Decontamination of Surfaces Exposed to Carbon-based Nanotubes and Nanomaterials

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Abstract

Contamination of surfaces by nanomaterials can happen due to accidental spillage and release or gradual accumulation during processing or handling. Considering the increasingly wide use of nanomaterials in industry and research labs and also taking into account the diversity of physical and chemical properties of different nanomaterials (such as solubility, aggregation/agglomeration, and surface reactivity), there is a pressing need to define reliable nanomaterial-specific decontamination guidelines. In this project, we propose and investigate a potential method for surface decontamination of carbon-based nanomaterials using solvent cleaning and wipes. The results show that the surfactant-assisted removal efficiencies of multi-walled carbon nanotubes, single walled carbon nanotubes and single walled carbon nano-horns from silicon wafers through wiping is greater than 95%, 90% and 78%, respectively. The need for further studies to understand the mechanisms of nanomaterial removal from surfaces and development of standard techniques for surface decontamination of nanomaterials is highlighted.

Another phase of experiments were performed to examine the efficiency of surfactants to remove multi-walled carbon nanotubes (MWCNTs) from silicon substrates with nano and microscaled features. In the first set of experiments, nanoscale features were induced on silicon wafers using SF$_6$ and O$_2$ plasma. Atomic force microscopy (AFM) was used to observe the surface topology and roughness. In the second set, well-defined microscale topological features were induced on silicon wafers using photo lithography and plasma etching. The etching time was varied to create semi-ellipsoidal pits with average diameter and height of ~ 7-9 µm, and ~ 1-3 µm, respectively. MWCNTs in the form of liquid solution were deposited on the surface of silicon wafers using the spin coating process. For the cleaning process, the contaminated surfaces were first sprayed with different types of surfactant or water. Then, the MWCNTs were wiped off using a simple wiping mechanism. The areal density of the MWCNTs was quantified prior to and after the removal
using scanning electron microscopy (SEM) and post-image processing. For a surface featured with nanoscale asperities, the removal efficiency was measured to be in the range 83-99% based on substrate type and surface roughness. No evident relationship was observed between the etching time and the removal efficiency. For microscale features, increase of the etching time significantly decreases the removal efficiency.

Keywords: carbon nano tubes(CNTs), multi walled carbon annao tubes (MWNT), single walled carbon nano tubes (SWNT), single walled carbon nano horns (SWNH), decontamination, removal efficiency, wipe, silicon wafer, micro scale feature, surfactant, Scanning electron microscope (SEM)
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Chapter 1

Introduction
1. Introduction

Since discovery of carbon nanotubes (CNTs) in 1991, they have attracted considerable attention due to their unique properties that include high stiffness, tensile strength, high Young’s modulus, exceptional electrical conductivity and excellent field emission [1-8]. The extremely small size and highly symmetrical structure of CNTs have allowed for remarkable quantum, magnetic and electronic effects that are still being translated into exciting applications in the semiconductor industry [9-11]. However, concerns have been raised due to their high reactivity, large surface area and needle like structure [12, 13] for health issues. CNTs are considered to be carcinogenic and cause malignancy in the human mesothelial cells [14]. Their geometrical structure has been compared and shown to possess similar properties to asbestos fiber [12]. It is estimated that nanotechnology will incorporate 15% of global manufacturing, totaling about $2.6 trillion by 2014 [15]. This ever increasing production of CNTs and potential health hazards due to their unwanted release into the work space have stimulated a demand for developing removal techniques for CNTs from contaminated surfaces.

In case of an accidental spillage or release of CNTs, the main challenge in the removal process would be to overcome the adhesion, which is often treated as the molecular coupling between two contiguous bodies; here CNTs and the surface [16]. More specifically, as the particle size shrinks to microscale, the surface forces such as adhesion and friction become increasingly critical and dominate over inertial and gravitational forces [17]. Due to the high surface contact area of CNTs, their removal is difficult without application of an external force [18-20]. Several researchers have conducted adhesion related studies involving carbon nanotubes and different substrates [21-23]. The microwave treatment of Ni/Ti/Au/SiO$_2$/Si surfaces have proven to have enhanced their adhesion to carbon nanotubes [24]. Adhesion of MWCNTs to
silicon oxide surfaces has been compared with the gecko’s ability to climb vertically [22]. Whittaker et al. have calculated the vertical force of adhesion by using an Atomic Force Microscope (AFM) tip to slide a CNT into a carefully fabricated trench on a silicon dioxide substrate [21]. Buehler et al. showed that a long CNT can self-fold due to strong adhesion on the surface of a substrate [25]. Adhesion of atmospheric dust is determined by contact conditions between the dust particle and the surface as these particles adhere due to gravitational force and hold on to the surface of the substrate by adhesion [26].

