA	NA
A	2400	x, y, z	NA
B	2400	x, y, z	100 NanoAQ
C	2400	x, y, z	987.5 DMF
D	2400	x, y, z	3 CTAB
E	2400	x, y, z	1.5 PVP-4
G	2400	x, y, z	NA; functionalized CNTs

* Amount of surfactant/solvent is doubled or tripled with an increase in amount of CNTs

In this study, the amount of sol gel involved in each sample is kept constant, while the experimental parameters of the CNTs (single-walled, multi-walled or functionalized multiwalled) and type and amount of surfactants/solvent for dispersion were varied for the experimental matrix. Sample B-E was repeated for single-wall carbon nanotubes (SWCNTs) for $x\text{mg}$ for comparison with the multi-wall carbon nanotubes (MWCNTs) of the same CNT weight content.

3.2.6 Spin-coating and curing of the film

With the completion in preparation of the wafer substrates and after sufficient ageing time, the sol-gel MWCNT composite films were then prepared by spin coating of sol-gel/CNT solutions onto 25.4 X 25.4mm² wafers. The thickness of the film was controlled by the spin speed of 1000rpm for 82s in two stages and the thickness of the spin coated films were estimated with a surface profiler to be in the range of 350 to 700 nm. The process of spin coating is shown in Figure 3-5 below.

Figure 3-5: A schematic of the spin coating process

The spin coating process can be divided into four main phases: dispensing of solution onto the substrate, spin-up, spin off and evaporation. First, the sol-gel is dispense onto the silicon wafer on the chuck of the spin coater. Then the spin coater starts its preset revolution or rotation of the chuck, causing the solution to spread out evenly and uniformly due to the centripetal force. The excess solution is spun off from the wafer substrate leaving a thin film to form on top of the silicon substrate. In the final phase, the evaporation of the solvent leaves the non-volatile portion of the solution behind to form the thin film composite.

At this stage the test samples were cured in a furnace. Curing of the thin films will promote the additional cross-linking of the composite films and result in the hardening and toughening of the film. The furnace used for the curing procedure was set to cure the composite films in the following temperature profile (Figure 3-6):

Figure 3-6: Temperature profile for curing of the thin film composites

- Stage 1: Ramp up to 100°C in 60 minutes from room temperature
- Stage 2: Holding at 100°C for 60 minutes
- Stage 3: Cooling down to room temperature from 100°C in 60 minutes

The gas medium used in the curing process is Nitrogen gas (N₂)

The curing of the films is important as it will inadvertently affect the mechanical, thermal and physical/chemical properties of the films. Therefore a standardized temperature profile is necessary to prevent the introduction of unknown parameters.

3.3 Materials Characterization

In order to characterize the thin films of sol-gel/CNT composite formed, a wide variety of characterization techniques can be used to determine the physical, chemical, mechanical and thermal stability of the spin coated films. Table 3-4 summarizes the approach for evaluation of the composite silica materials in this work. The experimental procedures for performing the characterizations are fully explained in the following sections.

Table 3-4: Characterization Techniques performed in this study and the properties measured.

Properties	Techniques	Remarks
Physical	FESEM, TEM and AFM, XRD, Raman spectroscopy,	Dispersion of aggregation of CNTs, film crystallinity, surface roughness could be determined with these instrumented techniques
Chemical	FTIR and XPS	Analyzing the chemical bonding, atomic compositions of CNTs and thin films formed
Mechanical	Nanoindentation and Nanoscratch	Extraction of the values of hardness, modulus, adhesion between the film and substrate.
Thermal	TGA and DSC	Determining the extent of cure reaction, thermal degradation behaviour of siloxanes sol-gel chemistry and influences of CNT on the thermal stability

Notations used:
FESEM: field emission scanning electron microscopy
TEM: transmission electron microscopy
AFM: atomic force microscopy
XRD: X-ray diffraction
FTIR: Fourier Transform Infra-read spectroscopy
XPS: X-ray Photoluminescence spectroscopy
TGA: Thermal gravimetric analyzer
DSC: Differential scanning calorimetry

3.3.1 Physical Characterizations: Topographical, Structural and Morphological

The FESEM, TEM, AFM and XRD were used for the physical characterizations of the sol-gel/CNT composite films in this work. The FESEM JEOL 6310 with an accelerating voltage of 5kV and current 12.5 μ A was used to examine the surface of the composite film surfaces and study the effectiveness of the achieved dispersion.

The qualitative nature of the MWCNTs dispersion in CTAB, PVP-4 and DMF was studied using transmission electron microscope (TEM JEOL 2010) at an acceleration voltage of 150kV at 600K magnification. The TEM samples were prepared by dripping the sol-gel/MWCNTs solution onto formvar carbon coated grids of 400 Mesh by a disposable plastic dropper and placed in a desiccator for drying of the samples in 24 hours.

The dielectric films were generally expected to be amorphous. Therefore an AFM in intermittent contact mode was used to record the three dimensional topography of the films surface and hence determine the planarity of the composite films formed. The AFM system used in this study is Digital Instruments Dimension 3000 series. The root mean square (RMS) roughness obtained from the AFM measurements is employed as the surface roughness within a given scanned area.

In addition, XRD was performed on the neat silica sol-gel to validate the amorphous structure of the silica sol. A Rigaku XRD machine with thin film attachment was used for the characterization of the films. The measurements were recorded over a range of 20-80° of 2 θ angle. A Renishaw Raman spectroscopy system with a 633nm light source with a He-Ne laser was used to investigate the structural changes (in the form of line intensities) of the carbon nanotubes by functionalization. Raman signal was collected by an attached CCD that was cooled by the liquid nitrogen.

3.3.2 Chemical Characterizations: FTIR and XPS

FTIR Spectroscopy

Fourier transfer infrared spectroscopy (FTIR) was performed on the MWCNTs (pristine, -COOH functionalized and silane functionalized) with Perkin Elmer Spectrum One, USA spectrometer. The MWCNTs in the various forms were compressed into KBr pellets and scanned from 400 to 4000 cm^{-1} . A total of 16 scans were averaged with a signal resolution of 4 cm^{-1} within the predetermined range. The CNT/sol-gel composite film samples were also examined with the FTIR using the same parameters. FTIR is a useful tool that can be extended to the analysis of solid films. Covalent bonds are not rigid and possess inherent vibrations, bending or even rotation. The crux of this technique is the irradiation of molecules with an infrared (IR) ray of continuous wavelength. Absorption of the IR with the same wavelength as the frequency of the molecules' innate vibration will cause an absorption peak to appear with the wave number. The bonds present in the particular sample could then be identified based on this inference.

X-ray Photoelectron Spectroscopy

XPS (X-ray Photoelectron spectroscopy) was also performed on the MWCNTs (pristine, -COOH functionalized and silane functionalized). It is based upon the photo-ionization and energy-dispersive analysis of the emitted photoelectrons to study the composition and electronic state of the surface region (~10 nm) of a sample. Firstly, a *survey scan* from binding energy of 0 to 1000 eV was done to determine the elements that are present in the specimen. This scan is low resolution with a scan step of 1.0 eV. It will then be followed by the *narrow scans* of all the present elements. The scan range is generally around 3 to 5 eV (but can be selected) around the characteristic peaks of the elements, and the scan resolution is ten times higher than survey scans (0.1 eV). The spectrum can now be analyzed using a suitable baseline. Normally a Shirley's baseline is suitable due to the shape of the spectrum caused by the inelastic scattering of photoelectrons. The peak areas are then determined and the atomic quantity or stoichiometry of the sample can then be made.

3.3.3 Mechanical Characterizations: Nanoindentation and Nanoscratch

Nanoindentation Tests for Hardness and Modulus

Nanoindentation either under load control or displacement control is widely used to measure the mechanical properties of thin films [117-119]. In this paper, the mechanical behaviour of the thin composite films were investigated using an instrumented nanoindenter MTS NanoXP® with a Berkovich tip to assess the effect of addition of CNTs on the composite film's modulus and hardness. A typical indentation test consists of three steps: the loading, the holding at peak load and finally the unloading step. The hardness and elastic modulus are measured with Continuous Stiffness Measurement (CSM) [120] (see also method of Oliver and Pharr [121]).

The hardness (H) of the material is defined to be the maximum applied load ($F_{\max}$) over the projected area (A_c) of the indentation and the film reduced elastic modulus is $(\sqrt{\pi}S)/(2\sqrt{A_c})$, where S is the contact stiffness measured from the slope of the unloading portion of the contact load versus indentation depth curve [121]. The reduced modulus, E_r is defined in terms of film and indenter moduli and Poisson's ratio as $E_r = \left[(1-\nu_s^2)/E_s + (1-\nu_i^2)/E_i \right]^{-1}$, where ν_i and ν_s are the Poisson's ratio and E_i and E_s are the elastic moduli of the indenter and the sample respectively. The bulk diamond indenter modulus and Poisson's ratio is taken as 1140GPa and 0.17 respectively. A continuous stiffness measurement technique at a constant loading rate of 0.05s^{-1} was applied on the thin films to measure hardness and modulus values as a function of indentation depth [120, 122, 123].

Nanoscratch Test for Adhesion Measurements

Nanoindenter MTS NanoXP® with a lateral force measurement option was used for the nanoscratch test to study the adhesion of the composite films. A conical indenter with a tip radius of 5µm was drawn across the film surface with increasing load until the film failed or delaminated. The scratch track for all the samples were defined to be 500µm and at a scratch velocity of 1µm/s. Each single nanoscratch test consists of a prescan, the actual scratch track, and a post scan. The prescan was performed with a small load to define the surface morphology of the film and establish the surface profile. The actual scratch test was characterized by the ramp loading of the diamond stylus to the preset 150mN load and the desired scratch length. This was followed by a postscan to profile the entire length of the scratch track. The most important parameter obtained from the scratch test is the critical normal load P_c which is the critical well defined value used in characterizing the interfacial adhesion of the films.

