Synthesis and Characterization of Graphene

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SYNTHESIS AND CHARACTERIZATION OF GRAPHENE

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Abstract

Graphene is an important nanoscale material with unique electronic and optical properties. Due to its many potential applications, graphene was the subject of a Nobel Prize in physics 2010; Andre Geim and Kostya Novoselov of Manchester University received the Nobel Prize for demonstrating the ability to create single atom thick graphene layers from bulk graphite. Since then, many alternative synthesis techniques and device applications of graphene have been explored. An important and unique property of graphene is its excellent thermal properties. Graphene has a two dimensional structure and the thermal properties are significantly different than three dimensional bulk materials. Using graphene by itself or as a composite for thermal management presents new opportunities for its impact on numerous applications including green technologies for power generation.

While graphene has been initially created using the exfoliation technique, it is widely believed that chemical vapor deposition (CVD) and plasma enhanced CVD (PECVD) techniques are better suited for large scale production of graphene. As such there has been significant effort in the synthesis of graphene by using these techniques. In particular, PECVD technique seems promising due to its lower growth temperature as it may be applied to a variety of substrates. Unfortunately, the quality of graphene created by CVD and PECVD techniques so far have been inferior to that made by the exfoliation technique; they are typically polycrystalline with grain size depending on specific process parameters.

The nanotechnology research group at UNLV has developed a technique for the synthesis of uniform diameter high quality carbon nanotubes by a process called catalyst engineering where a
nanoparticle of the catalyst is used instead of a thin film. Since nanoparticle catalysts have better
efficiency compared to thin films, this process has allowed the synthesis of superior quality
carbon nanotubes. We believe that similar catalyst engineering can be applied for the synthesis
of superior quality graphene tin films. Copper thin films are widely used as catalyst for the
synthesis of graphene. In this project, we use copper nanoparticles to synthesize graphene using
the PECVD technique in UNLV’s unique cluster tool Nanosys. While scanning electron
microscope imaging shows synthesis of some carbon structures, the formation of graphene could
not be confirmed by Raman spectroscopy measurement, possibly due to the small mass of the
structures. From our investigation, it became apparent that a more systematic approach with
additional resources will be needed to synthesize graphene by this method. As such, the focus in
this research was redirected towards the development of another platform for the synthesis of
graphene using catalyst engineering.

The nanotechnology research group has extensive experience in the synthesis of nanostructures
using anodized alumina as a template. In this research, we investigated and developed a platform
for the fabrication copper nanowires using an anodized alumina template that can be used for the
synthesis of graphene using the PECVD technique. The project also investigated adhesion
properties of such structures on the substrate. In addition, an interesting outcome of this project
is the development of a new technique for the fabrication of nanoporous thin film membranes.
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Table of Contents
Abstract.............................................................................................................................................. iii
Acknowledgements .............................................................................................................................. v
Table of Figures.................................................................................................................................. vii
Chapter 1: Introduction ......................................................................................................................... 1
Chapter 2: Synthesis and Characterization of Graphene .............................................................. 15
Chapter 3: Anodized alumina based platform for graphene synthesis ........................................ 39
Chapter 4: Thin Film Nanoporous Alumina Membranes................................................................. 53
Appendix A ...................................................................................................................................... 60
References ........................................................................................................................................ 64
Curriculum Vitae ................................................................................................................................. 70
### Table of Figures

| Figure 1.1 | Honeycomb Structure of Graphene | 4 |
| Figure 2.1 | Picture of NanoSys, a cluster tool for the fabrication of nanoparticle based devices | 19 |
| Figure 2.2 | Schematic diagram and photograph of Nanoparticle deposition system (rotated 180 degrees from previous pictures), developed for the manufacturing of nanoparticle based electronic and photonic devices | 22 |
| Figure 2.3 | Schematic diagram of the Nanocluster source. Top sketch shows qualitative plot of a normal distribution curve representing the size-variation of nanoclusters within the aggregation region. Schematic diagram of a Quadrupole Mass Filter with the top sketch showing the qualitative picture of a sharp size-distribution of nanoparticles after filtration through the QMF | 23 |
| Figure 2.4(a) | FESEM image of Cu nanoparticles with QMF turned OFF. Inset: Size-distribution of the nanoparticles. (b) FESEM image of Cu nanoparticles with QMF turned ON and set to 9.0 nm size selection. Inset shows the size-distribution of the nanoparticles. Grain boundaries of the deposited aluminum can be seen in the background | 28 |
| Figure 2.5 | Photograph of nanoparticle deposition system showing different units | 31 |
| Figure 2.6 | Scanning electron micrograph of the copper nanoparticles deposited on silicon substrate | 32 |
| Figure 2.7 | PECVD chamber in cluster tool for growth of graphene using catalytic nanoparticle | 33 |
| Figure 2.8 | Scanning electron micrograph of the result of PECVD growth on silicon substrate with copper nanoparticles | 34 |
| Figure 2.9 | Raman spectroscopy system used for the characterization of the graphene sample | 35 |
| Figure 2.10 | Raman spectra of graphite for reference | 36 |
| Figure 3.1 | Schematic top and cross-sectional views of pores formed by anodization of aluminum. Pore formation steps and concurrent potential-time characteristics providing an insight into pore formation process for thin films of aluminum. The potential-time curves and the aluminum film thickness can be used to determine the pore formation rate which is experimentally determined to be proportional to the anodization current density | 41 |
| Figure 3.2 | Structure for the anodized alumina based platform for the synthesis of graphene | 44 |
| Figure 3.3 | Anodization apparatus and chamber showing details of the sample holder | 45 |
| Figure 3.4 | Voltage-time characteristics obtained during the anodization of aluminum under constant current condition | 46 |
| Figure 3.5 | Scanning electron micrograph of copper nanowires synthesized inside anodized alumina pores | 48 |
| Figure 3.6 | Test results for alumina on silicon and, for comparison, aluminum on silicon | 51 |
| Figure 3.7 | Scratch test results for Cu-Alumina/Silicon structure | 52 |
Figure 4.1 (a) top and (b) bottom Scanning electron microscope images of two different alumina membranes created in these experiments

Figure 4.2 (a) top. Folded alumina membrane showing both top and bottom surfaces. Membrane top surface shows regular hexagonal array of pores. (b) bottom. Higher magnification image of membrane bottom surface showing presence of pores confirming that the pores go all the through the membrane.