The conventional approach for removal of residues from contaminated surfaces, generally known as solvent cleaning method, involves dispersion of contaminants in a cleaning medium and then removal of the cleaning medium with considerably less effort and higher efficiency due to the weaker bonds between solid and liquid phases. Two general approaches are used to disperse carbon nanotubes in various solvents: mechanical methods that involve either sonication (ultrasonic cleaning) or high shear mixing to mechanically disperse the CNTs [27], and physical or chemical methods that alter the surface energy of CNTs [28, 29]. In general, mechanical methods are not feasible for the purpose of decontamination since they have proven to be time-consuming and less efficient [27]. Furthermore, such energetic methods may lead to the wider spread of contamination [30, 31]. Chemical methods, also referred to as covalent treatment methods, involve using surface functionalization of carbon nanotubes at elevated temperatures and pressures to improve their solubility in solvent [32], making them unsuitable for in-situ decontamination of the work space. Physical methods, which also are referred to as non-covalent treatment methods, use surfactants, solvents or polymers to disperse CNTs. These methods are widely used to disperse nanotubes since they absorb various groups of carbon nanotubes without altering the $\pi$-system of grapheme [28, 29]. A variety of surfactants has been
examined for this purpose such as octylphenol ethoxylate (Triton X-100) [33],
dodecyltrimethylammonium bromide (DTAB) [34], sodium dodecylbenzenesulfonate (SDBS)
[35] and sodium dodecylsulfate (SDS) [36]. These agents weaken the physical bond between
surfaces and attached particles by reducing the surface tension and suppress particle re-adhesion
by creating a repulsive zone by their amphiphilic (polar) mechanism [37]. It has been proposed
that CNTs-surfactant complexes form spherical micelles in which CNTs form the core and
surfactant molecules extend radially from the core [38-40]. Another morphology proposes that
surfactant hemi-micellar aggregates cover carbon nanotubes [35, 41]. Angle of contact, chirality,
diameter of CNTs and concentration of SDS surfactant are important factors affecting CNT-
surfactant adsorption [40, 42].

In this project, the removal of multi-walled carbon nanotubes (MWCNTs) from
contaminated silicon wafers was carried out using sodium dodecylsulfate (SDS), sodium
dodecylbenzenesulfonate (SDBS), Gum Arabic and calcium carbonate (CaCO₃). Silicon wafers
were spin coated with MWCNTs. Scanning electron microscope (SEM) imaging and subsequent
image processing were performed to estimate an average areal density prior and after cleaning.
For cleaning, a fibrous material was soaked with each of the aforementioned chemicals and
wiped across the surface. Moreover this experiment is done for single walled carbon nanotubes
(SWNT) and single walled carbon nanohorn (SWNH) with using surfactant and water. Also,
another Experiments were performed to examine the efficiency of surfactants to remove multi-
wa lled carbon nanotubes (MWCNTs) from silicon substrates with nano and microscaled
features.
Chapter 2

Chemical cleaning
2. Chemical cleaning (or solvent cleaning)

2.1. Introduction

Chemical cleaning (or solvent cleaning) is used conventionally for the removal of residues, contaminants, or soils deposited on or attached to a substrate surface. The basic concept of chemical cleaning is to dissolve or suspend the contaminants and to eliminate them by the removal of the cleaning media. Studies on the solubility of nanomaterials have shown that many engineered NMs have minimal solubility and dispersibility in water or many common solvents [43-46]. For example, CNTs are shown to be neither soluble nor wettable by water or many other solvents, making them hard to be physically dispersed which in addition to cleaning is critical for obtaining individual CNTs for research and other applications [47-49]. Therefore, various surfactants [36, 43, 47, 50-53], solvents [54-59] and polymers [60-62], as well as DNA [63-65] have been explored to non-covalently dissolve and disperse CNTs into a liquid phase. Figure 1 summarizes the solubility of single-walled CNT in various solvents as reported in the literature. In general, surfactants (short for surface active agents) are more effective for dissolving higher quantities of single-walled and multi-walled CNTs in water compared to most available solvents. The use of surfactants for the cleaning process is particularly of high interest for a number of reasons; water is a safe and convenient substance, and surfactants are cheap, commercially available and easy to use. The highest solubility is currently reported for an aqueous solution of gum Arabic (15% wt), where 3% wt. (~30 mg/mL) solubility was obtained using sonication at 50 W and 43 kHz for a relatively short duration of 15-20 minutes [62]. We have also explored the available data on solubility of other common carbon-based NMs. In Figure 2, we have summarized the available results on the solubility of C\textsubscript{60} fullerene in different solvents. Motivations for studying the solubility of fullerenes in solvents include exploring chemical reactions pathways for fullerene, their purification methods, and extracting higher fullerenes [44, 66-78]. Also, the aqueous solubility of fullerenes with use of surfactants has been investigated for potential biological applications and the results are included in Fig. 2 [79-83]. The
differences in the reported solubility of fullerenes in a specific solvent in different studies can be attributed to the effects of temperature, illumination or sonication during the solving process. Extraordinary temperature dependence is observed in the solubility of fullerene C₆₀ in some solvents, reaching its maximum magnitude near 280 K and decreasing remarkably by increasing the temperature above this value [74, 84, 85]. In addition, there are studies investigating the solubility of higher order fullerenes [67, 68, 70, 73-75] or combinations of different order fullerenes [70] in various solvents. Studies performed on the solubility of fullerenes in aqueous media suggest that the solubility rates of fullerene in water-surfactants are several orders of magnitude less than the solubility rates obtained by successful solvents.