3.3.4 Thermal Characterization: TGA and DSC

Thermal analyses of the sol-gel films and its analogous composites with CNTs impregnation were studied using thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC). TGA is a technique where a sample mass is monitored against variation in time or temperature, while the material is heated, cooled or held at a constant temperature in a controlled environment. This technique is commonly employed to determine changes in weight in relation to changes in temperature, to identify the material's degradation temperatures, the level of inorganic and organic components, the absorbed moisture content and the decomposition thresholds of the solvent residue in the material.

On the other hand, DSC provides measurements of heat flow in endothermic and exothermic transitions as a function of temperature under a controlled environment. The DSC curve provides useful information on enthalpy, heat of reaction and the percentage of crystallinity. The films in the thermal characterizations were cured at 100°C and scrapped off from a glass petridish. Sample weights were between 10-20mg and the experiments were performed in a dynamic mode, at a heating rate of about 5°C/min from room temperature to about 700°C, in an inert nitrogen environment.

3.4 Summary

This chapter presents an overview of the experimental procedures and techniques utilized in this work. The idea of the protective composite film is proposed and the routes for synthesizing of silica sol-gel CNT composites (by physical and chemical surface modification) were outlined here. Although various techniques were used to characterized the thin film composites, emphasis was accorded to the nanomechanical properties as this is currently one of the most important weakness in low k materials which was to be solved in this work.

4 RESULTS AND DISCUSSION

4.1 Introduction

While low-k materials in use at the 130nm and 90nm node are CVD organosilicates (OSG), the spin-on coatings have better extendibility to lower technological nodes of 45nm and below as it allows the introduction of porosity into dielectric materials to achieve ultra low-k values ($k < 2.0$) [124]. One of the promising candidates for ultra low-k dielectric materials is sol-gel synthesized silica xerogel film because the skeletal network structure of SiO_2 gives excellent dielectric properties and thermal stability [111].

Silica xerogels with their high porosity allows ultra low-k values to be achievable. In addition, there is a possibility to tailor their dielectric constant to vary from between dense silica to near air (4.0 to 1.2) by adjusting the porosity of the silica from low to high. This would allow the extendibility of the xerogels to be used in more than one device generation without having to change the basic silica matrix itself. However, the mechanical properties of these porous structure degrade when compared to their solid cell wall materials. There is a need to balance the porosity without compromising the mechanical properties.

The unique structure of CNTs with its high aspect ratio, low density, high strength, good thermal and mechanical properties make them ideal for development of novel material systems such as reinforcing fillers in nanocomposites [80, 125]. The development of CNT composites has been impeded by the efficiency and ease of dispersion of the CNT inclusions in the matrices. The difficulty has been attributed to the smooth, non-reactive, chemically inert surface of the CNTs.

Moreover, the inter-tube Van der Waals' forces of attraction also results in significant aggregation of CNTs which prevents the transfer of the desirable nanotube properties to the matrix itself. For the effective reinforcements in nanocomposites, homogenous dispersion of CNTs in the host matrix as well as a strong interfacial bonding between the CNTs and the matrix is necessary for efficient load transfer.

In order to dispel the aggregation of pristine CNTs, their surface modification is necessary either by physical or chemical means. For physical surface modifications, some form of surfactant or solvents are employed to disperse the CNTs [126, 127]. However, the resulting dispersions may not be able to sustain its homogeneity over time [128]. On the other hand, chemical surface modification or functionalization of CNTs is emerging as a more attractive alternative [129, 130], involving the attachment of functional groups or aliphatic carbon chains resulting in a marked improvement in dispersion as well as chemical compatibility between nanotube and matrix material.

This chapter focuses on the synthesis and characterization of sol-gel silica and functionalized carbon nanotubes. Sol-gel nanotube composite films were then fabricated from addition of pristine, physically modified and chemically functionalized carbon nanotubes into the so-gel silica xerogel solution. The chemical, nanomechanical and thermal characteristics of the composite dielectric films were evaluated to determine the most optimal CNT reinforcement method to achieve the film fabrication.

4.2 Microstructure characterization of Sol-gel

Figure 4-1 shows a typical XRD scan of the synthesized xerogel cured by the temperature profile as described in Chapter 3. The XRD pattern obtained shows a broad peak from 20 - 30°, typical of the amorphous structures commonly found in silica xerogels [131]. The amorphous nature of silica is partly attributed to the two step acid base catalyst step used in the synthesis of the sol-gel. Therefore, there is no distinct orientational plane of the pores in the xerogel and hence no distinct peaks are observed.

Figure 4-1: XRD pattern of a typical xerogel film cured at 100°C and aged 3 days

The surface morphologies of the cured xerogel films were measured using AFM in tapping mode with the surface roughness measured to be 0.8nm (see Figure 4-2). The smooth and featureless morphology is supportive of an amorphous structure..

Figure 4-2: AFM in tapping mode with (a) plan view and (b) three dimensional view, having a scan area of 20 by 20μm of the xerogel films with an ageing time of 3 days cured at 100°C.

The effect of processing parameters on the chemical structure of xerogel films were investigated using FTIR spectroscopy. The spin coated sol-gel films with ageing times of 3 days; at a cure temperature of 100°C, were taken to be the reference samples. From the FTIR spectrum of a 3 day aged silica film as shown in Figure 4-3, several points of interest could be noted as explained below.

The silica films after polycondensation reaction and thermal curing were composed of mainly siloxane Si-O-Si bonding represented by the intense peak absorption detected at 1070cm^{-1} due to the transverse optical vibration mode corresponding to asymmetric stretching of the skeletal SiO_2 network. The peak centered around 1150cm^{-1} corresponds to the longitudinal optical vibration mode of the Si-O-Si linkage [124, 131]. The peak located at 775cm^{-1} is associated with the symmetric stretching of the Si-O-Si linkage [124]. No weak signals of alkyl group at 1270cm^{-1} for Si-CH₃ symmetric were detected and broad absorption peak at 3327cm^{-1} indicates the presence of -OH stretching. The -OH related vibration is due to physisorbed moisture on the surface of the xerogel [124].

Figure 4-3: FTIR spectra of xerogel films cured at 100°C using solutions with different ageing time.

Examining the ratio of the Si-O-Si peaks for the 3, 4, 6 solution aging days, it was calculated that they have peak height values of 1:1.01:1.19 respectively. This signifies that, with an increase in ageing time, a slightly stronger absorbance of Si-O-Si bonding could be detected which points to a more complete silylation reaction [131]. However, no obvious differences between the FTIR spectra of these films were observed. For all three samples, Si-OH and Si-O-Si, bands appeared. After ageing for 6 days, there is increased peak intensity around 3300 cm^{-1} , which may be due to the -OH stretching. The C_nH_{2n} alkyl group stretching, and temporary stabilization of oligomers [132] (a sharp peak) could have been obscured due to the overlapping and coverage of the broad -OH peak.

The resultant silica films were also monitored for normal moisture uptake in ambient conditions. An incorporation of water or moisture into the film would increase the dielectric constant due to the polar nature of H_2O molecule. While dielectric constant measurements were not performed in this work, it is crucial to ensure the stability of the xerogel films with time. Figure 4-4 shows the FTIR spectra of 3, 7, 14 and 21 days of cured sol gel storage in ambient conditions. There is no significant increase in the $-\text{OH}$ peak with storage time which points to the fact that there is no significant absorption even after 21 days.

Figure 4-4: FTIR spectra of stability study of 3 day aged xerogel films cured at 100°C with FTIR spectrum taken at 3, 7, 14 and 21 days.

The effect of curing temperature on the spin-coated silica films is shown in Figure 4-5. With an increase in curing temperature, the peaks due to the organic species weaken considerably. In addition, the broad absorption peak at 3327cm^{-1} corresponding to silanol, SiOH or $-\text{OH}$ bonds revealed a decrease in intensity when

the curing temperatures were raised. The decrease is due to the elimination or evaporation of hydroxyl groups at high temperature [124]. The ratio of Si-O-Si absorption peak at 1085 cm^{-1} for 60, 100, 150, 200 and 300°C is 1:1.279:1.249:1.250:1.488. This proves that with increasing curing temperature, more Si-O-Si bonds are formed due to the higher tendency of cross-link. A window period of three days at a 100°C cure temperature was selected as the optimum parameters for synthesis similar to that reported by Cahyadi et. al.[133] .

Figure 4-5: FTIR spectra of 3 day aged xerogel films cured at 60 °C, 100 °C, 150 °C, 200 °C and 300 °C.

4.3 Surface Modification of Carbon Nanotubes (CNTs)

4.3.1 Chemistry of Functionalized CNTs

The production methods of CNTs also generate defects during synthesis. Around 1-3% of the carbon atoms are in the vicinity of a defect site. An often encountered defect of the six membered ring carbon structure of the nanotubes such as the inclusion of two pairs of five and seven membered rings in the network is referred to as a Stone-Wales defect (7-5-5-7) [130]. Chemical modification approaches usually target defects, end caps and sidewalls. As a result, esterification and amidation of oxidized nanotubes have become one of the emerging areas of covalent attachment of chemical groups onto the tubular nanotube structures [129, 130].

The general chemical functionalization of CNTs for surface modification is usually performed in two steps [129]: Initially, carboxylic acid groups COOH can be introduced to the surface defect sites and end caps of CNTs after oxidation with either nitric or sulphuric acid. The attached COOH groups are then able to form covalent coupling between the tubes and other active groups such as amide, ester groups and other functional moieties. The tailoring of suitable groups to the otherwise chemically inert CNTs will result in the formation of chemical bonds which will help the host matrix to realize the efficiency of load transfer from the impregnated CNTs as well as the exfoliation of the nanotubes from bundles.