Figure 4.3 Scanning electron microscope images of membrane edges at two different angles (a) top and (b) bottom showing high degree of bending of the nanochannels
Chapter 1: Introduction

1.1 Graphene and its properties

Graphene possess very unique properties. Graphene has been propelled in to the research and engineering arena since its recognition in 2010 when two researchers were awarded Nobel Prize for the experiments they conducted.

Graphene is an atomic-scale honeycomb lattice made of carbon atoms. What make graphene unique are its structure and the associated properties.

Its structure is one-atom-thick planar sheets of carbon atoms that are densely packed in a honeycomb crystal lattice. Graphene is most easily visualized as an atomic-scale chicken wire made of carbon atoms and their bonds (Figure 1.1). The crystalline or "flake" form of graphite consists of many graphene sheets stacked one on top of another.

The carbon-carbon bond length in graphene is about 0.142 nanometers [4]. Graphene sheets stack to form graphite with an inter-planar spacing of 0.335 nm. Graphene is the basic structural element of some carbon allotropes including graphite, charcoal, carbon nanotubes and fullerenes.

According to research Novoselof. et al, 2012) “graphene has extraordinary material properties. He states that at room temperature electron mobility of $2.5 \times 10^5$ cm$^2$ V$^{-1}$S$^{-1}$ approaches the theoretical limit of approximately $2.0 \times 10^5$ cm$^2$ V$^{-1}$S$^{-1}$, high thermal conductivity above 3000WmK$^{-1}$, complete impermeability to any gases, ability to sustain extremely high densities of current( a million times higher than copper) high Youngs modulus.
Summary of properties of graphene

Electronic properties

Graphene has exhibited very high electrical conductivity

“Carbon atoms have a total of 6 electrons; 2 in the inner shell and 4 in the outer shell. The 4 outer shell electrons in an individual carbon atom are available for chemical bonding, but in graphene, each atom is connected to 3 other carbon atoms on the two dimensional plane, leaving 1 electron freely available in the third dimension for electronic conduction. These highly-mobile electrons are called pi (π) electrons and are located above and below the graphene sheet. These pi orbitals overlap and help to enhance the carbon to carbon bonds in graphene. Fundamentally, the electronic properties of graphene are dictated by the bonding and anti-bonding (the valance and conduction bands) of these pi orbitals.” (Graphanea, n.d.)

“Tests have shown that the electronic mobility of graphene is very high, with previously reported results above 15,000 cm²·V⁻¹·s⁻¹ and theoretically potential limits of 200,000 cm²·V⁻¹·s⁻¹ (limited by the scattering of graphene’s acoustic photons). It is said that graphene electrons act very much like photons in their mobility due to their lack of mass. These charge carriers are able to travel sub-micrometer distances without scattering; a phenomenon known as ballistic transport. However, the quality of the graphene and the substrate that is used will be the limiting factors. With silicon dioxide as the substrate, for example, mobility is potentially limited to 40,000 cm²·V⁻¹·s⁻¹.” (Graphanea, n.d.)

Mechanical Properties
Due to the strength of its 0.142 Nm-long carbon bonds, graphene is the strongest material ever discovered, with an ultimate tensile strength of 130,000,000,000 Pascals (or 130 gigapascals), compared to 400,000,000 for A36 structural steel. Not only is graphene extraordinarily strong, it is also very light at 0.77 milligrams per square meter (for comparison purposes, 1 square meter of paper is roughly 1000 times heavier). It is often said that a single sheet of graphene (being only 1 atom thick), sufficient in size enough to cover a whole football field, would weigh under 1 single gram. These values are theoretical values. To test these values requires flawless graphene which currently is very hard to be commercially produced. (Graphanea, n.d.)

Optical properties

Graphene’s ability to absorb a rather large 2.3% of white light is also a unique and interesting property, especially considering that it is only 1 atom thick. This is due to its aforementioned electronic properties; the electrons acting like massless charge carriers with very high mobility. (Graphanea, n.d.)
Figure 1.1 Honeycomb Structure of Graphene

Source: Graphene :https://en.wikipedia.org/wiki/Graphene
Source: Dutta & Shalaev Purdue University, College of Engineering, ECE 695S Dutta Graphene orbital interactions.
Graphene has very high thermal conductivity, which can be used for advanced heat sinking applications for integrated circuits and chips. As the focus of this research is to develop graphene based structures for such applications, such properties are explored more details below.

Heat transfer takes place through Conduction, Convection, or Radiation.

(The following is excerpted from Wikipedia)

**Conduction** occurs within boundaries of the body by diffusion of its internal energy. Energy is transferred from high energy molecules to low energy molecules when adjoining molecules collide. Heat flows in the direction of decreasing temperature. The heat conducted in differential equation form is according to Fourier’s law:

\[ q = -k \nabla T \]

Where:

- \( q \) is local heat flux \( \text{W.m}^{-2} \)
- \( k \) is material thermal conductivity \( \text{W.m}^{-1}.\text{K}^{-1} \)
- \( \nabla T \) is the temperature gradient \( \text{K.m}^{-1} \)

For general discussion here \( k \) is assumed to be constant to be exact thermal conductivity varies with temperature but for most materials the variation is small. For anisotropic materials (a property of being directionally dependent as opposed to isotropy which means identical properties in all directions. Example of anisotropy is light through a polarizer another example of
an anisotropic material is wood, directional properties along grain are different than across the grain. Most metals are isotropic that is they have same properties in all directions.)

Fourier law in one direction can be simplified as

\[ q_x = -k \frac{dT}{dx} \]

The differential equation when integrated for homogeneous material of 1D geometry between two end points yields the heat flow rate as:

\[ \frac{\Delta Q}{\Delta T} = -kA \frac{\Delta T}{\Delta x} \]

Where \( A \) is the cross section surface area

\( \Delta T \) is the temperature difference between ends

\( \Delta x \) is the distance between the ends.