Since CNTs are one of the most common carbon-based NMs, we have discussed the efficiency of different solvents for dissolving CNTs in the following sections in more details:

2.2. Surfactants as the cleaning media

Surfactants can weaken the strong bond between particles and substrate by reduction of the surface tension, prevention of particle re-adhesion by creating a repulsive zone between the particles and substrate, and suspension of the particles in the solution by their amphiphilic mechanism [86]. When surfactants are available in adequate concentrations in the solution, they get adsorbed on the surface of CNTs, forming cylindrical micelles or hemimicelles which make CNTs soluble in water [87]. It is necessary that the amount of surfactant dissolved in the aqueous media be far exceeding the surfactant critical micelle concentration to ensure that enough surfactant molecules can be absorbed onto the surface of the nanotubes to make them suspended and dissolved in the water. For example, Sun et al. [53] obtained the optimum concentration of some surfactants for suspending CNTs as equal to 10 mg/mL. However, critical micelle concentrations for these surfactants from the literature are far less than 10 mg/mL [53]. In the use of surfactants as the cleaning media combined use of surfactants and mechanical removal might be necessary to fully overcome the adherence of NMs to substrates [86, 88].
Islam et al. [47] investigated the solubility of single-walled CNTs in water with different anionic, cationic, and nonionic surfactants by using a long-duration (16-24 hr) sonication procedure. They showed that the anionic surfactants sodium dodecylbenzene sulfonate (NaDDBS), and a close chemical relative sodium 4-n-octylbenzene sulfonate (NaOBS) had high solubility of single-walled carbon nanotubes, with the solubility of up to 20 mg/mL and 8 mg/mL of CNTs, respectively. Using a different solubilization technique, Moore et al. [52] reported the relatively high ability of NaDDBS, and a close relative sodium dodecylsulfonate (SDSA), and sodium dodecyl sulfate (SDS) to individually suspend nanotubes in water [89]. However, of much interest for the purposes of cleaning, they showed that the difunctional block copolymer nonionic surfactants with high molecular weight have high suspendibility (19.2 – 28.2 mg/mL) but relatively lower individual dispersion quality compared to other surfactants. They concluded that the high dispersion rate of copolymers such as Pluronic F 98 and PEO-PBO-PEO triblock copolymer (EBE) is related to the enhanced steric stabilization by long polymeric groups. The solubility of multi-walled carbon nanotubes in SDS was studied by Yu, et al [41]. They reported 1.4 wt% (14 mg/mL) as the maximum concentration of multi-walled CNTs that can be homogenously dispersed in the aqueous solution. It is noteworthy that the reported quantities for a single surfactant in different studies might be significantly different due to various factors related to the amount of surfactant used, test temperature, mechanical forcing and CNT type and manufacturing method.

2.3. Polymers as the cleaning media

Polymers appear as promising options for solving CNTs in aqueous media in high concentrations with relatively low agitation [52, 60-62]. O’Connell et al. [61] studied the solution of SWNTs in water by non-covalently associating them with linear polymers such as polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS). They suggested that the high concentration solution of CNTs (2% wt., ~ 20 mg/mL) can be obtained by the robust association/wrapping of polymer layers to the nanotubes.
2.4. Solvents as the cleaning media

The use of solvents as cleaning agents to remove nanomaterials is questionable for a number of reasons. First, many of the proposed solvents to disperse nanotubes have some level of toxicity. Second, the solubility/dispersibility of many of the proposed solvents is below 0.1 mg/mL, far less than the solubility of surfactants. Parra-Vasquez et al. [58] investigated the solubility of SWNTs obtained by different methods of production in superacids (e.g., fuming sulfuric and chlorosulfonic acids) and showed that high concentrations (> 100 mg/mL) of SWNTs are spontaneously dispersed in acids within minutes. However, the use of acids as the cleaning media in the cleanup process does not seem reasonable because of the hazards in handling and usage and removal of acids and also the potential damage to the substrate.

![Diagram](image)

**Fig. 1.** High concentration surfactant, polymer, and solvent based suspensions of SWCNT as reported in the literature [36, 47, 52-58].
Fig. 2. Solubility of $C_{60}$ in the most effective $C_{60}$ solvents at 298° K, as reported in the literature [44, 66, 76-78, 85, 90]
Chapter 3

Removal Efficiency of CNT Chemical Cleaning
3. Methodology of experiments and Removal efficiency of different types of CNTs