One of the recent functionalization routes is the chemical modification of the surface of the nanotubes with organosilanes[134-136]. These organosilane agents are able to link two different materials, inorganic and organic material together by establishing

chemical bonds or physical interactions which are water resistant at the interface of the two dissimilar materials. The organosilane agents exist as

where R is an organo-silane group attached to silicon while R' react with Si-O bonds and easily hydrolysed to form trisilanol, $-\text{Si}(\text{OH})_3$. Trisilanol, $-\text{Si}(\text{OH})_3$ reacts readily with hydroxyl groups (OH) formed on the surface of oxidized carbon nanotubes. In this work, an alternative chemical approach was applied albeit with the same objective. The silane agent used in this work is:

where R'' is a trimethylsilyl, $\text{Si}-(\text{CH}_3)_3$. Si is attached to three methyl groups CH_3 . The chemical nature of the functionalized moieties were studied through FTIR, Raman, XPS and thermogravimetry in the subsequent sections along with the probable mechanism of chemical reactions that occur. Non-covalent functionalization of CNTs by adsorption of surfactants and solvents on the pristine CNTs present more easily accomplished dispersions by sonication. Hence, no rigorous chemical characterizations except visual inspection of the CNTs in the sol-gel solution is needed for verification.

4.3.2 Chemical Functionalization of MWCNTs and Probable Mechanism

From the COOH functionalized CNTs, the OH peak and the asymmetric and symmetrical C=O bonds stretching appeared at $1740\text{--}1660\text{ cm}^{-1}$ and $1687\text{--}1625\text{ cm}^{-1}$ concluded that COOH bonding exists. C-O bond stretching occurs at around 1350 cm^{-1} mainly due to COH in-plane deformation. There are also negative peaks due to loss of water content after drying. From the silane functionalized CNTs, there is an obvious peak of Si-O-CH₃, Si-O skeletal vibration. The Si-O-Si bond and CH₃ band are indexed at 1064 cm^{-1} and 2974 cm^{-1} respectively. The end group Si-CH₃ band appeared at 1255 cm^{-1} and 1405 cm^{-1} due to CH₃ symmetric and asymmetric stretching. CNH bonds of stretching open and stretch-bending occurs at $1490\text{--}1400$ and $1570\text{--}1510\text{ cm}^{-1}$. This shows that C=O-NH₂ band exists hence it is conclude that CNTs functionalization is complete. Peaks were referenced from [137].

Figure 4-6: FTIR spectra of COOH and silane functionalized MWCNTs. See Figure 4-10 on page 88 for silane compound chemical structure.

The surface states of the MWCNTs before and after functionalization were also verified with XPS analysis. Figure 4-7 represent the XPS survey spectra of pristine, COOH functionalized and silane functionalized MWCNTs. The elemental compositions of the CNTs summarized in Table 4-1 reveal the presence of mainly carbon as well as the existence of some oxygen. When functionalized with silane groups, the atomic percentage of N1s increased from 2.72 to 10.59%. and also Si2p was detected at 3.69at%.

Figure 4-7: XPS spectra of (a) pristine, (b) –COOH and (c) silanized nanotubes

Table 4-1: Summary of the elemental atomic composition of the MWCNTs

Element (atom %)	C (1s)	O (1s)	N (1s)	Si (2p)
Pristine	94.17	5.51	-	0.32
COOH functionalized	90.70	6.58	2.72	-
Silane functionalized	71.19	14.53	10.59	3.69

As the attachment of the silane functional group is vital in the overall chemical scheme, additional analysis was performed to confirm the presence of silane covalently grafted onto the nanotubes. The C1s XPS spectra of pristine, -COOH and silane functionalized MWCNTs were deconvoluted into five contributing curves as presented in Figure 4-8. For pristine MWCNTs, the peaks were identified at 284.6, 285.43, 286.52, 289.28, 291.21eV. The last component corresponds typically to a shakeup of the aromatic structures present in CNTs [135, 136]. The peaks for –COOH and silanized tubes were at the following binding energy values; 284.60, 285.64, 288.225, 286.91, 291.4 and 284.6 288.31, 286.40, 284.43, 282.78eV respectively.

From the contribution attributed to the Si-C appearing at 282.78eV along with the elemental composition of silicon, it is possible to deduce the presence of silane on the MWCNTs after silanization of the –COOH moieties. It was also reported that amides have binding energy in the range of 399.5 to 400.2eV [138] which was detected by the XPS scan. Therefore it can be acknowledged that the peak energies of N1s are complementary to the results obtained by FTIR spectra in confirmation of the final product formed.

Figure 4-8:C1s XPS spectrum of (a) pristine, (b) –COOH and (c) silanized MWCNTs

Raman spectroscopy was also performed on the MWCNTs in their pristine, -COOH functionalized and silane functionalized states in order to understand the effect of functionalization on the structural properties of the MWCNTs. The Raman spectra exhibit two distinct bands at 1300 and 1580 cm^{-1} which are identified as the D and G bands respectively. The D line intensity is a representation of disorder in the MWCNTs and is related to the presence of amorphous carbon that adhere to the defects present in the pentagonal and hexagonal graphitic walls. On the other hand, the G line intensities are characteristic of the graphitic bands representing the C = C bonds of the MWCNTs.

The Raman spectra show that the structures of the nanotubes have largely been preserved despite the oxidative treatment followed by the silanization process. It is also noted that from the comparisons of the relative areas of the intensity of the D and G peaks that with chemical surface modification, the D bands are widened which implied the generation of surface defects in the crystalline MWCNTs structure. The spectrum of the COOH-MWCNTs and the silane-MWCNTs do not differ significantly due to the fact that the electronic structures of the nanotubes are intact. This observation indicates that silanization can only take place at the defects, disorder and surface active sites of the MWCNTs that have been generated by the acidic treatment with nitric acid.

The proposed functionalization scheme is as shown in Figure 4-10. The COOH MWCNTs were suspended in EDC and succinimide in an ultrasonic bath similar to a process described by Weiwei et al. [138]. The organic reactions allowed the formation of transitional amine terminated nanotube species that could easily be substituted in a second reaction by the silane coupling agent with the trimethylsilyl groups. While only one side group was illustrated in the Figure 4-10, in reality, many side groups or end caps with COOH could eventually be converted to the silane functionalized groups. The attachment of bulky side groups would assist in the dispersion (or solubility in the macroscopic sense) of the nanotubes.

Figure 4-10: Proposed functionalization route and mechanism

The thermogravimetric analysis (TGA) of pristine, COOH functionalized and silane functionalized MWCNTs were shown in Figure 4-11. From the TGA analysis, the functionalized MWNTs can be seen to decompose at a faster rate, followed by MWNT-COOH and finally the pristine MWNTs. The different rates of thermal decomposition implicitly suggests there are different side groups attached to the CNTs hence it proves that different thermal stabilities for different functionalized and non functionalized carbon nanotubes. The TGA curve of the pristine MWCNTs, distinctly illustrated that the onset of thermal degradation of MWCNTs occurred at about 620°C , which was in good correlation with previous studies by Shanmugharaj [139]. The weight loss for the pristine MWCNTs is about 10% at 700°C.

Figure 4-11: TGA curves of (a) pristine, (b) COOH functionalized and (c) silane functionalized carbon nanotubes

COOH functionalized CNTs on the other hand demonstrated a gradual degradation over a broad range of temperatures. The initial weight loss when the temperature is increased for 30-550°C is probably due to the evaporation of moisture, degradation of the amorphous carbon and COOH acid groups attached to the surface of the CNTs. The complete removal of these groups is followed by a steeper weight loss which represents the onset of MWCNTs itself.

For the silane functionalized CNTs, multiple stepped thermal degradation indicates complex reactions occurring when the CNTs were subjected to the controlled temperature program. The initial degradation peak between the range of 150-200°C can be assigned to the burning off silane groups that have been freely adsorbed on the MWCNTs surface after functionalization. Further increase in temperature leads to the elimination of silane and OH groups present in the functionalized CNTs. In addition, the weight loss may be due to the breaking down of other organic groups present in the functionalized CNTs as well as possible moisture due to exposure to air, which finally leads to a 60% weight loss of the original product.

Morphology of functionalized CNTs

The morphology of the MWCNTs before and after functionalization is studied with the aid of a field emission scanning electron microscope (FESEM). The original pristine MWCNTs in Figure 4-12(a) are aggregated together due to the Van der Waals forces of attraction between the MWCNTs. However, impurities attributed to catalyst particles were not observed. After functionalization with silane coupling agent, the f-MWCNTs were observed in Figure 4-12(b) to possess a mat-like morphology, aggregating together in the form of bundles. A similar observation by

Zhang et al. [140] ascribed the formation of such morphology to the hydrogen bonding and cross-linking of the silane groups between adjacent MWCNTs

Figure 4-12: Morphology of (a) pristine and (b) silanized MWCNTs prepared by chemical functionalization.

4.4 Characterization of the Sol-gel/CNT Composite Films

4.4.1 Hardness and Modulus measurement

Nanoindentation tests were performed with the continuous stiffness measurement (CSM) technique at a strain rate of 0.05 (1/s) on all the fabricated sol-gel/CNT composites. A typical load – indentation depth curve for a silica sample indented using a Berkovich indenter is shown in Figure 4-13. A series of 10 indentation tests to a depth of 500nm were performed on each sample at a spacing of 50 μ m (to prevent interference between the indentation zones and all showed good repeatability).

Figure 4-13: A typical set of 10 load versus indentation depth curves of the reference silica sol-gel silica film.

An effort was made to study the indentation region under SEM. But, none of the indentation marks were clearly detected. The data of the ten indents (elastic modulus and hardness) were averaged and the error bars in the CSM curves represent the standard deviation of the calculated values of the hardness and reduced modulus. The Poisson's ratio for the composite films was taken to be 0.2 as this is the adopted 'rule of thumb' value for ceramics. At shallow indentation depths ($<10\text{nm}$), the hardness and modulus values are not so stable due to the surface roughness of the films.

With subsequent increase in the depth of indentation up to $\sim 100\text{nm}$, the modulus and hardness curve approach a constant value, indicating the inherent nanomechanical properties of the film. With further increase in the indentation depth to the maximum of 500nm , the hardness and modulus values increase in response to the stiffness and hardness of the silicon substrate.

The following section discusses the effect of ageing and curing temperature on the hardness and elastic modulus on sol-gel silica. Also the effect of the addition of CNTs to the sol-gel silica matrix through various dispersion techniques, their mechanisms and the effectiveness of the dispersion on the mechanical properties is explained.