Stated another way:

\[ Q = \frac{kA\Delta T}{s} \]

Where

\( A \) = heat transfer area ( m\(^2\) )

\( k \) = thermal conductivity
\( \Delta T \) = temperature difference across material

S = material thickness (m)

Note: Thermal conductivity vs. Specific heat. Thermal conductivity a measure of an object’s ability to conduct heat (when two objects at different temperatures come in contact atoms or molecules collide and thus create heat); the amount of energy necessary to increase the temperature of a given mass of a substance is called its specific heat.

A couple of other definitions need to be reviewed before our discussion of thermal properties of graphene.

Thermal conductance; it is time rate of steady state flow through a unit area of material induced by a unit temperature difference between the body surfaces in W/m\(^2\).

Conductance = \( \frac{\text{thermal conductivity}}{\text{thickness of material}} \)

And is a reciprocal of thermal resistance.

Convection occurs in fluid by mixing. There is free convection and forced convection. For purposes of distinguishing the above discussion (conduction) the magnitude of heat flux normal to solid surface by free convection (such as in case of air and water in contact with the surface) is

\[ q_n = hA_h(T_h - T_f) \]

Where
H is the convection coefficient (typical values for air and water are 5-25 and 500-1000 $\frac{W}{m^2.K}$ respectively.

Radiation heat transfer occurs by electromagnetic radiation between surfaces of a body and the surrounding medium.

The magnitude of heat flux normal to a solid surface by radiation is

$$q_r = \varepsilon \sigma A_r (T_r^4 - T_m^4)$$

Where

$T_r$ is absolute temperature of the body surface?

$T_m$ is the absolute temperature of surrounding medium.

$A_r$ is the body surface area subjected to radiation

$\sigma = 5.6703 \times 10^{-8} (W/m^2K^4)$

$\varepsilon = $ surface factor (=1 for perfect black body)$^i$

Heat in a material is typically associated with phonons, which is a quantum description of a special type of vibrational mode in which lattice oscillates with the same frequency. A normal mode is important because any arbitrary lattice can be considered as a superposition of elementary vibrations (Fourier analysis). Mathematical treatment of phonons is addressed in literature referenced herein. There exists a minimum energy that must be supplied to the
harmonic oscillator to move it to the next energy level. This is quantum of energy is called phonon (a photon is quantized electromagnetic field). Energy levels (harmonic oscillator eigenvalues)

\[ E_n = \left( \frac{1}{2} + n \right) \hbar \omega_k, \quad n=0, 1, 2, 3 \]

\[ \omega_k = \sqrt{2 \omega^2 (1 - \cos(ka))} \]

a= distance between atoms

\[ k_n = \text{wave number of phonon} = \frac{\text{wave number}}{\text{wavelength}}, \quad \text{it has quantized values because the number of atoms is finite.} \]

\[ \omega = \text{natural frequency of harmonic potentials.} \]

A qualitative description of phonon and how heat spreads is referenced in this report.

Heat and sound both are vibration of atoms and molecules. Low frequency vibrations correspond to sound and higher frequencies correspond to heat. At each frequency, quantum mechanics principles provide that vibrational energy is a multiple amount of energy called a quantum which is proportional to frequency. This basic level of energy is called phonons.

Phonons are important in understanding the behavior of heat and sound in crystals (phonon in graphene is discussed below this discussion). In a crystal the atoms are neatly arranged in a uniform repeating structure and when heated the atoms oscillate at specific frequencies. The bonds (reference materials in this report provide sources for review of different
types of bonds) between the atoms behave like springs. When one of the atoms gets pushed and or pulled it sets of a wave (a phonon) travelling through the crystal. In practice most materials are filled with a chaotic mix of phonons that have different frequencies and are travelling in different directions all superimposed on each other. Their behavior can be analyzed by Fourier analysis.

Unlike photons (that carry electromagnetic radiation), generally do not interact if they have different wavelengths; phonons of different wavelengths can interact and mix when they bump into each other producing a different wavelength.

Like photons of a given frequency can exist only at certain specific energy levels exact multiples of basic quanta, phonons also have the same characteristic.

Behavior of phonons gives us insight of heat dissipation and is important concept in removal of heat.

Some additional concepts and terminology review

Heat sink is a passive component that cools a device by dissipating heat into the surrounding air. The performance of heat sink is given by

\[ R_{hs} = \frac{\Delta T}{P_{th}} - R_s \]

Where
\( R_{hs} \) = maximum thermal resistance of heat sink to ambient \(^0\text{C/W (K/W)}\)

\( \Delta T \) = temperature difference \( \text{In} \(^0\text{C} \)

\( P_{th} \) = thermal power(heat flow) in watts

\( R_s \) = thermal resistance of heat source in \(^0\text{C/W} \)

Interfacial thermal resistance is also known as thermal boundary resistance or also called Kapitza resistance is a measure of interface’s resistance to thermal flow. This thermal resistance differs from contact resistance at it exists even at atomically perfect surfaces. Due to differences in electronic and vibrational properties in different materials when an energy carrier (phonon or electron) attempts to transverse the interface it will scatter at the interface. For example metal to metal interface electron scattering will dominate thermal boundary resistance as electrons are primary thermal carriers in metals.

Acoustic phonons are main heat carriers in graphene while optical carriers are used for counting number of atomic planes in Raman experiments with few layer graphene.

For a constant flux applied across an interface the interfacial thermal resistance will lead to a finite discontinuity at interface. Using Fourier’s law

\[
Q = \frac{\Delta T}{R} = G\Delta T
\]

Where

\( Q \) = applied flux
\[ \Delta T = \text{the temperature drop} \]

R= thermal boundary resistance (Kapitza resistance)

G=thermal boundary conductance

According to author (phonon transport in graphene) the transport properties of phonons – the energy dissipation and scattering rates are substantially different in quasi two dimensional system (graphene) compared to the three dimensional bulk crystals. Because of the unique nature of a two dimensional structure phonon transport provides unusual heat conduction in graphene.

In solid materials heat is carried by acoustic phonons (ion –core vibrations in a crystal lattice) and electrons

\[ k = k_p + K_e \]

Where \( k_p \) and \( K_e \) are phonons and electron contributions.

In metals \( k_e \) is dominant owing to large concentrations of carriers. Measurements of electrical conductivity (\( \sigma \)) define \( k_e \) through Wiedemann Franz law.