3.1. Multi walled carbon nanotubes

In this section, experimental investigations were performed to assess the removal efficiencies of CNTs deposited on the surface of silicon wafers using different cleaning media. The CNTs used for this study were combustion chemical vapor deposition (CCVD) grown, acid purified carbon nanotubes dispersed in Polyvinylpyrrolidone (PVP) surfactant. The average length and diameter of the MWCNTs used in this study were measured 250 nm and 15 nm, respectively. The averaged length and diameter of SWCNTs were 200 nm and 1.2 nm, respectively. In the experiments, carbon nanotubes in the form of pristine liquid solution were deposited on surface of silicon wafers (orientation, Nitrogen/Phosphorus doped, P/E surface, and with mechanical grading) using the spin coating process. The wafers were 3” in diameter and the spin coating was performed for 1 min at 3000 RPM. After spin coating, the CNT deposited wafers were heated at 105 °C for 90 sec in order to dry the wafer surface completely. A total number of 30 images with equal magnification and resolution were taken from different spots of each wafer surface using scanning electron microscope (SEM) imaging. The CNT surface aerial concentration for each image was then determined using an image processing program incorporated in MATLAB© software. Average CNT aerial density from 30 different images of each wafer was obtained and used in the analysis. The average aerial density of the wafers, denoted by AD was approximately 34% for SWCNTs and 36% for MWCNTs after the spin coating.

First, we have assessed the multi-walled CNT removal efficiency of two surfactants (i.e. SDBS (sodium dodecylbenzene sulfonate) and SDS (Sodium dodecyl sulfate)), one polymer (gum Arabic), one mineral salt (Calcium Chloride), and pure water in a simple wipe cleaning method. The concentrations of SDBS, SDS, CaCl₂, gum Arabic (GA) were 1.5%, 4%, 11% and 10% wt, respectively. The mineral salt Calcium Chloride was specifically chosen since it was shown to be capable of transforming dispersed
CNT in aqueous environment into aggregates [91]. The CNT-coated wafers were first treated by different cleaning media and then cleaned with a piece of non-woven polyester/cellulose fabric. In the experiments, first the cleaning media was sprayed on the surface of the wafer. After 2 minutes, the wafer was manually wiped once and unidirectionally. The estimated hand pressure and wiping duration were 2 kPa and 5 sec, respectively. The wafer was dried using Nitrogen gas after the cleaning. After cleaning, the wafers were imaged using SEM and the average final area density for each wafer was obtained by post processing the images as explained above. The removal efficiency was defined as the difference between the initial and the final average CNT aerial densities. Figure 5A shows the quantitative comparison of MWNT surface removal efficiency by different cleaning media used in this study. Figure 5B shows the SEM images of MWCNT-coated wafer surfaces before and after cleaning using different cleaning media. The two surfactants used in the experiments, SDS and SDBS, showed the highest MWCNT removal rates among all the solvent cleaning media with the removal efficiencies greater than 95%. The high removal efficiencies in using the surfactant as the cleaning media can be attributed to the role of surfactant micelles on suspending the CNTs in aqueous media and increasing the soaking ability of water by decreasing the water surface tension. Pure water has the removal efficiency of almost 65% on the silicon wafer substrate. Gum Arabic and CaCl$_2$ have comparable removal efficiency of approximately 76% and 80%, respectively, standing between the removal efficiencies of pure water and surfactants solutions.

3.2. single-walled carbon nanotubes

As the next step, we measured the single-walled CNT removal efficiency of two surfactants (i.e. SDBS (sodium dodecylbenzene sulfonate) and SDS (Sodium dodecyl sulfate)), and pure water in the same wipe cleaning method. The two surfactants were chosen since they showed the highest efficiencies for the removal of MWCNTs from the surface of silicon wafer in the last section. The same deposition and wiping methods were used. In figure 6A a quantitative comparison of SWNT surface removal efficiency by different cleaning media is given. The two surfactants showed high SWCNT removal
capability with efficiencies greater than 90%. Wiping after pure water spray resulted in a removal efficiency of approximately 61%. Figure 6B shows sample SEM images of SWCNT-coated wafer surfaces before and after cleaning.

### 3.3. Single walled carbon nano-horns

#### 3.3.1 Introduction:

In previous experiments some types of CNTs such as MWNTs and SWNTs were studied. In this new phase of experiments, the removal efficiency for Carbon nano horn are studied. Single-walled carbon nanohorn (SWNH), was seen in 1999 for first time. These SWNHs with about 40–50 nm in tubule length and about 2–3 nm in diameter are derived from SWNTs and ended by a five-pentagon conical cap with a cone opening angle of ~19. [92]

![Fig.3.](A) TEM images of carbon nanohorns. (B) The insert shows a schematic diagram of a typical hornlike outer part of CNHs.[93]

There is wide range of possible applications for SWNHs such as energy management system, medical, gas absorption and compound material.

SWNHs show high dispersion in ethanol. It keeps more than 2 weeks. [94]
Fig. 4. Carbon Nano-horns are dispersed in ethanol, it is sonicated for 15 minutes by a conventional ultrasonic ethanol.