(a)

(b)

Figure 4-14: Variation of (a) hardness and (b) modulus with indentation depth of sol-gel silica films using 3, 4, 6 and 200°C cured (3 day aged) solutions.

4.4.2 Effect of Ageing time and curing temperature

The average values of Young’s modulus and hardness taken over the range of 10-20nm of Figure 4-14 are shown in Table 4-2. The values of hardness and modulus demonstrate that when the sol-gel solution was allowed to age for a longer time before spin coating, the modulus and hardness of the neat sol-gel thin films increases.

Table 4-2: Hardness and Modulus values obtained for xerogel films with 3-6 day aged solutions

Sample	Modulus, E (GPa)	Hardness, H (GPa)
3 day aged	22.25±1.07	1.27±0.14
4 day aged	24.61±2.31	1.40±0.49
6 day aged	27.93±1.76	1.86±0.26

These observations due to longer ageing time and higher curing temperatures indicate these factors create alterations in the TEOS sol-gel chemistry. Indeed, from the FTIR peaks of increase ageing time and higher thermal cure, the intensities of the Si-O-Si peak also amplify correspondingly (i.e. more cross-links). Therefore to ensure a fair bench mark against other sol-gel CNT composite films, 3 day age sol-gel thin films cured at 100°C was chosen as the reference sample. During the fabrication the set curing temperature is high enough to remove the residual solvents.

4.4.3 Effect of CNT reinforcement

In this section, the effect of MWCNTs reinforcement in sol gel silica on the composite mechanical properties is investigated through microstructural observations. Further, the efficacy of CNTs dispersion using various surfactants is explored. Recall from table 3-3 that the samples prepared using surfactants are named as A, B, C, D, E and F. The weight fraction of CNTs is limited to 0.04wt% in order to avoid the aggregation of CNT fillers. The measured modulus and hardness values for various surfactant treated/functionalized CNT sol-gel composites as a function of CNT weight fraction are listed in Table 4-3. (See figure 4-15 for actual measurements).

Table 4-3: Hardness and Young’s Modulus values obtained for different films

Sample	CNT type*/ content (wt %)	Modulus, E (GPa)	Hardness, H (GPa)	Surface roughness (R _{rms}) (nm)
Silica sol-gel	0	22.25±1.07	1.27±0.14	0.830
(sol-gel/CNT)/A	0.01	21.63±2.80	1.74±0.37	0.848
	0.02	23.01±6.54	1.61±0.62	0.874
	0.04	24.51±1.45	1.86±0.22	1.136
(NanoAQ)/B	0.01	20.52±4.69	1.56±0.52	6.113
	0.02	15.15±1.42	1.16±0.35	6.135
	0.04	14.65±4.62	0.82±0.46	7.972
(DMF)/C	0.01	28.25±1.77	1.88±0.23	1.340
	0.02	27.89±2.59	1.50±0.77	0.840
	0.04	27.70±3.17	1.43±0.29	0.976
(CTAB)/D	0.01	28.65±1.07	1.97±0.26	2.499
	0.02	23.18±1.70	1.80±0.27	2.545
	0.04	21.01±1.38	1.42±0.57	2.489
(PVP-4)/E	0.01	30.46±3.40	2.13±0.76	1.905
	0.02	24.24±1.72	1.75±0.29	0.631
	0.04	22.00±2.54	1.66±0.4	0.631
(functionalized)/F	0.01	23.75±1.97	1.18±0.18	0.362
	0.02	24.62±1.29	1.48±0.14	0.706
	0.04	33.38±1.09	1.84±0.32	0.605

(a)

Figure 4-15: Variation of (a) hardness, and (b) modulus with indentation depth of sol-gel silica composites (including neat reference sample) with various surfactants.

To observe the effect of MWCNTs reinforcement into the sol-gel matrix, it is necessary to compare the reference neat silica sol against the other five MWCNTs sol-gel nanocomposites labeled as A, B, C, D and E. With the exception of sample A and B, general trends showed that the modulus and hardness of the nanocomposite increases with the addition of MWCNTs of 0.01wt%. For samples A and B which show lower modulus but higher hardness as compared to the reference sol-gel silica sample, the incongruity in mechanical properties could be due to nanostructural differences in the morphology of the sol-gel MWCNTs spin-coated film (as in sample A) or due to the influence of surface roughness (as observed from the relatively high R_{rms} in sample B) [141].

The surface morphologies of various sol-gel/MWCNTs obtained using field emission scanning electron microscope (FESEM) were analyzed. With the aid of these micrographs, the morphology of the thin films was studied to gain insight into the presence or absence of reinforcing ability of the MWCNTs.

Considering sample A, where no solvent/surfactant was used for the dispersion of MWCNTs, the presence of MWCNTs in the sol gel matrix degrades the modulus due to the poor adhesion between the MWCNTs and the sol gel matrix. Cracks are observed on the silica film surface as a result of the aggregation of MWCNTs (see Figure 4-16).

Figure 4-16: Bundling of CNTs due to poor dispersion of fillers in sample A

When the sol gel does not serve as a cementing matrix, the displacement of the individual MWCNTs occurs easily. This makes the perceived hardness and modulus values much lower than it should be when MWCNTs were effectively reinforced into the matrix for load sharing. The reinforcing of MWCNTs alone does not improve the mechanical properties of the silica composite film. Stirring and sonication are crucial steps in the process of CNT dispersion to prevent the aggregation of MWCNTs. However, if the Van der Waals forces of attraction between the MWCNTs are greater than the sonication energy provided then the MWCNTs are not separated. The result leads to MWCNTs forming bundles in the TEOS/ethanol solution. These aggregations of MWCNTs disrupt the SiO_2 network of the sol-gel and cause cracks to form in an otherwise planar and defect free film.

From the nanoindentation tests, sample B with NanoAQ surfactant show a decrease in modulus in comparison with the pure sol-gel reference sample. The modulus of the NanoAQ treated sample decreased by about 7% for the CNT weight fraction of 0.01wt %. This indicates that the sol gel composite film produced using NanoAQ surfactant leads to a mechanically inferior thin film and thus not a suitable solvent for the use of dispersing CNTs in sol-gel solutions.

The microstructure observation under the FESEM (see Figure 4-17) of the surface of the spincoated film indicates the non-planar nature of the film with aggregated black areas of CNTs coupled with voids. The surface of the NanoAQ based silica CNT composites is very rough with an RMS value of 6.1 nm.

Figure 4-17: The sol-gel film fabricated using NanoAQ as a dispersing agent

The nanomechanical properties of samples C, D and E are superior to those found in A and B and also surpass that of the sol-gel silica matrix film. This is a clear indication that the CNTs have succeeded in reinforcing silica composites. Further confirmation rests in their surface morphology as seen in Figure 4-18, 4-20 and 4-22, showing even dispersions of CNTs throughout the matrix. No excessive aggregations were noticed in these three CNT composite films like in the case of sample A, which is a vital criteria in the formation of CNT reinforced inorganic sol-gel silica composite. The planarity and continuity of the film was also preserved unlike that of sample B. As such the nanotube matrix interaction is enhanced and hence a more efficient load transfer is afforded from the nanofillers to the matrix.

The mechanisms assisting the dispersion of the MWCNTs for samples C, D and E are quite different. For sample C, solvent assisted dispersion using DMF was used to scatter the aggregation tendencies of MWCNTs as the DMF solvent molecules adsorb onto the nanotubes and overcome the Van der Waals attraction between the tubes. The TEM image in Figure 4-19 clearly shows the wetting of the solvent upon the nanotubes. The purpose of the solvent is therefore to render the otherwise chemically inert MWCNTs soluble by interaction and subsequent dispersion with the solvent molecules in the sol-gel mixture.

Figure 4-18: DMF assisted dispersion of CNTs in sol-gel matrix

Figure 4-19: TEM micrograph of DMF dispersed MWCNTs

Sample D employs the aid of a positive cationic surfactant, Hexa Cetyltrimethylammonium Bromide (CTAB). The CTAB surfactant molecules adsorbed onto the MWCNTs, as seen by the presence of the small dark molecules in Figure 4-21. The interactions of the like cationic charges inadvertently result in steric repulsions which exist to separate the CNTs while in solution form. These positive forces of repulsion due to the cationic CTAB ions between the CNT-CNT exceed those Van der Waals forces of attraction thus giving rise to an improvement in dispersion. The CTAB surface modified MWCNTs reinforced sol-gel silica possesses an increase in modulus by 29% and hardness by 55% when compared to the pure silica sol-gel. Jinwei et al.[111] also observed that CTAB treated CNT based silica composites resulted in enhanced mechanical properties in the form of fracture toughness.

Figure 4-20: Surface of sol-gel/CTAB dispersed MWCNTs

Figure 4-21: Adsorb CTAB molecules shown by the dark spots on the CNTs

The improvement in the mechanical properties of sample E is due to a polymer assisted dispersion technique using poly(4-vinylpyridine) (PVP-4), first suggested by Rouse [142] for sol-gel nanotube composite formation. The PVP-4 polymers chains wrap around the CNTs, effectively isolating them from each other and in the process contributed to the debundling of the CNTs in the sol-gel silica. The micrograph in Figure 4-22 and 4-23 qualitatively shows the extent of separation provided through this mechanism. A further advantage of this process route is that PVP-4 polymer promotes adhesion between the inorganic SiO_2 network and CNTs [142]. This increased efficiency of load transfer is reflected by the corresponding improvement in modulus and hardness over the reference sample by 37% and 68% respectively. The adhesion promotion mechanism of the polymer also serves to improve the mechanical properties of sample E over those of sample C and D.

Figure 4-22: Micrograph of PVP-4 dispersed CNTs in sol-gel silica.

Figure 4-23: TEM of polymer wrapped MWCNTs in sol-gel silica

All the dispersion routes and techniques for samples B-E involved physical surface modifications by surfactants or solvents of CNTs in sol-gel solution followed by sonication. The key advantage of physical dispersion techniques are the easily accomplishable dispersions and the ability to initiate the exfoliation of nanotubes from the aggregated bundles. This is achieved by attaching various groups of functional molecules without the disruption of the π system of the graphene sheet(s) that would compromise the mechanical, electrical and other properties unique to only CNTs. However, the residual surfactants/solvents that remain may affect the properties of the composite as they are difficult to fully eliminate.