Heat conduction in carbon materials is dominated by phonons (also for graphite which exhibits metal like properties). This is explained by strong covalent \( sp^2 \) bonding resulting in efficient heat transfer by lattice vibrations. In nanostructures \( K \) is reduced by scattering from boundaries.
An example of the benefit of advanced heat transfer is improved efficiency of solar cells. Substantial improvements can be made in PV (photovoltaic) solar cells and the timing for research and building a device is ripe. Currently the PV solar cells have an efficiency of about 15% in converting absorbed light into electricity. Absorbing light PV cells convert about 70% of solar energy to heat. This heat must be efficiently removed from the cell to prevent degradation of performance and/or damage to a cell. The temperature rise degrades the power conversion efficiency in PV cells approximately linearly with a coefficient of .23W/°C in temperature range from 25°C to 70°C for crystalline Si. This corresponds to ~20% reduction in power due to thermal build up. Other studies have indicated ~.5% efficiency loss per 1°C increase in cell temperature. If we assume the highest temperatures of PV solar panels are ~70°C the overall efficiency loss is very significant. According to some studies a reduction in cell temperature by 15°C at one sun illumination boosts ~6% increase in output power. Optimized mixture of graphene and MLG hold a good prospect for improving the efficiency of PV solar cells. (Shahil & Balandin, 2012)

1 Power ; 1 W= 1 Joule/sec, 1 Btu/sec = 1055 W

0°C=32°F= 273K

1 BTU/ft. h 0°F= 1.731 W/mK=1.488kcal/ (h m°C)

1 Term $hc = \left(1.99x10^{-29} \text{ joules} - m\right) \frac{1 \text{ ev}}{1.602 x 10^{-19} \text{ joules}} = 1.24x 10^{-6} \text{ e V} - m$
1 micrometer (\(\mu m\)) = \(10^{-6} m\) also called micron

1 nanometer (nm) = \(10^{-9} m = 10^{-3} \mu m\)

1 Angstrom (Å) = \(10^{-10} m\)

Pressure units: 14.7 psia = 0 psig = 29.92 in Hg = 33.95 ft. H\(_2\)O = 2116.8 lbs/sq.ft

1 atm = 1.013 bar = 14.696 psi = 33.9 ft of H\(_2\)O

1 inch of Hg = 12.8 mm of H\(_2\)O
Chapter 2: Synthesis and Characterization of Graphene

Mechanical exfoliation leads to the discovery and recognition of graphene. This simple technique uses a sticky tape which is wrapped or interfaced with a lead pencil. The tape is removed and it has traces of graphite/graphene (graphite is several layers of graphene stacked together). The sticky tape is folded over and peeled open. This operation is repeated several times to obtain a thin film from the residue on the sticky tape. While the exfoliation technique provided high quality of graphene for research purposes, it is not a viable technique for manufacturing of graphene based devices. Towards such goal it is believed that chemical processes such as Chemical Vapor Deposition (CVD) is more appropriate. Several researchers have commented that CVD is a viable method for such applications (Kataria et al., 2014). CVD involves introducing precursor gases at a low pressure in to a reaction chamber. At a very high temperature approximately 1000-1200°C (Munoz et. al., 2013). The decomposition is thermal because the C-H bonds are strong- 440kJmol⁻¹) Copper melting point is 1000°C. The gases that are generally used are hydrogen and a gas for the source of carbon. That gas is generally methane. (Methane is an alkane and has single bonds to hydrogen and carbon). Based upon literature other alkanes have not been used or considered such as ethane, propane, butane etc. Also Alkenes- two bonds and Alkynes- 3 bonds have not been used to date because low solubility of carbon in copper the graphene growth is restrained in the surface (Vlassiouk, 2011). Graphene growth is ‘Strongly dependent on the hydrogen contribution which seems to serve as a double role as an activator of surface bound carbon that leads to monolayer growth and as an etching reagent that controls the morphology and the size of graphene.” (Vlassiouk, 2011).
Hydrogen helps to reduce the native surface oxides on copper surface which deters the growth of graphene (Kataria, 2014). Then graphene then has to be transferred to another substrate. The transfer can degrade the quality of the film by introducing defects and contamination (Chugh et al., 2015). Copper is typically used as the catalyst for the growth of graphene. CVD has been used for the growth of graphene on copper and other substrates.

CVD growth of graphene typically requires very high temperature, which may not be suitable for many substrates or structures. As an alternative, Plasma Enhanced Chemical Vapor Deposition (PECVD) has been explored for the low temperature growth of graphene. PECVD allows lower temperature as the energy required to break the bonds is supplied through plasma. (Chugh, et al., 2015). In his experiments he used temperatures of 650°C to decompose CH4 by plasma for a range between 1-15 minutes. He used RF plasma (13.56 Mhz). The gases were introduced at a the pressure was 1 m Torr and a flow rate of 6 sccm. The system was cooled down at a rate of approx. 15°C / min in a 100sccm flow of argon at a pressure of 1 Torr. He uses Horiba Labram HR 800 for characterization. The author states that while copper was used to speed up the process as a catalyst it is not necessary condition to grow graphene. He states low temperature; rapid, non-catalytic synthesis is needed for industrial mass production of graphene devices (Chugh, et. al, 2015)

While CVD and PECVD techniques are considered methods of choice for the growth of large area graphene sheets, needed for device applications, the quality of such films to date has been inferior to that created by the exfoliation technique. CVD and PECVD grown graphene are
typically polycrystalline, with grain size depending on the specific growth process. As such there is significant on-going effort towards improving the crystalline quality of the graphene. We believe that catalyst engineering can be an effective approach towards improving the crystalline quality of graphene. The UNLV nanotechnology research group has significant experience in using catalyst engineering for the controlled growth of carbon nanotubes. In this technique, nanoparticles of the catalyst material are used for growth instead of a thin film of the catalyst. The UNLV group has successfully grown carbon nanotubes of uniform diameter using this technique; the diameter of the nanotube being determined by the nanoparticle diameter. We believe that the catalyst engineering can be used for the growth of high quality graphene, since catalyst nanoparticles provide significantly more surface area compared to thin films. As a result, we decided to use copper nanoparticles for the PECVD growth of graphene as described below.