3.3.2. Methodology

At the first step, 8 silicon wafers with 3” diameter were spin coated for 1 min at 3000 RPM. After spin coating, deposited wafers were heated at 105 °C for 90 sec in order to dry the wafer surface completely. A total number of 30 images were taken from different spots of each wafer surface using scanning electron microscope (SEM) imaging. The SWNHs surface aerial concentration for each image was then determined using an image processing program incorporated in MATLAB© software. As it is shown in figure 7, the two surfactants used in the experiments, SDS and SDBS, showed the highest SWNH removal rates among the other solvent cleaning media. The high removal efficiencies in using the surfactant as the cleaning media can be attributed to the role of surfactant micelles on suspending the CNTs in aqueous media and increasing the soaking ability of water by decreasing the water surface tension. Pure water has the removal efficiency of almost 43% on the silicon wafer substrate. Ethanol has removal efficiency of approximately 59%.
3.4. Results

The removal efficiency of SWNHs from silicon surface is less than MWNTs and SWNTs for all solvents. The results show that the removal efficiencies for single- and multi-walled carbon nanotubes from silicon wafers sprayed with water-surfactant solutions prior to mechanical wiping is greater than 90% and 95%, respectively. SWNHs show about 87% removal efficiency for SDS and 77% for SDBS, respectively.

Fig. 5. (A) MWCNT removal efficiency of SDS, SDBS, CaCl₂, gum Arabic (GA), water, and dry wiping as discussed in section 4. (B) Sample SEM image of the surface of Multi-walled carbon nanotubes deposited silicon wafers before cleaning (AD = 36%), and after wipe cleaning with pure water (AD = 12.5%), gum Arabic (AD = 8.5%) and SDBS surfactant (AD = 1.5%). The average pre-cleaning areal density was approximately 34% for all samples.
Fig. 6. (A) SWCNT removal efficiency of SDS, SDBS and water as discussed in section 4. (B) Sample SEM image of the surface of SWNTs deposited silicon wafers before cleaning (AD=38%), and after wipe cleaning with pure water (AD=14.7%), SDBS (AD=3.2%) and SDS surfactant (AD=2.1%). The average pre-cleaning areal density was approximately 36% for all samples.
Fig. 7. (A) SWNH removal efficiency of SDS, SDBS, ethanol and water as discussed in section 4. (B) Sample SEM image of the surface of SWNTs deposited silicon wafers before cleaning (AD=48%), and after wipe cleaning with pure water (AD=27.3%), ethanol (AD=20.1%) and SDBS surfactant (AD=10.8%).
Chapter 4

Macro and nano feature

On silicon wafer
4. Macro and nano feature

4.1. Nano scale patterns making

Two different experimental methodologies were employed to create nano and microscale features on the surface of silicon wafers. In the first set of experiments, the surface of silicon wafers (Nitrogen/Phosphorus doped, P/E [polished and etched] surface, mechanical grade) were subjected to either of two different plasma treatments regimes, namely, SF$_6$ (20 sccm SF$_6$, 10 sccm O$_2$, 10 sccm Ar) and O$_2$. The SF$_6$ plasma treatment was carried out in an Inductively Coupled Plasma (ICP) at 22°C, 10 mTorr, helium backside cooling. The experiments with O$_2$ treatment were performed in the Anatech SP-100 Plasma System. The plasma etching time was varied between 30 and 90 sec, and the dependence of the amplitude of the created patterns on the etching time was quantified using non-contact high resolution atomic force microscope (AFM). Figure 1 shows a 3D image of a silicon surface of 2.7 $\mu$m $\times$ 2.7 $\mu$m along with a graphical interpretation of the surface profile in the X and Y directions, respectively, after 30 sec plasma treatment with SF$_6$. The amplitude presented in Fig. 8A for the sample silicon substrate was measured by averaging the amplitude of the profile over an area of 5.72 $\mu$m$^2$ using XEI (Park Systems AFM software). The surface has nanoscale peaks and valleys with average amplitude of about 4 nm. Figure 9 shows the results for the O$_2$ plasma treatment. In general, treatment by the SF$_6$ plasma creates rougher features on the surface of the silicon wafer compared to the O$_2$ plasma treatment.
Fig. 8 Surface analysis of silicon wafer after plasma etching for 30, 60 and 90 sec. (A) Mean surface amplitude versus plasma etching time (sec). Error bars indicate one standard deviation value; (B) AFM image of silicon substrate after surface was plasma (SF₆) etched for 30 sec.

Fig. 9 Surface analysis of silicon wafer after oxygen plasma treatment for 30, 60 and 90 sec. (A) Mean surface amplitude versus plasma etching time (sec). Error bars indicate one standard deviation value; (B) AFM image of silicon substrate after surface was oxygen plasma etched for 30 sec.
MWCNTs (dispersed in polyvinyl pyrolidone) were spin-coated on the etched wafers using a Laurell Spinner at 500 rpm for 60 sec and then heated to 105°C (Glass transition temperature of polyvinylpyrolidone (PVP)) for 90 sec. Similar to our previous study [95], SEM imaging was performed before and after wiping with cellulose fabric soaked in SDBS. MATLAB software was used for image processing to estimate the areal density of MWCNTs on the wafers.