On the contrary, sample F utilizes the chemical surface modification route by functionalizing the COOH-CNTs with an amino silane group. It should be noted at this point that direct comparisons of the mechanical properties with samples A-E may not be possible as the COOH functionalized CNTs were obtained from Nanocyl as opposed to the pristine CNTs supplied by Shenzhen Nanotech.

However, the modulus of the silanized CNT sol-gel composites exhibited an increase of 6% in modulus as compared to the reference sol-gel film but there were no observed improvements in hardness for 0.01 wt% functionalized composites. Micrographs with FESEM were unable to capture any images of the CNT inclusions at 0.01 wt% in Figure 4-24(a) although these were observed for 0.04wt% of CNT loading in Figure 4-24(b).

Figure 4-24: Sample F with (a) 0.01wt% functionalized CNTs and (b) 0.04wt% functionalized CNTs.

Notwithstanding, the improved elastic modulus reflects the function of the silane group attached onto the CNTs acts as an interface between the organic CNTs fillers and the inorganic sol-gel silica matrix to chemically couple/link the two materials together. A schematic illustration of the coupling mechanism is shown in Figure 4-25.

Figure 4-25: The silane coupling mechanism where the Si atom acts as an interface between two different materials and link them together.

The silane functionalized CNTs (f-CNTs) were prepared according to the chemical reaction scheme proposed in Section 4.2 in which the silane group was first grafted covalently onto the CNTs. The f-CNTs were then dispersed into the sol-gel solution. It has been suggested that the functional groups enhance the dissolution process by the formation of intervening moieties that surmount the intrinsic van der Waals attraction between CNTs. In this work, the trimethylsilyl groups attached to the silane agent accounts for the homogenous dispersion of f-CNTs in the sol-gel solution.

Under aqueous conditions, the three $-\text{O}-\text{Si}(\text{CH}_3)_3$ groups undergoes hydrolysis revealing the $\equiv\text{Si}$ group that can react with the Si-O chains in the sol-gel silica xerogel solution due to its chemical compatibility. Due to the chemical similarity, silane covalently anchors onto MWCNTs would help the MWCNTs to disperse more uniformly in the precursor, and in the final thin film. The homogenous dispersion would increase the interacting surface area of the nanotube with the silica matrix. The silane acted as a covalent “hinge”, which would offer stronger interfacial interactions between MWCNTs and the sol-gel matrix [140].

Chemical functionalization is often carried out with the covalent attachment of chemical groups through chemical reactions on the π conjugated skeleton of CNT. Defects induced can lead to tube shortening due to the ‘cutting’ of nanotubes at regions of defects leading a decrease in tube length. The mechanical properties of CNTs are functions of their aspect ratios (tube diameter and length). A decrease in its length diminishes the effect of reinforcement as fillers. This could partially explain the lesser extent of mechanical enhancement of functionalized CNTs (at 0.3mg/0.01wt %) as compared to the other non-covalent physical dispersion routes (also at 0.3mg/0.01wt %). However, at higher weight percentage of f-CNTs, the mechanical properties did improve as shown from the measurement of hardness and modulus in Figure 4-26.

Figure 4-26: Variation of (a) Modulus and (b) Hardness with indentation depths for sol-gel silica CNT composites with increasing weight percentage of f-CNTs content.

4.4.4 Effect of CNT Weight percentage

The reinforcing effects of CNTs as fillers were studied by varying the CNTs from weight fraction 0.01, 0.02wt and 0.04wt% for all samples A-F. In this section we assess the nanomechanical properties (hardness and modulus) and discuss the parameters influencing the mechanical reinforcements by CNTs which is summarized by the bar chart in Figure 4-29.

The addition of CNTs proves that an increase in modulus and hardness to the sol-gel matrix occurs as compared to the neat silica sol-gel sample although in some cases there may be slight change (i.e. sample C) or a drop (i.e. sample B) in modulus. Such a trend is consistent for both functionalized and non-functionalized CNTs when the loading of CNTs are increased for A and F.

For sample A(0.01wt%) which show lower modulus but higher hardness (21.63GPa and 1.74GPa respectively) as compared to the reference sol-gel silica sample, the incongruity in mechanical properties could be due to nanostructural differences in the morphology of the spin-coated film. This proves to be higher than hardness value obtained for sample A(0.02wt%) (1.61GPa).

Figure 4-27: Variation of (a) Modulus and (b) Hardness with indentation depths for sol-gel silica MWCNT composites A-F for 0.01wt%, 0.02wt% and 0.04wt%. The dashed line indicates the modulus and hardness of the reference sol-gel sample.

The decrease in the modulus for sample A(0.01wt%) is due to the nano dimensions that CNTs possess such as large surface area and high aspect ratio. Van der Waals forces are prominent between the CNTs, causing them aggregate into bundles as observed under the FESEM. Furthermore, CNTs are extremely hydrophobic and coupled with the lack of chemical compatibility introduced a poor dispersion of CNTs. The aggregations observed on the film surface contribute to disruption of the silica network and degrades the film modulus due to poor interfacial interaction between the CNTs and the matrix which leads to little or no improvement in mechanical properties. While there are some increase in modulus and hardness for sample A(0.02wt%) and A(0.04wt%), the effect is minimal due to the poor load transfer efficiency.

On the contrary, the surfactants and solvent assisted dispersion experienced a degradation in mechanical properties when the amount of CNTs introduced into the matrix increase from 0.01wt% to 0.04wt%. The sol-gel nanocomposites exhibited maximum hardness and modulus at B-E(0.01wt%) that did not increase with nanotube reinforcements. Even the best physical dispersion route attained by PVP-4 for sample E showed a reduction in modulus and hardness from 30.46GPa and 2.13GPa to 22.00 and 1.66GPa respectively.

The decrease in mechanical properties at higher filler contents can be attributed to an increasingly poorly dispersed aggregation of MWCNTs or due to the deleterious effect of the solvent or surfactant used to disperse the CNTs [126]. The solvent effect have been studied by researchers recently [143] related the reduction of mechanical properties as being due to the plasticity to the film caused by the dispersion agents used.

Functionalization that involves the covalent grafting of specific chemical groups on the surface of the nanotubes showed a better and more consistent trend in that with increase in CNT content both the hardness and modulus also increase. The selection of the type of functional group is crucial in order to optimise the potential of the functionalised CNTs in fulfilling the designated objective to enhance the bonding of CNTs and the silica matrix, to promote better dispersion of CNTs, interfacial interaction and load transfer.

The functionalized CNT composites sample F has a good improvement in modulus and hardness as compared to the reference sol-gel sample. A content of 0.04wt% f-CNTs led to an increase in modulus and hardness from 22.25 GPa and 1.27GPa to 33.38GPa (+50%) and 1.84GPa (+45%) respectively. Sample F(0.04wt%) also demonstrated the highest modulus achieved among all the sol-gel CNT thin film composites formed. While the hardness of F(0.04wt%) is lower than that of sample E(0.01wt%) by 0.29GPa, it should be noted that having an extremely hard film will also result in brittle behavior and lead to film cracking during indentation.

In addition to the enhancement in CNT dispersion, the improved compatibility between the CNT-matrix interfaces as a result of the functional groups grafted onto the CNTs, enhances interfacial interaction and in turn, load transfer mechanism. Interfacial stress transfer is a key requirement for effective reinforcement in composite materials. The functionalisation of CNTs establishes chemical bonding with the matrix and such bonds are strong enough to overcome the effects of Van der Waals forces which promote homogeneous distribution of CNTs in the sol gel matrix and in turn, better interfacial interaction.

More importantly, with these chemical bonding increases the CNT-silica matrix interfacial strength and translate into an improvement in modulus and hardness of the film. The results obtained for the functionalized MWCNTs are in good agreement with reported literature [144, 145] where an increase in CNT loadings were performed.

4.4.5 Interfacial Adhesion Measurement

Microelectronic chips often consist of multi-layered structures bonded together. These layers are fabricated using various thin film deposition processes available in industry today such as atomic layer deposition (ALD), physical vapour deposition (PVD), chemical vapour deposition (CVD), spin coating, ion implantation and etc. However, with the increasing miniaturization of electronic packages, reliability issues, particularly interfacial delamination are largely responsible for the failure of the Cu/low-k dielectric systems. Interfacial failures of Cu and low-k layers occur during chemical mechanical polishing (CMP) and result in failures of the semiconductor packages. Therefore, understanding of the interfacial strength is a vital component for the integration of the dielectrics into the interconnect fabrication process.

A variety of thin film adhesion measurement techniques have been developed [146]. However, sample preparation itself is a challenging task for many of these methods. Nanoscratch test is one of the simplest ways to measure the practical work of adhesion of sol-gel CNT films adhesion to the Si substrates. The nanoscratch technique allows easy semi-quantitative comparisons of adhesion strength among the different films deposition on similar substrate systems. The thin films were spin-coated onto the substrates and cured before performing the scratch test. Figure 4-28 illustrates the typical scratch test adhesion results obtained from the nanoscratch tester on sol-gel silica reinforced with CNTs.

Figure 4-28 (a) – (i): Nanoscratch tests with load and friction force along scratch direction vs scratch distance for 0.01wt% composite films. Only silane functionalized CNT sol-gel films (g) – (i), 0.01, 0.02 and 0.04wt% respectively are shown. The load is the monotonic linear line while the friction force is represented by the other line.

As the load linearly increases from 0mN to a maximum of 150mN monotonically, the frictional force exerted on the surface of the film increases likewise. A sudden fluctuation of the tangential frictional force recorded on the plots represent the critical load at which the film delaminates or peels off from the surface of the substrate. The phenomena could be correlated with the help of the FESEM observation of the scratch track shown in Figure 4-29.

Using the reference sol-gel silica as an example, the measured distance from the start of the film fracture to the end of the scratch track corresponds exactly to the abrupt fluctuation point. The elastic deformation regime is usually not observable as it recovers after the removal of the load. With the linear increase in load, the film experiences irreversible plastic deformation. Upon reaching the critical load denoted as P_{cr} , fracture initiates on the film and with further loading it propagates leading to the cracking of the film.