The PECVD growth of graphene using catalyst engineering was carried out in the Nanosys cluster tool as described below. NanoSys was developed to facilitate prototype development for the manufacturing of nanoparticle based devices and was designed to be flexible. The system consists of a nanoparticle deposition system, a 4-pocket electron-beam evaporation unit, a sputtering unit, a transfer chamber to facilitate substrate transfer without breaking vacuum, and a PECVD unit. NanoSys currently handles 2 inch substrates, however, the substrate size can be easily scaled up to 6 inches and higher. Some of the features of NanoSys are: (i) allows deposition of nanoparticles of any metal, semiconductor or insulator of diameters ranging from 1nm to 70nm with less than 5% size variation on any arbitrary substrate, metallic, semiconducting or insulating (ii) in-situ deposition of four different nanometer scale thin films with less than 5% thickness uniformity, (iii) in-situ deposition of thick layers of insulators,
semiconductors or metals including isolation dielectrics, and (iv) in-situ PECVD growth without breaking vacuum.

The NanoSys has been used to deposit nanoparticles of Ni, Fe, Co, Au, Ag, Cu, Si, CdTe, CdSe, ZnS and many other metals and semiconductors on a variety of substrates including silicon, silicon dioxide coated Si, metal coated silicon, quartz, sapphire. Since the nanoparticle deposition system is based on sputtering, nanoparticles can be formed from any material that can be sputtered. In addition, since nanoparticle deposition is carried out at room temperature, and the process is substrate-independent, nanoparticles can be deposited on a variety of substrates including flexible substrates.
Figure 2. Picture of NanoSys, a cluster tool for the fabrication of nanoparticle based devices.
NanoSys is unique equipment that allows the fabrication of nanoparticles of any metal, semiconductor or insulator with dimensions as low as 1 nm with less than 5% size variation on any kind of substrate. The uniqueness of this system lies in the fact that beside the nanocluster source, it consists of an electron-beam evaporation system; a pulsed DC sputtering unit as well as a PECVD unit is installed in the same system. Thus, ohmic contacts and isolation dielectrics can be formed in an integrated manner without breaking the vacuum. In addition, the deposited nanoparticles can be used as catalysts for the growth of carbon nanotubes. A major strength of this system is that the equipment and the process are compatible with the silicon CMOS IC process lines, thus making this technique suitable for volume manufacturing.

The schematic diagram as well as a picture of the nanoparticle deposition system is shown in Fig. 2.2. Nanoparticle deposition system consists of a nanoparticle unit that provides the capability to deposit nanoparticles of any metal, semiconductor or insulator of diameters as low as 1 nm with less than 5% size variation on an arbitrary substrate. A load-lock is used for transferring the substrate to and from the ultra-high vacuum chamber. The substrate is mounted on a rotating substrate holder that can be heated up to 800°C. An important objective in the development of NanoSys was commercial viability of the nanoparticle based devices. Since it is widely believed that for nanoparticle based devices to be commercially viable, at least in the near future, the fabrication process has to be compatible with the silicon IC CMOS process, special attention was given to make all processes in NanoSys to be silicon IC compatible. While electron-beam evaporation and pulsed DC sputtering are standard techniques used by the silicon IC industry, the selection of the nanoparticle source required serious considerations. (Das, et al. 2007)
The nanoparticle unit consists of a (i) nanocluster source that generates nanoparticles of different dimensions, and a (ii) quadrupole mass filter (QMF) that acts as a band-pass filter and allows only a pre-selected mass (and thus size) of nanoparticles to pass through for deposition.

**Nanocluster Source**: The nanocluster source consists of a dc magnetron sputtering unit, an aggregation region, an aperture through which nanoclusters are channeled to the QMF, gas feed-throughs, cold trap and water cooling systems, differential pumping arrangements and a linear motion drive to adjust the length of the aggregation region. A schematic diagram of the nanocluster source is shown in Fig. 8. The system is specifically designed for UHV environment. The D.C. magnetron discharge is used to generate clusters from the target, connected to the magnetron assembly. The magnetron is designed for high operating pressure and high sputter rate. The magnetron-based source has the advantage over all other types of cluster source in terms of the wide cluster size range, which varies from fraction of a nanometer to few tens of nanometers. The variation of cluster size is dependent on several parameters, such as the length in which the clusters aggregate, the power to the magnetron, the flow rate(s) of the aggregation gas(es), the temperature and pressure of the aggregation region and type(s) of the aggregation gas(es) being used, etc. Another important feature of the nanocluster source is the presence of ionized clusters in the aggregation region, which is suitable to form highly adherent and uniform coatings even on insulating substrates by the so-called technique of energetic cluster impact. (Das et al 2007)
Figure 2. Schematic diagram and photograph of Nanoparticle deposition system (rotated 180 degrees from previous pictures), developed for the manufacturing of nanoparticle based electronic and photonic devices. (Das, et al. 2007).
$A = \alpha + \beta \cos(2\pi vt)$

where,

$\alpha \rightarrow$ dc component,

$\beta \rightarrow$ amplitude of the ac part

Figure 2. Schematic diagram of the Nanocluster source. Top sketch shows qualitative plot of a normal distribution curve representing the size-variation of nanoclusters within the aggregation region. Schematic diagram of a Quadrupole Mass Filter with the top sketch showing the qualitative picture of a sharp size-distribution of nanoparticles after filtration through the QMF. (Das et al, 2007).
Typically, sputtered clusters are cooled and swept through the liquid nitrogen cooled aggregation region by argon and (or) helium gases, where these clusters nucleate to form a distribution of nanoclusters of various sizes as shown in the Fig. 2.3. The residence time within the aggregation zone can be varied by varying the length of the aggregation region with the linear motion drive. By controlling the aggregation length, and thus the residence time, one can control the distribution of the nanocluster size within the aggregation region. Several theoretical and experimental works have been carried out to explain the growth of the clusters within the aggregation region. Generally, the nanocluster size follows a normal (Gaussian) distribution, with significantly large standard deviation, as shown in the inset of Fig. 8. Therefore, if these nanoclusters are allowed to deposit on substrates within the main deposition chamber, without using any filter, the size variation of the deposited nanoclusters will also be quite significant. But fabrication of useful nanodevice requires uniformly distributed nanoparticles with well-defined sizes. Hence, a size-selector is essential to select nanoclusters of specific size from the distribution, which is the purpose of the QMF. The QMF acts as a band pass filter and allows only nanoparticles of pre-selected size to pass through. The QMF selects a specific value of the particle size (say, $x_1$) from the normal distribution, which is represented by the thin slice around $x_1$ shown in the inset of Fig. 2.3. The width of the slice, $\Delta x$, depends on the resolution of the QMF. (Das, et al 2007)