4.2. Micro scale patterns making

In the second set of experiments, micro scale patterns were created on the surface of silicon wafers using a photolithography and plasma etching process as shown in Fig. 10 A. Positive photoresist (Rohm Haas 1813) was spin-coated at 500 rpm for one minute. The wafer was then subjected to photolithography for ten seconds in a Quintel 4000 mask aligner to pattern mask features on the wafer surface. The wafer was later immersed in photoresist developer (MF-319 Rohm Haas) for 35-40 seconds. Plasma etching with SF$_6$ was performed on the wafer for 30 to 120 seconds (time range) in ICP plasma therm. Afterwards, the silicon wafers were immersed in a photoresist stripper solution (Shipley Microposit Remover1165) at 85°C for 5 minutes to remove the remaining photoresist polymer. Figure 10 B shows the dependence of the induced pattern diameter and etched depth on plasma treatment time. The inset shows the schematic of the mask patterns. The mask included 5 µm diameter circular holes separated by 5 µm space between adjacent patterns. Sample wafers with different etching times were cut in cross section and SEM imaging was performed to measure width and depth of etch as shown in Fig. 10 B. The average depth of the created patterns was varied between 1 and 3 µm for etching times of 30 and 120 sec, respectively. The average pattern depth increases approximately linearly with increasing
etching time. The average diameter of the created patterns increases slightly with increasing etching duration. The plasma etching process has some distinct advantages over other etching methods as it is easily repeatable, less sensitive to temperature changes and easier to start and shut down the procedure [96]. In the ICP plasma system a high density plasma discharge is generated by applying Radio Frequency (RF) power that is magnetically supplied through electromagnetic induction of an electric field. Figure 10 C shows examples of the created patterns after plasma etching for 30 and 120 sec.

Fig. 10 (A) Schematic of fabrication steps for creating surface topography on silicon wafers: (I) Spin coating positive photo-resist on silicon wafer; (II) Photolithography to pattern the mask; (III) Plasma etching; (IV) Stripping
photo-resist. (B) Average diameter and pattern depth as a function of etching time. (C) SEM images of wafer side views, showing the surface features after etching for 30 and 120 sec.

The physiochemical properties of the surface can greatly influence the adhesion of carbon nanotubes to the substrate. This is particularly manifest in Fig. 11, which illustrates the surface of a silicon wafer deposited with MWCNT after the etching process. The photoresist polymer still covers the non-etched portion of the wafer, whereas the rest of the photoresist free, imparting non-uniformity to the surface properties of silicon. As highlighted in Figs. 11 A and B, when MWCNTs were coated on the substrate their distribution was observed mostly in the proximity of circular pattern walls. Figure 11 C shows a cross section of a pattern that indicates strong adherence of nanotubes to the walls possibly due to different crystal orientations in the walls compared to the lower surface of the hole. In order to create a more uniform surface, a photoresist stripper was used to strip off the photoresist polymer from the “top” surface of the wafer. Also, plasma treatment was once again performed for 120 seconds to make sure that the whole surface is plasma etched and has uniform surface properties.
Fig. 11 SEM images show distribution of MWCNTs around the walls of etched patterns. (A) and (B) show the wafers top view at different magnifications. (C) shows the side view of the wafers. The etching time was 60 sec.

4.3. Effect of angular velocity during coating process

MWCNTs were spin coated on these surfaces at 500 and 3000 rpm. Figures 12A and 12B show comparison of spinning speed; the areal density of MWCNTs after spinning at 500 rpm is much greater than at 3000 rpm. Figure 12A is a graph of areal density distribution of MWCNTs in topological features created by plasma etching that indicates a higher number of nanotubes in the bottom surface (where were exposed to etching gases) as compared to the top surface (where were protected by photoresist from etching gases) of the etched pattern.
Fig. 12 (A) Initial areal density distribution of MWCNTs at the top and bottom surfaces of the etched pattern after spin coating MWCNTs at different rpms, i.e., 500 and 3000; (B) SEM images of 30 sec etched pattern shows the distribution of MWCNTs at 500 and 3000 rpm spinning at different magnifications.
4.4. Results for nano and micro scale pattern

The ability of different surfactants to remove CNTs from patterned surfaces was quantified by the removal efficiency parameter, defined as the difference between the initial and final areal density of MWCNTs divided by the initial areal density. Figures 13A and 13B show the efficiency of SDBS to remove MWCNTs from nano-patterned surfaces which were treated by the SF$_6$ and O$_2$ plasmas, respectively, versus the etching time. The efficiency of SDBS surfactant in removing MWCNTs for SF$_6$ plasma treated wafers is in the range of 83-93%, which is lower than the removal efficiency for the wafers treated with O$_2$ with efficiencies in the range of 95-99%. This can be attributed to higher roughness of the SF$_6$ plasma etched wafers, which creates higher resistance to the removal process. SEM images of MWCNTs on silicon wafer treated with the SF$_6$ plasma can be seen in Fig. 13C before and after removal.