Figure 4-29: FESEM micrograph of nanoscratch track of 500 μm of the neat sol-gel silica using a 5 μm conical diamond tip.

There are two distinct phases in the micrograph. In the initial stages of the actual nanoscratch segment, the stylus ploughs the surface of the film and the interface face occurs ahead of the film. However, the coating is suppressed by the indenter surface traversing across the scratch track and prevents the flaking of the film material (Figure 4-30(a)). When the load increases to a critical value, the interfacial failure and flaking occurs simultaneous and in front of the stylus path [147].

Figure 4-30: Schematic representations of (a) initial plastic deformation and (b) chipping failure which comprises of spalling and buckling. Adapted from [148].

The preceding compressive field causes the spallation (adhesive failure) and buckling (partial delamination) of the film in a semicircular arc in front of the traversing stylus (Figure 4-30(b)). The proximity of the failures to the leading edge of the stylus allows the previous film failures to be embedded in the track below. This causes regions beyond the scratch to be free to spalling and leads to cracking with regular chipping on both sides of the scratch track [148] as seen in Figure 4-31.

Coatings may fail in several ways when subjected to nanoscratch testing and can be easily categorized upon the basis of the hardness of both the substrate and coating (Figure 4-31) [149]. In general soft coating (hardness<5GPa) fail by plastic deformation whereas hard coatings (>5GPa) can fail by interfacial failure, bulk fracture or through thickness fracture.

Figure 4-31: Schematic of the scratch test failure modes as a function of coating and substrate hardness [149].

In the context of this study, the critical load P_{cr} at which the films failed and the hardness are summarized in Table 4-4. The hardness fall in the range of 0.8GPa to 2.13GPa which is conclusive that the sol-gel composites were all soft coatings.

Table 4-4: Experimental results for the nanoscratch tests

Sample	CNT type*/ content (wt %)	Critical load, P _{cr} (mN)	Hardness, H (GPa)
Silica sol-gel (sol-gel/CNT)/A	0	111.16	1.27±0.14
	0.01	80.13	1.74±0.37
	0.02	89.70	1.61±0.62
	0.04	47.36	1.86±0.22
(NanoAQ)/B	0.01	22.99	1.56±0.52
	0.02	19.59	1.16±0.35
	0.04	18.93	0.82±0.46
(DMF)/C	0.01	71.01	1.88±0.23
	0.02	56.11	1.50±0.77
	0.04	57.31	1.43±0.29
(CTAB)/D	0.01	53.34	1.97±0.26
	0.02	67.11	1.80±0.27
	0.04	53.23	1.42±0.57
(PVP-4)/E	0.01	50.35	2.13±0.76
	0.02	75.00	1.75±0.29
	0.04	53.21	1.66±0.40
(functionalized)/F	0.01	107.30	1.18±0.18
	0.02	104.43	1.48±0.14
	0.04	116.70	1.84±0.32

The results showed that the reference sol-gel sample has an extremely high P_{cr} as compared to the sol-gel CNT composites obtained by the various physical dispersion strategies. While the nanomechanical properties of hardness and modulus are extremely promising, the adhesion of the composite films to the Si substrate distinctly shows the inferior adhesion properties to the substrate. Silica xerogel has good chemical compatibility and adhesion to the substrate.

The introduction of CNTs as physically dispersed entities would probably result in a disruption to the prevalent silica dielectric three dimensional network structure. Despite the thermal curing and additional cross-linking afforded, only physical

bonding exists between the silica inorganic network and the pristine CNTs resulting in a limited load transfer ability. This results in the poor P_{cr} obtained from the CNT dispersed samples with values below 80mN as compared with the reference sol gel silica (~120mN).

The functionalized CNT sol-gel composites showed an entirely opposing scenario. With an increase in f-CNTs, the P_{cr} increases. It could be observed from Figure 4-28 (g), (h) and (i) that all the P_{cr} attained were at least 100mN and above with the F(0.04wt%) having approximately the same critical load as that of the neat sol-gel. The most probable justification for this observation is that in the chemical functionalization process, the f-CNTs are strongly bonded to the matrix allowing a more effective load transfer from the matrix to the nanotubes. The strong interfacial bonding allows the complete incorporation of the CNTs to become part of the integral part of the silica matrix.

Figure 4-28 shows the typical graphs for critical load measurements. P_{cr} was obtained from the corresponding distance value where the friction force showed abrupt changes indicating film failure and delamination from the Si substrate (soft coating on hard substrate system). The scratch tests provide only relative values for comparison of scratch resistances. From the data obtained, it could be observed that scratch resistances of the reference silica sol gel and sample F were much higher than those obtained for samples A-E. The general rule of thumb for scratch tests is to take the fluctuations in friction force as indications of film failure at the interface [146-147]. An increase in the P_{cr} implies that a greater minimum load must be applied in order to remove the coating from the substrate on which it is being deposited.

4.4.6 FTIR spectra of cured films

The FTIR spectra of the cured CNT sol-gel films were analyzed for the purpose of attempting to correlate their molecular chemical structures to the mechanical and thermal properties. Pristine CNTs present in sample A are not expected to affect the Si-O-Si bonding in the sol-gel. Figure 4-32(a) shows the spectra of B-E(0.01wt%) and sample F (0.01wt%, 0.02wt% and 0.04wt%) having approximately similar absorption bands as the neat/reference sol-gel film as in Figure 4-3. The presence of the predominant Si-O-Si peak at 1170cm^{-1} is indication that the surfactants or solvents cannot destroy the siloxane structure of the silica xerogel.

Figure 4-32: FTIR spectra of the cured sol-gel CNT film with 0.01wt% of MWCNTs using the dispersion techniques, cured at 100°C at 3 day ageing.

While the intrinsic nature of the sol-gel film may be preserved despite the presence of surfactants and did not show any particularly distinguishable features on the FTIR spectra, the use of surfactants and solvents did lead to a degradation of film properties, particularly with higher weight percentage of CNTs and a larger amount of surfactants/solvent use, the ideal solution would be to use the silane functionalized CNTs as the residual surfactant or solvent is of little consequence in these cases. Figure 4-33 compares FTIR spectra of the neat sol-gel silica to the functionalized CNTs impregnated into the silica matrix.

Figure 4-33: Functionalized sol-gel CNT composites at 0.01wt%, 0.02wt% and 0.04wt% silanized CNT content compared with the neat sol-gel sample.

Figure 4-34 illustrates the silanized CNTs before impregnation (Figure 4-34(a)) and after insertion into the silica matrix (Figure 4-34(b)) of a 0.3mg f-CNT composite. The FTIR results indicate the excellent chemical compatibility of the functionalized tubes in the sol-gel matrix. The peaks associated with the functionalized CNTs were not observed in the composite film is probably the result of coverage by the strong absorbance of the Si-O-Si peak.

Figure 4-34: FTIR spectra of silane functionalized nanotubes (upper) and functionalized CNTs (0.01wt%) in sol-gel silica matrix.

4.4.7 AFM morphology

From Table 4-2, it was observed that the surface morphologies of most of the films were generally smooth with an root mean square surface roughness in the range of 0.362 – 1.340nm except when the surfactant CTAB and NanoAQ were used for the dispersion. The RMS versus the weight percentage of CNTs was plotted in Figure 4-35. From the trends observed, it was deduced that film roughness was independent of the addition of CNTs but showed a greater reliance on the dispersion route used in fabrication.

The RMS of NanoAQ dispersed films showed the highest roughness values in between 3.813 – 7.972nm indicating a poor film thickness uniformity. The CTAB films have rms in the range of 2.489 – 2.545nm which has the lowest surface roughness. CTAB are known to be porous templating agents for low-k materials and so the roughness is in an acceptable range. The roughness is probably caused by the burning out of the CTAB molecules that may create porosity in the silica material resulting in the aggregation of some of the silica matrix when air pores were formed.

AFM images of functionalized CNT sol-gel composites as well as DMF sol-gel composites were also presented as a means of evaluating the surface morphology of the formed materials and compared against those of NanoAQ and CTAB. These were shown in Figure 4-36. The RMS value is an important dimension of measurement especially for nanoindentation and nanoscratch tests as a large RMS would invalidate the results and render the obtained data inaccurate. In this experiments, morphology with less than 10nm RMS would be quite acceptable as limits for nanomechanical tests.

Figure 4-35: The root mean square (RMS) roughness of the samples A-F with comparisons to the sol-gel film.

Figure 4-36: Selected AFM surface morphologies of (a) Sample B(0.04wt%) (b) Sample D(0.01wt%) , (c) Sample F(0.01wt%) and (d) Sample C(0.01wt%). Comparisons of (a) and (b) with (c) and (d) showed a more undulating microstructure with peaks and troughs indicative of a rougher topology.

4.4.8 Thermal characterization (TGA and DSC) of composites

Thermal characterizations of the neat sol-gel and sol-gel CNT composite films were performed to evaluate their degradation behaviour under the influence of heat. TGA and DSC techniques were employed for thermal studies. While the TGA curves provides the identification of the degradation temperatures with the weight loss together with the amount of material degraded, DSC measures the endothermic or exothermic heat of reactions and the heat flows associated with the transitions occurring within the nanocomposite material. The complementary analysis of these two techniques supplement each other to produce accurate assessment of the thermal stability and nature of the sol-gel nanotube composites.

The degradation of pure sol-gel silica and the sol-gel CNT composites are performed in nitrogen environment and the obtained TGA measurements of Sample A were presented in Figure 4-37. The low temperature weight loss between 50°C to 100°C was an indication of solvent evaporation and decomposition of the low molecular weight species. Although curing of the film was performed, the solvent evaporation could be attributed to adsorbed water molecules and residual ethanol [150]. Between 200 to 500°C, the dielectric composite experiences high temperature weight loss due to the degradation of pyrolysis of the organic components such as the residual alkyl and organic species [151].