**Quadruple Mass Filter (QMF)**: The quadrupole mass filter, introduced between the aggregation region and the main deposition chamber is used to analyze, electrostatically manipulate and filter charged nanoparticles from the nanocluster source. It has been designed specifically for the purpose of high-resolution measurement, manipulation and filtering of nanoclusters between 50
and 3x10^6 a.m.u. rather than only to detect the presence of elemental or low-mass compound materials. A schematic diagram of the QMF is shown in Fig. 2.3. It consists of four cylindrical rods, with alternating voltages applied to the opposite pairs of the rods. Nanoclusters of various sizes from the aggregation region enter into the QMF through the entrance aperture, which shields the cluster beam from the end of the quadrupole rods and also help to define the beam. The cluster beam is then allowed to flow through the quadrupoles along the axes of the rods. Positive and negative ac voltages are applied to the opposite pairs of the QMF poles, and the cluster ions are selected according to their charge-to-mass (e/m) ratio. Ionized clusters, with different e/m ratios follow different spatial trajectories due to the external alternating electric field and only a specific particle size is allowed to pass through the exit aperture. Ideally, a QMF consists of a set of four parallel electrodes with hyperbolic cross-sections, with potentials of ±A/2, applied across them as shown in Fig. 2.4a. This structure gives rise to a two-dimensional hyperbolic field, E(x, y) = A [x^2 – y^2] / 2r_o^2, where 2r_o is the shortest distance between the rods (r_o is also called characteristic radius). Driven by an alternating potential, A = α + β cos (2πvt), this field provides mass-dependent focusing of ionized clusters passing along the central line of the QMF. In practice, hyperbolic shaped electrodes are very difficult to produce, hence cylindrical rods are used with good approximations to the theoretical profile by considering electrode radius r_e as 1.148 times larger than the inscribed circle, r_i, as shown in Fig. 2.4b. The parameters which can be varied to allow clusters of particular mass (and thus diameter of spherical particles) to pass through are the amplitude of the ac voltage (β), frequency (ν) and the dc component of the applied potential (α). The ratio (α/β), called resolution, defines the cluster mass- (or diameter-) band transmitted through the filter. Higher the value of α/β, narrower is the band transmitted through the filter. Details of the design and working principle of the QMF are
available in various articles. Theoretically, the resolution of the QMF can be better than 0.01%, but in reality the optimum resolution is determined by a number of other parameters including the mechanical construction (diameter, tolerance, length and alignment of the poles), variations in the initial cluster ion energy, electrical imperfections etc. Therefore, typical usable cluster size resolution of the system is ~2% to 6%. (Das, et al 2007). The full-width-and-half-maximum of this distribution depends on the resolution of the QMF. Another important feature of this system is the X, Y deflection plates present after the QMF. Neutral particles present in the incoming flux, which will not be affected by the QMF, can be separated from the ionized clusters by applying suitable voltages in the X, Y deflection plates. (Das, ET .al 2007)
Our research group has deposited nanoparticles of a variety of metals (such as Ni, Cu, Fe, Au, Ag), elemental semiconductors (such as Si) and compound semiconductors (such as CdS, CdSe) using NanoSys. Fig. 2.4(a) shows the FESEM image of Cu nanoparticles deposited on Al-coated Si substrates with the QMF in the OFF condition. Fig. 2.4(b) represents the same with QMF turned ON and set to a particle size of 9 nm. In both cases the Ar flow-rates were 70 sccm. The insets of both the figures represent the size distribution of the nanoparticles obtained from the respective images. These two figures were used to determine the resolution and accuracy of the QMF. The size distribution of nanoclusters with QMF-OFF, shown in the inset of Fig. 2.5(a), is determined from the image analysis of FESEM micrograph, assuming the cluster area to be the projection of a spherical particle. The column charts are the experimental data measured from Fig. 2.4(a). The data are well approximated by Gaussian distribution with peak diameters of 11.07 nm. The size variation, obtained from the distribution is found to be around 10 %. Physically, this distribution is a representative of the cluster distribution present within the aggregation region of the nanocluster source under the applied operating conditions. By changing operating conditions, such as sputtering power, pressure, gas flow, aggregation length etc. the peak value as well as the distribution of clusters can be changed, which can be used to calibrate the nanocluster source for optimum performance. Inset of Fig. 2.4(b) represents the particle size distribution of Cu-nanoparticles with QMF-ON and set to 9.0 nm size, as mentioned earlier. The distribution is well-fitted with Gaussian distribution with a peak diameter of 9.4 nm and a size variation of 4.4 %. This demonstrates the power of the mass filter to get accurate, narrow size-distribution of nanoparticles.
Figure 2. (a) FESEM image of Cu nanoparticles with QMF turned OFF. Inset: Size-distribution of the nanoparticles. (b) FESEM image of Cu nanoparticles with QMF turned ON and set to 9.0 nm size selection. Inset shows the size-distribution of the nanoparticles. Grain boundaries of the deposited aluminum can be seen in the background (Banerjee et. al.).
A photograph of the relevant parts of the nanocluster source is shown in Figure 2.5. In this project, a 2 inch silicon substrate was loaded in the nanocluster source and the system pumped down. The substrate was next loaded in the growth chamber as shown in Figure 2.5 using a load lock. The growth chamber is typically maintained at ~ $10^{-8}$ torr in order to create high purity nanoparticles and to protect the nanoparticle surfaces from oxidation. Argon and helium gases are next introduced into the nanocluster source; the argon produces the plasma for the sputtering and the helium gas acts as an agglomeration gas for the formation of nanoclusters of different size, as explained in more detail. A plasma was next activated by providing the necessary voltage to the sputtering unit (the gate valve to the chamber is closed during this period). The quadrupole mass filter is next activated. The quadrupole mass filter acts as a filter and allows only certain preselected sized nanoparticles to the growth chamber. The quadrupole mass filter is computer controlled and allows the selection of a specific nanoparticle size and size distribution. In our experiments, we have typically use size distributions in the range of 5% to 10%. The gate valve to the gate chamber was next opened to allow the selected size nanoparticles to the substrate. The nanoparticles are typically carried to the substrate by the helium gas due to a differential pressure in the system. However, a bias may be applied to the substrate for improved deposition rate. Since the nanoparticles emitting from the quadrupole mass filter are charged particles, the application of a substrate bias can enhance the deposition rate. The substrate was rotated during deposition for uniform particle density. The deposition of nanoparticles was carried out for 15-30 minutes. The nanoparticles were next characterized by field emission SEM to determine size and size distribution.
Fig 2.6 shows a scanning electron micrograph of the copper nanoparticles deposited on silicon substrate. As can be seen from the figure, the nanoparticle density was quite high as desired. Also, from a preliminary examination, the size distribution of the nanoparticles was found to be within the range expected. The substrate was then transferred to the PECVD chamber (Fig 2.7) for the growth of the graphene layer. The PECVD system was modified to allow vertical as well as side-ways growth of material. This was accomplished by changing the orientation of the substrate holder with respect to the anode. Next, acetylene was introduced into the system for the growth of graphene. The fabrication parameters were obtained from the literature. PECVD was carried out at a temperature of 650°C with gas pressure at 1 mTorr and gas flow rate of 6 sccm. Deposition was carried out for 25 minutes.