To study the effect of removal from the microscale mask patterns, photolithography and SF6 plasma etching were used along with the micro fabrication techniques described in the previous section. The etching time was varied between 30 and 120 sec and three samples were fabricated for each etching time step. The chart in Fig. 14 shows a comparison of the removal efficiencies obtained by using two surfactants and water for different etching times from 0 to 120 sec. The bars represent the removal efficiency averaged over the bottom and top surfaces which were created during the plasma etching. The removal efficiency on the top is constant for various etching times (and is represented by bars at etching time equal to 0) since the mask prevented any treatment on the top surfaces. As the result of plasma etching, the bottom surfaces were etched from 1 µm at the etching time of 30 sec to 3 µm at the etching time of 120 sec. As expected, increasing the etching time results in a decrease in the removal efficiency for all cleaning media due to increased surface roughness. There was no significant removal of
MWCNTs inside the holes due to lack of contact between the wipe and contaminated surface, whereas the removal efficiency was much higher for the top surface because of sufficient removal force. This result highlights the important role of mechanical force in the decontamination process. SDS and SDBS both have greater removal efficiency than water. SDS shows slightly better decontamination efficiency compared to SDBS.
Fig. 13 Cleaning efficiency analysis of silicon wafer surface subjected to uniform plasma treatment. (A) Plot of initial and final areal density and cleaning efficiency as a function of plasma (SF$_6$) etching time. (B) Plot of initial and final areal density and cleaning efficiency as a function of plasma (O$_2$) treatment time. (C) Sample SEM images of MWCNTs deposited on plasma treated silicon wafers after etching for 30 and 90 seconds before and after cleaning.
Fig. 14 Removal efficiency of MWCNTs from top and bottom surfaces of Silicon wafers as a function of etching time; using water, SDS and SDBS
Chapter 5

Different wipes
5. Wipes effect on removal efficiency

5.1. Introduction

In previous chapters some important factors such as different type of surfactant and roughness of the substrate surfaces were studied. In this new phase of experiments, pre-saturated wipes with different saturation properties and different surfactant concentration are examined. Pre-saturated wipes with surfactant showed great function in cleaning process of surfaces like silicon surface.

5.2. Methodology

At the first step, 16 silicon wafers with 3" diameter were spin coated for 1 min at 3000 RPM. After spin coating, the CNT deposited wafers were heated at 105 °C for 90 sec in order to dry the wafer surface completely. A total number of 30 images were taken from different spots of each wafer surface using scanning electron microscope (SEM) imaging. The CNT surface aerial concentration for each image was then determined using an image processing program incorporated in MATLAB© software.

In this set of experiments, pre-saturated wipes were used. Two types of wipes were used. (i.e. EcoClean 60- Non-Woven cotton And MicroPolx MT2012, Polyester/ Nylon Microdenier).

8 different types of wet wipes were used:

1) Polyester/ Nylon Microdenier with 4% SDS and 65% saturation 
2) EcoClean 60- Non-Woven cotton And MicroPolx MT2012 with 4% SDS and 65% saturation 
3) Polyester/ Nylon Microdenier with 4% SDS and 45% saturation 
4) EcoClean 60- Non-Woven cotton And MicroPolx MT2012 with 4% SDS and 45% saturation 
5) Polyester/ Nylon Microdenier with 1% SDS and 65% saturation 
6) EcoClean 60- Non-Woven cotton And MicroPolx MT2012 with 1% SDS and 65% saturation 
7) Polyester/ Nylon Microdenier with 1% SDS and 45% saturation
Each experiment ran on two wafer samples to reduce the possible error (total 16 samples). Each wafer was manually wiped once. The estimated hand pressure and wiping duration were 2 kPa and 5 sec, respectively. After cleaning, the wafers were imaged using SEM and the average final area density for each wafer was obtained by post processing the images.

5.3. Results

The results show that removal efficiency is in direct relationship with the saturation of the pre-saturated wipes. It means that regardless of wipe type and concentration of SDS, the removal efficiency increases by increasing the pre-saturation from 45% (light blue) to 65% (dark blue) in Fig.15.

Moreover, 1% concentration of SDS shows better removal efficiency compare to 4% concentration. This result is in agreement with previous results reported in the literature [28]. If the surfactant concentration increases, the surfactant molecules shape micelles whose sizes increase by increasing surfactant concentration. This is due to the interaction between micelles with same polarity. If the surfactant concentration surpasses an optimum value, surface of micelles becomes so high which cause the portions of surfactant molecules interact with each other instead of CNTs [97]. If outer layer of surfactants orients in such a way that the hydrophobic tales extend into the solution, surfactants surface energies decreases and CNTs dispersion also decreases, consequently. This phenomenon is known as Flocculation (Fig. 16) [98]. For example, Sun et al. [53] obtained the optimum concentration of some surfactants for suspending CNTs equal to 1% and Rastogi et al. [28] found it equal to 1.3% for SDS.

Fig. 17 shows sample SEM images of MWCNT-coated wafer surfaces before and after cleaning.
Fig. 15. Removal Efficiency of different wipe types

Fig. 16. Mechanism of flocculation of CNTs via surfactant molecules (Taken from [28])
**Fig. 17.** Sample SEM image of the surface of MWNTs deposited silicon wafers. 

(a) EcoClean 60- Non-Woven cotton And MicroPolx MT2012 with 4% SDS and 45% saturation. 