In the case of samples B-E, the high temperature weight loss was ascribed to the remnant surfactant or solvent species. While the initial weight loss was about 13-15%, the weight loss registered a decrease in only about 4-5% at high temperatures. The rate of weight loss also decreased considerably after solvent evaporation. The TGA plots showed a continuous weight loss and there is no distinct change of further degradation mechanisms with temperature.

This could be attributed to the inorganic silica network of the dielectric that exhibit good thermal stability as well as rigidity that make the dielectric material stronger as compared to organic dielectrics. For the ease of quantification, the neat sol-gel and sol-gel composites with CNTs (no surfactants/solvents) were appended in the Figure 4-37. Similar trends were also observed for samples B-F.

Figure 4-37: Effect of CNTs on the TGA footprint of the sol-gel dielectric composite materials, for sample A.

The results showed that with an increase in weight percentage of CNTs, the thermal stability of the material was not affected as there is no improvement in the degradation temperatures. The onset temperature could not be determined from the TGA curves. There was also no distinction for the maximum rate of degradation (50°C to 100°C) for the different types of sol-gel CNT composites. The main distinguishing factor from the TGA curves above is the difference in final residual content. The weight loss from initial room temperature to 700°C of sample A is tabulated in Table 4-5:

Table 4-5: Residual weight content for sol-gel and sol-gel CNT samples

Sample	CNT type*/ content	Residual content
Silica sol-gel	0 wt %	20%
(sol-gel/CNT)/A	0.01 wt %	18.5%
	0.02 wt %	18.2%
	0.04 wt %	14.0%

The increase in residue was probably due to the higher weight content of CNTs in the sol-gel matrix. Even after oxidation, the CNTs would be converted to carbonaceous material and along with the original sol-gel material could not be further degraded due to the high thermal stability nature of these materials. Such results are in contrast to studies to investigate the effects of CNT wt% variation on polymer composites thermal stability as reported in recent works [152, 153] where the addition of CNTs enhances the thermal stability of the composite as reflected in the shift in the degradation temperatures in the TGA curves.

For DSC studies of the sol-gel CNT composites, no significant trends or relationships were observed as opposed to polymer CNT composites. Figure 4-38 shows an example using Sample A. The broad major exothermic peaks occur at between 90 to 125°C for all of the CNT composite films, a clear indication that CNTs effect on the temperature at which exothermic reaction takes place. The thermal stability of the sol-gel does not improve with addition of CNTs as the silica matrix is itself relatively thermally stable. The variance of the DSC characteristics of the composites depends very much on the solvents/surfactants used to disperse the CNTs which can increase or decrease the peak temperatures at which the heat of reaction takes place.

Figure 4-38: Dynamic DSC thermograms for the exothermic heat of reaction for sample A (0.01, 0.02 and 0.04wt %).

5 CONCLUSIONS AND FUTURE WORK

5.1 Conclusions and Findings

In order to improve the reliability of *Cu*/low-*k* interconnect structure an alternative low-*k* material is proposed. Essentially, carbon nanotubes (CNTs) were reinforced in the sol-gel silica dielectric matrix by (i) physical dispersion and (ii) chemical functionalization of CNTs. The neat silica xerogel used as the matrix material was synthesized using a two step acid base catalyst procedure and examined using FTIR, XRD and AFM in order to determine the chemical and structural qualities of the spin-coated film. Then using commercially available surfactants such as DFM, CTAB, NanoAQ, PVP-4 etc CNT were dispersed in the sol-gel silica and cured. Finally, in chemical dispersion of the fillers, silane coupling agent (3-Aminopropyl)tris(trimethyl siloxy) silane is used to chemically alter the surface structure of CNTs. FTIR, Raman, XPS, TGA and FESEM micrographs were used to identify and affirm the functionalized moieties and confirm the presence of covalently bonded silane functional groups onto the CNTs.

The sol-gel nanotube composite films formed by the two routes were investigated for their physical, mechanical, chemical and thermal behaviour to evaluate their suitability and reliability for process integration into the packaging environment. The major findings of the project are summarized below:

- Nanomechanical properties (such as modulus, hardness and film peel-off load) of CNT reinforced sol-gel silica composite thin films were measured by nanoindentation and nanoscratch tests. The results showed that CNTs treated and dispersed using PVP-4 surfactant showed better modulus and hardness properties

when compared to the silica matrix properties, while NanoAQ dispersed sol-gel films showed the worst mechanical behaviour for composites prepared in physical dispersion. Surprisingly, when the CNTs reinforcement was increased from 0.01 wt% to 0.04 wt%, the properties again degraded due to poor CNTs-silica matrix interaction and ineffective dispersion of CNTs in the sol-gel silica.

- Nanoscratch tests results revealed that silica composites obtained through physical dispersion of CNTs had inferior adhesion strength to the substrates as compared to the neat silica sol-gel sample. This is probably due to the strong sol-gel chemical nature and compatibility to the substrate. The presence of CNTs, although could improve indentation properties offered a lesser degree of scratch resistance as the CNTs may well have contributed to the disruption of the three dimensional silica network.
- The silica composites with functionalized CNT fillers had shown excellent nanomechanical properties for at all three weight fractions (ie 0.01, 0.02 and 0.04 wt%). This is made possible as a result of the covalent linkage of the functionalized tubes that form strong chemical covalent bonds that resist the scratch force applied (i.e. increase scratch resistance).
- The physical roughness of the films formed were generally well below 3nm, indicating their smoothness and planarity, except for Sample B (which used NanoAQ dispersing agent) with RMS value in between 6-7nm. This roughness was determined with FESEM which reveal voids and numerous peaks and troughs in the scanned area showing extremely rough nature of the film.

- FTIR spectra of the formed films were also analyzed to determine the chemical nature of the films fabricated. The routes (i) and (ii) of ensuring the homogeneity of the dispersions did not appear to interfere with the sol-gel Si-O networks as predominant peaks of Si-O-Si absorbance were recorded on the FTIR system.
- Thermal analysis of the CNT reinforced sol-gel composites were also examined after curing them at 100°C. The results show that the siloxane chemistry afforded great thermal stability to the silica network and no improvement in degradation properties were observed on the dynamic temperature TGA thermogram curves. Similarly, the exothermic peaks obtained using DSC did not indicate any clear trends or shifts to higher temperature with addition of CNTs. It was noted that the exothermic peaks for composites were larger as compared to the neat sol-gel but still hovered about the range of 80-100 °C.
- The results showed that film reliability should be justified by the analysis with different characterization techniques. This would allow a comprehensive knowledge to enable and determine selection of the appropriate film to act as a reinforcement layer. In the context of this work, Sample F(0.04wt%) showed the best improvement in mechanical properties as well as an unrivalled chemical compatibility to the matrix network and is proposed for use in the design of the interconnect structure which has been patented. (See appendix).

5.2 Recommendations for Future work

The work in this report focused on designing a interconnect structure as a protection mechanism for the underlying weak dielectrics and metal lines thin film stacked structures. CNTs were used by physical dispersion and as well as chemical surface modification by a technique developed in this work. While the mechanical reliability, chemical and thermal stability of the films were investigated, additional recommendations for research should be performed before integration of the structure into the BEOL. Two important areas for further investigations concern the electrical and thermal properties of the sol-gel dielectric.

The electrical properties of the CNT/sol-gel should be investigated to reveal the role of CNTs in electron conduction and its effects on the C - V (Capacitance-Voltage) properties of the composites particularly the dielectric constant of the sol-gel material. As CNTs offer good thermal conductivity over the dielectric materials, it should act as heat sinks to draw the heat away from the dielectric materials and thus prevent the onset of joule heating which is a prevalent problem for many low- k materials. In addition, the modeling of the interconnect structure with the CNT/dielectric will be done to achieve the correlation with the experimental results and provide the application in backend packaging.

An alternative solution could also be proposed to the current structure by growing horizontal CNTs on the surface of the dielectric so that dispersion of CNTs is not needed, eliminating the problem of residual surfactants/solvents or difficult functionalization but an industrially compatible process of growing the CNTs such as CVD method.

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PATENT

7 APPENDIX

INTEGRATED CIRCUIT AND METHOD FOR ENHANCING METAL/LOW-K DIELECTRIC INTERCONNECT RELIABILITY USING CARBON NANOTUBES

Inventors:

Tong Yan Tee
Blk. 408, Hougang Ave 10, #07-1082
Singapore 530408
Citizen of Malaysia

Xueren Zhang
#09-41, Block 266, Toh Guan Road
Singapore 600266
Citizen of China

Shanzhong Wang
Blk. 345, #14-99, Kang Ching Road
Singapore 610345
Citizen of China

Valeriy Nosik
Blk. 806, #13-16, Thomson Road
Singapore 298189
Citizen of the Russian Federation

William A. Munck
Davis Munck Butrus, P.C.
Three Galleria Tower
13155 Noel Road, Suite 900
Dallas, Texas 75240
(972) 628-3600

Jijie Zhou
98 Nanyang Crescent, #04-01
Singapore 637665
Citizen of China

Sridhar Idapalapati
57A, Nanyang Terrace
NTU Campus
Singapore 639734
Citizen of India

Subodh Mhaisalkar
9 Sin Ming Walk
#18-01 The Gardens
Singapore 575578
Citizen of Singapore

Zhi Yuan Shane Loo
66 Jalan Lembah Thomson
Singapore 577534
Citizen of Singapore

DOCKET NO. 06-SIN-010 (STMI01-06010)

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**INTEGRATED CIRCUIT AND METHOD FOR ENHANCING METAL/LOW-K
DIELECTRIC INTERCONNECT RELIABILITY USING CARBON NANOTUBES**

TECHNICAL FIELD

[0001] This disclosure is generally directed to integrated circuits and more specifically to an integrated circuit and method for enhancing metal/low-K dielectric interconnect reliability using carbon nanotubes.

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BACKGROUND

[0002] Many integrated circuits today include interconnect structures formed from metal and dielectric material. For example, conventional interconnect structures were often formed using aluminum and silicon dioxide. However, integrated circuits are being continuously scaled so that they are smaller and smaller (such as device scaling from the 90nm node to the 65nm node), and conventional interconnect structures often suffer from electrical resistance and parasitic wiring capacitance. These problems are major factors that limit the speed of high performance integrated circuits.