The graphene sample was then characterized using SEM and Raman spectroscopy. The SEM image is shown in Fig 2.8, which shows a variety of structures, including some small pieces of thin films oriented at different angles. The samples were then characterized using Raman spectroscopy, the image of the spectrometer in use is shown in Figure 2.9. A piece of graphite was first characterized to act as reference, the spectrum of which is shown in Figure 2.10. Unfortunately, no Raman signal above noise level could be observed for the graphene samples. This is attributed to the small volume of material that can be seen in the SEM micrograph.
Figure 2. 5 Photograph of nanoparticle deposition system showing different units.
Figure 2. 6 Scanning electron micrograph of the copper nanoparticles deposited on silicon substrate.
Figure 2. 7 PECVD chamber in cluster tool for growth of graphene using catalytic nanoparticle.
Figure 2.8 Scanning electron micrograph of the result of PECVD growth on silicon substrate with copper nanoparticles.
Figure 2. 9 Raman spectroscopy system used for the characterization of the graphene sample
Figure 2. 10 Raman spectra of graphite for reference
The results can be summarized:

- PECVD synthesis of graphene using copper nanoparticles show growth of carbon structures.
- Raman spectroscopy measurement did not result any confirmed signal above noise, so nature of the particles could not be confirmed.
- It appears that there are multiple categories of carbon structures present.

It became evident from research that growth of graphene using copper nanoparticles will require more systematic long term approach with more resources. A proposal is under development using the preliminary data towards that goal.

As such, the focus in this research was redirected towards the development of another platform for the synthesis of graphene using catalyst engineering.

The nanotechnology research group has extensive experience in the synthesis of nanostructures using anodized alumina as a template. Anodized alumina a great intermediate layer due to its high insulation properties and also for the platform for creating nanostructures. However, anodized alumina has poor thermal conductivity approximately around 0.7W/m/K (Ogden, 1987), which requires an improved thermal conduction mechanism for heat sinking applications.

In this research, we investigated and developed a platform for the fabrication copper nanowires using an anodized alumina template that can be used for the synthesis of graphene using the PECVD technique. The project also investigated adhesion properties of such structures on the substrate. In addition, an interesting outcome of this project is the development of a new
technique for the fabrication of nanoporous thin film membranes. The work is described in chapter 3.
Chapter 3: Anodized alumina based platform for graphene synthesis

Anodized alumina has been the topic of great interest for the low cost fabrication of semiconductor and metal nanostructure arrays with applications ranging from nanoscale electronics to high-performance flat panel displays (Das, et al. 2000; Xiao, et al., 2002; Jain, et al., 2002). This material system uses natural self-organization for the creation of periodic arrays of nanoscale structures. When aluminum is anodized in a suitable oxidizing acid (e.g., sulphuric acid), a two-dimensional hexagonal lacework of $\text{Al}_2\text{O}_3$ cells with uniform tubular pores is formed as shown in Figure 3.1 Das, et al., 2000. The pore diameter and the cell wall thickness depend on the anodization conditions, such as type and pH of the anodizing acid, and the anodizing current density, and can be precisely controlled over a wide range. The technique can be used to create templates with pore diameters ranging from 4 to 200 nm, pore length from 10 to 1000s of nm, and pore density in the $10^9$ – $10^{11}$ cm$^{-2}$ ranges. In addition, such templates can be created on aluminum substrates, silicon substrates and glass (soda lime) substrates, and a pore diameter variation of $\pm$10% can be achieved. In recent years, researchers have reported self-organized pore growth leading to a nearly perfect, densely packed hexagonal pore structure for a narrow set of processing parameters. A systematic investigation suggests that the cause of this self-ordering behavior is mechanical stress which leads to a repulsive interaction between neighboring pores. Such self-organized pore growth allows even more stringent control over the diameters of the nanostructures. The pore diameter and the inter-pore spacing depend on the anodization conditions such as electrolyte pH, type of acid, anodization current/voltage, electrolyte temperature and the substrate parameters. The pore diameter can be varied between 4 nm to 100s of nm and the pores can be several microns deep Parkhutik, et al., 1990; Wada, et al. 1986; Ono, et al, 1990; Treverton, et.al, 1990). Due to the excellent
periodicity of the pores, and the ability to control the pore diameters, such anodized alumina films can be used as templates for the fabrication of periodic arrays of nanostructures. Since alumina (Al₂O₃) is electrically insulating (10¹⁸ Ω-cm resistivity), optically transparent over a wide spectra, and chemically robust, it is an ideal embedding material for optical and electronic devices (Das, et al. 2000). The pores in alumina templates can be used to synthesize a variety of metal and semiconductor nanostructures (Routkevitch, et al, 1996). In addition, the template can be used as a mask for pattern transfer to create periodic arrays of pores on a substrate. In summary, this technology, allows economic fabrication of large periodic arrays of nanostructures that allow (a) the size and composition of the nanostructures to be varied, (b) encapsulation of nanostructures in a rugged host material, (c) flexibility to use a variety of substrate materials, and (d) compatibility with standard silicon fabrication technique.