(b) Polyester/ Nylon Microdenier with 1% SDS and 65% saturation
Chapter 6

Different substrates
6. MWNTs on stain steel surfaces

6.1. Introduction:

These days according to increasing usage of Carbon nanotubes (CNTs) in different industrial, the concern about the contamination of these materials are grown. Finding efficient method to decontaminate surfaces are exposed to CNTs seems vital. In previous experiments some important factors such as different type of surfactant, roughness of the substrate surfaces, pre-saturated wipes with different saturation properties and different surfactant concentration were studied. In this new phase of experiments, the goal is to study that if substrate change from silicon to stain steel the results how will change. Because in different work place, different substrate are in contact with CNTs, it is necessary to study about different substrate materials especially stain steel regarding to huge applications of it.

6.2. Methodology

2 types stain steel 304 EP samples were prepared rectangular shape with 2*5 cm and 0.5 cm thickness. One is AM 118 and the other is AN 031, both are stain steel 304 EP. As previous experiments these samples were spin coted for 1 min at 3000 RPM. After spin coating, the CNT deposited wafers were heated at 105 °C for 90 sec in order to dry the wafer surface completely. A total number of 30 images were taken from different spots of each wafer surface using scanning electron microscope (SEM) imaging. The stain steel surface make harder SEM imaging and the quality of images is not as good as silicon wafer. The CNT surface aerial concentration for each image was then determined using an image processing program incorporated in MATLAB© software.

In this set of experiments, the wet wipe which shows the best Removal Efficiency in last set of experiment was used. The polyester/ Nylon Microdenier with 1% SDS and 65% saturation showed 88.24% Removal Efficiency on silicon wafer coated by MWNTs. Each experiment ran on two samples to reduce the possible error. Each sample was manually wiped once. The estimated hand pressure and
wiping duration were 2 kPa and 5 sec, respectively. After cleaning, the wafers were imaged using SEM and the average final area density for each wafer was obtained by post processing the images.

6.3. Results

The results generally show that Removal Efficiency for stain steel is lower than Silicon wafers. Maybe it is because that the rougher surfaces of stain steel samples in compared with silicon wafers.

In Fig.18, the Initial and final aerial density of MWNTS on 2 different type of stain steel are shown.

In Fig.19, the Removal Efficiency of stain steel AM-118 and stain steel AN-031 and silicon wafers are shown.

In Fig.20 the sample SEM images of pre-cleaning and post cleaning are shown.

![Fig.18. Initial and final densities of MWNTS on stain steel surfaces](image-url)
Fig.19. Removal Efficiency of different surfaces types

Fig.20. Sample SEM image of the surface of MWNTs deposited stain steel AM-118 A) pre-cleaning. B) post cleaning
Chapter 7

Conclusion
7. Conclusion:

We proposed solvent cleaning as a technique for surface decontamination of carbon-based NMs such as CNTs, which can potentially be used for removal of nanomaterial adhered to surfaces caused by unwanted spillage and release or the gradual accumulation during the processing or handling. The role of cleaning media (i.e. surfactants, solvents, etc.) in facilitating the mechanical removal of single- and multi-walled CNTs from contaminated surfaces was discussed. The challenges associated with this technique include the high levels of agglomeration of CNTs and extremely low solubility in water and many common solvents, which tend to lower the efficiency of this method. Based on our results, the removal efficiency of multi-walled carbon nanotubes, single walled carbon nano tubes and single walled carbon nanohorns using two different water-surfactant solutions from a highly smooth surface of a silicon wafer through wiping are greater than 95%, 90% and 78%, respectively. The higher removal efficiency for multi-walled carbon nanotubes can be attributed to the larger value of the binding energy density holding the nanotube aggregates together for MWCNTs compared to SWCNTs [99]. The effectiveness of CNT removal using the solvent cleaning technique for CNTs obtained by various production methods, with different chemical modifications or attached on different substrates.

This research addresses the issue of MWCNTs removal from contaminated surfaces featured with controlled micro and nanoscale asperities. The amplitude of the nanoscale asperities was varied between 1 and 15 nm by the etching time. The etching induced microscale semi-ellipsoidal pits had an average diameter and height of ~ 7-9 µm, and ~ 1-3 µm, respectively. The results show no evident correlation between the size of nanoscaled features and the removal efficiency. By varying the etching time, the removal efficiency is in the range of 83-93% and 95-99% for SF₆ and O₂ plasma etched surfaces, respectively. However, microscale morphological asperities on the substrate have the capacity to hold a great numbers of MWCNTs, which are difficult to remove by the wiping procedure. Increasing the size of these features significantly
decreases the removal efficiency. Surfactants (SDS and SDBS) show a significant improvement in removal efficiency compared to water. The results of our study show that surfactant-saturated wipes can remove MWCNTs efficiently from contaminated surfaces, however their function is limited by the presence of micron-scale substrate roughness. Also, with optimizing the concentration of surfactant and the saturation of wet wipe, we can increase the removal efficiency of surfactants. Moreover, surfactants (SDS and SDBS) showed good function in decontamination of other substrate such as stain steel. In conclusion, surfactants are economical, commercially available and easy to use. These factors make surfactants a good candidate for the removal of CNTs deposited on surfaces.
Chapter 8

References
8. References