[0003] Because of these problems, integrated circuit manufacturers have begun moving away from using aluminum and silicon dioxide in interconnect structures. Some manufacturers have started using a "Copper Damascene" process, where copper and low-K dielectric material are used to form an interconnect structure. The copper helps to lower the resistance of the interconnects and increase their reliability, while the low-K dielectric material helps to reduce the parasitic capacitance of the interconnects.

[0004] A problem with these types of interconnects is

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that the interconnects often experience strain or stress when the integrated circuits undergo further processing. For example, the interconnects may experience compressive force during a subsequent ball bond process or shear stress during bumping in a flip chip process. These strains or stresses could cause damage or destruction of the interconnects, such as by causing the dielectric material to collapse or by causing interfacial delamination of the copper and the dielectric material.

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SUMMARY

[0005] This disclosure provides an integrated circuit and method for enhancing metal/low-K dielectric interconnect reliability using carbon nanotubes.

[0006] In one aspect, an interconnect structure, integrated circuit, and method are provided. In general, an interconnect structure includes a metal, low-K dielectric material, and a protection layer. The protection layer includes vertically aligned carbon nanotubes. The carbon nanotubes help to reduce or prevent damage to the interconnect structure, such as by reducing or preventing collapse of the low-K dielectric material or delamination of the metal and the low-K dielectric material.

[0007] Other technical features may be readily apparent to one skilled in the art from the following figures, descriptions, and claims.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0008] For a more complete understanding of this disclosure, reference is now made to the following description, taken in conjunction with the accompanying drawing, in which:

[0009] FIGURE 1 illustrates a conventional interconnect structure;

[0010] FIGURE 2 illustrates an example interconnect structure according to one embodiment of this disclosure;

[0011] FIGURE 3 illustrates carbon nanotubes having different alignments according to one embodiment of this disclosure;

[0012] FIGURE 4 illustrates an example relationship between protection layer strength and protection layer composition according to one embodiment of this disclosure;

[0013] FIGURE 5 illustrates an example Four-Point Bend test structure according to one embodiment of this disclosure;

[0014] FIGURE 6 illustrates example results obtained using the Four-Point Bend test structure according to one embodiment of this disclosure; and

[0015] FIGURE 7 illustrates an example modeling of a

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flip chip ball grid array (FCBGA) to quantify a cohesive crack phenomenon according to one embodiment of this disclosure.

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DETAILED DESCRIPTION

[0016] FIGURE 1 illustrates a conventional interconnect structure 100. In this example, the conventional interconnect structure 100 includes a metal 102, such as a layer of copper. One or more low-K dielectric materials 104-106 are disposed above and below the metal 102. The one or more low-K dielectric materials 104-106 could include any suitable number or type of dielectric material, including one or more silicon oxycarbides, organic polymers, or fluorosilicate glass. A silicon nitride layer 108 is disposed over the metal 102 and the low-K dielectric material 106.

[0017] Damage to the conventional interconnect structure 100 may be caused by compressive forces, shear stresses, or other strains or stresses. The damage could include collapse of the low-K dielectric materials 104-106 or interfacial delamination between the metal 102 and either or both of the low-K dielectric materials 104-106. Interfacial delamination may be caused, for example, by a weak adhesion strength at the metal/dielectric interface.

[0018] FIGURE 2 illustrates an example interconnect structure 200 according to one embodiment of this disclosure. The embodiment of the interconnect structure

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200 shown in FIGURE 2 is for illustration only. Other embodiments of the interconnect structure 200 could be used without departing from the scope of this disclosure.

[0019] In this example, the interconnect structure 200 includes a metal 202 (such as copper) and one or more low-K dielectric materials 204-206 (such as silicon oxycarbides, organic polymers, or fluorosilicate glass). A silicon nitride layer 208 is disposed over the metal 202 and the low-K dielectric material 206.

[0020] In addition, a protection layer 210 is disposed over the silicon nitride layer 208. The protection layer 210 includes one or more dielectric materials 212. The protection layer 210 also includes vertically aligned carbon nanotubes 214. Carbon nanotubes may represent cylindrical carbon molecules with novel properties that make them potentially useful in a wide variety of applications (such as nano-electronics, optics, and materials applications). Carbon nanotubes often exhibit extraordinary strength and unique electrical properties and are often efficient conductors of heat. For example, carbon nanotubes may have a high Young's modulus (1 TPa) and high tensile strength (100 GPa). FIGURE 3 illustrates scanning electron microscope images of example carbon

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nanotubes. In particular, image 302 in FIGURE 3 illustrates vertically aligned carbon nanotubes, while image 304 in FIGURE 3 illustrates non-aligned carbon nanotubes.

[0021] The vertically aligned carbon nanotubes 214 may have any suitable pattern in the protection layer 210. For example, in some embodiments, the vertically aligned carbon nanotubes 214 are arranged in a honeycomb pattern in the protection layer 210. In the illustrated embodiment, the carbon nanotubes 214 are used to improve the mechanical properties of the interconnect structure 200. As an example, the carbon nanotubes 214 could be positioned to act as cushions or nano-springs, where their high modulus and stiffness are able to absorb impact, shear stresses, or other strains or stresses caused to the interconnect structure 200.

[0022] Among other things, the use of the protection layer 210 may help to address concerns regarding the adhesion and mechanical reliability of metal/low-K dielectric interconnect structures, such as the interconnect structure 200 of FIGURE 2. For example, the protection layer 210 may help to shield the interconnect structure 200 from compressive forces that are imposed

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onto the interconnect structure 200. The protection layer 210 may also help to reduce accumulated strain or stress at the interfaces between the metal 202 and the dielectric materials 204-206. This allows the protection layer 210 to reduce or eliminate collapse of the low-K dielectric materials 204-206 and interfacial delamination of the metal 202 and either or both of the dielectric materials 204-206. Also, the high Young's modulus of the carbon nanotubes 214 may help to strength the protection layer 210 and pin the top interface, reducing strain of the metal-dielectric interface. In particular embodiments, as shown in FIGURE 4, the strength of the protection layer 210 may be roughly proportional to the percentage of the protection layer 210 formed from the carbon nanotubes 214.

[0023] The interconnect structure 200 shown in FIGURE 2 could be incorporated into or used in any suitable integrated circuit. Also, an integrated circuit could include any number of interconnect structures 200. In addition, the interconnect structure 200 could be used for any suitable purpose in an integrated circuit.

[0024] Various techniques could be used to fabricate the interconnect structure 200 of FIGURE 2. For example, a catalyst could be deposited on the silicon nitride layer

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208, and carbon nanotubes 214 could be grown on the silicon nitride layer 208. In particular embodiments, the carbon nanotubes 214 have a spacing of 100nm or less. After that, one or more dielectric materials 212 may be deposited in the spaces between the carbon nanotubes 214 to form the protection layer 210. Any other suitable technique could be used to form the interconnect structure 200 of FIGURE 2.

[0025] Although FIGURE 2 illustrates one example of an interconnect structure 200, various changes may be made to FIGURE 2. For example, materials other than copper and silicon nitride could be used in the interconnect structure 200. Also, the particular sizes and shapes of the various components in the interconnect structure 200 are for illustration only. The components in the interconnect structure 200 could have any other suitable size or shape.

[0026] Interfacial adhesion energy of the copper and low-K dielectric interfaces (reinforced by the protection layer 210) may be studied using a Four-Point Bend test structure (shown in FIGURE 5) or using nano-scratch/nano-indentation tests. Example results using the Four-Point Bend test structure are shown in FIGURE 6. In addition, a

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finite element method may be used to model the interconnect structure 200. FIGURE 7 illustrates the modeling of a flip chip ball grid array (FCBGA) to quantify a cohesive crack phenomenon, allowing the effective strain contours to be compared. Sites #2 and #3 (the two sites located underneath the bump corners) may be the most critical ones. Moreover, with the considered patterning, these results highlight that the most strained layers may be located at the extreme inter-metal dielectric (IMD) layers (IMD1 and IMD4). As a result, the most likely areas for a cohesive crack initiation may be found to be the top and bottom low-k dielectric layers just below the two bump corners. The use of the interconnect structure 200 may help to avoid these types of cohesive cracks.

[0027] The interconnect structure 200 has good mechanical reliability with low-K dielectric materials due to the carbon nanotubes 214 providing reinforcements in the protection layer 210. Based on the effects of carbon nanotube material composition, process parameters, and testing conditions on interfacial material reliability, different design guidelines can be used to optimize the interfacial material reliability by varying the structure

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and properties of the carbon nanotubes 214.

[0028] It may be advantageous to set forth definitions of certain words and phrases used throughout this patent document. The terms "include" and "comprise," as well as derivatives thereof, mean inclusion without limitation. The term "or" is inclusive, meaning and/or. The phrases "associated with" and "associated therewith," as well as derivatives thereof, may mean to include, be included within, interconnect with, contain, be contained within, connect to or with, couple to or with, be communicable with, cooperate with, interleave, juxtapose, be proximate to, be bound to or with, have, have a property of, or the like.

[0029] While this disclosure has described certain embodiments and generally associated methods, alterations and permutations of these embodiments and methods will be apparent to those skilled in the art. Accordingly, the above description of example embodiments does not define or constrain this disclosure. Other changes, substitutions, and alterations are also possible without departing from the spirit and scope of this disclosure, as defined by the following claims.

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WHAT IS CLAIMED IS:

1. An interconnect structure incorporating every feature shown and described.
2. An integrated circuit incorporating every feature shown and described.
3. A method incorporating every feature shown and described.

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**INTEGRATED CIRCUIT AND METHOD FOR ENHANCING METAL/LOW-K
DIELECTRIC INTERCONNECT RELIABILITY USING CARBON NANOTUBES**

ABSTRACT OF THE DISCLOSURE

In one aspect, an interconnect structure, integrated circuit, and method for enhancing metal/low-K dielectric interconnect reliability using carbon nanotubes are provided.

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FIGURE 1 100

FIGURE 2 200

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