Although the pore formation mechanism is not yet fully understood, it is believed to take place in the following steps. During the first 3-5 s of anodization, a thin non-porous layer of alumina (Al₂O₃) is formed on top of the aluminum layer. As anodization is continued, an array of pores develops on the alumina layer, and grows in diameter until reaching the final dimension determined by the anodization conditions. Once the final diameter is reached, the diameter of the pores do not increase any further, and as the anodization is continued, the depth of the pores increase in proportion to the anodization current. While most of the work in this area has been restricted to bulk aluminum, we have extended this technique to create Al₂O₃ templates on silicon and glass substrates through the deposition of an aluminum thin film. This approach
Figure 3. Schematic top and cross-sectional views of pores formed by anodization of aluminum. Pore formation steps and concurrent potential-time characteristics providing an insight into pore formation process for thin films of aluminum. The potential-time curves and the aluminum film thickness can be used to determine the pore formation rate which is experimentally determined to be proportional to the anodization current density (Das, et al., 2000).
Provides the possibility of nanostructure integration on silicon substrates, and provides us with a tool for precisely controlling the nanostructure depth by monitoring the voltage-time characteristics during anodization, as shown in Figure 3.1. During anodization, the potential increases initially during the formation of the top layer of Al₂O₃, then decreases during pore widening, and then levels off at the onset of pore propagation. Next, when the pores propagate through the complete layer of aluminum film, and contacts the silicon substrate, the potential rapidly increases. Since the thickness of the aluminum film is accurately known, and the time from the beginning to the end of pore formation can be determined from the potential profile, the pore formation rate can be precisely determined in this system. Therefore, in addition to providing control over the diameter of the pores, our approach also provides precise control over the length of the pores.

The objective of this research was to develop an anodized alumina based platform for the PECVD synthesis of graphene. A schematic diagram of the structure to be developed is shown in Figure 3.2. The structure consists of an anodized alumina template created on a substrate (silicon in our case), with the pores filled with copper. The advantage of this structure is that it provides a nanostructure platform for graphene synthesis, with the benefit of improved catalytic efficiency provided by nanostructures. This specific structure has many additional advantages such as lower cost, ease of fabrication, control of nanostructure size. In addition, this method can be used to grow graphene on sensitive substrates as the alumina layer acts as a protective barrier. This structure is also advantageous for heat sinking applications as the copper nanowires can help heat conduction from the substrate to the graphene layer.
In our experiment, we used silicon substrates for the creation of the proposed structure. Silicon substrates were first cleaned, and then immersed in a 1% HF bath, rinsed, and dried in N2. Then, a 100 nm layer of Al was sputter deposited on the back of the wafer, followed by annealing at 450° C for 30 minutes to form an ohmic back contact. Next, a 100 nm layer of Al was deposited on the top of the wafer, which was then annealed at 400° C for 30 minutes to ensure good adhesion. The wafers were then anodized in 20% sulfuric acid at a constant current condition at current density of 30 mA/cm². The acid solution was circulated using a pump and chilled to prevent heat buildup at the aluminum/electrolyte interface. The anodization process was monitored by observing the voltage-time characteristics.

A picture of the anodization apparatus is shown in Figure 3.3, which also shows a close-up of the sample holder. The sample is mounted on the chamber so as to be liquid sealed; the chamber is cooled using a water bath circulating around it that is pumped through the pump. This ensures a constant temperature of the anodization bath as the porosity can be adversely affected by varying bath temperatures. The anodization in this project was carried out at a constant temperature of around 10°C. During anodization, the voltage-time characteristics is monitored to obtain an insight into the anodization process and also to obtain an end point for the anodization process. Figure 3.4 shows a typical voltage-time characteristics obtained during anodization. The voltage-time characteristics show the steps of pore initiation, pore formation, pore propagation and termination of the pores on the substrate.
Figure 3. 2 Structure for the anodized alumina based platform for the synthesis of graphene
Figure 3.3 Anodization apparatus and chamber showing details of the sample holder.
Figure 3. 4 Voltage-time characteristics obtained during the anodization of aluminum under constant current condition.
The anodization process leaves an insulating layer of aluminum at the bottom of the pores, known as the barrier layer. While the barrier layers are usually very thin, they prevent any DC current flow due to their insulating nature. This barrier layer can be removed by the process of “pore widening”, which involves dipping the structures in 5% phosphoric acid for 3 to 6 minute durations. In addition to removing the barrier layers, the pore widening process also creates improved uniformity of the pores. In our research, the pore widening process was carried out for 5 minutes.

Following the pore widening, the pores in the anodized alumina were filled with copper by DC electrochemical deposition. The sample was remounted and the electrodeposition was carried out in 0.5 M CuSO₄ aqueous solution with a copper rod as the counter electrode (anode) and the alumina template on silicon as the cathode. The electrodeposition was carried out at room temperature. Electrodeposition of copper is an established process, and the deposition parameters were selected from the literature. A current of 2 mA was sent between the electrodes for 7 minutes, which worked well to fill the pores of the alumina template. A thin layer of the alumina was removed by etching in NaOH solution. Figure 3.5 shows the top view and a cross-sectional image of the structure. As can be seen, the pores in the alumina template were filled with copper and the structure provides a nanostructured catalyst for the synthesis of graphene.
Figure 3. 5 Scanning electron micrograph of copper nanowires synthesized inside anodized alumina pores.
Scratch Test

As a part of the project, we also investigated the adhesive property of copper filled alumina templates on silicon, which is important for practical applications. To investigate the adhesive properties, scratch tests were performed using a nano-scratch tester instrument manufactured by Micro photonics Inc. The scratch test is done by generation of scratches using a spherical stylus (Rockwell C Diamond, tip radius 2um). Scratch test was also performed on the adjacent metallic aluminum layer (from which the porous alumina was formed) to evaluate the adhesiveness of metallic aluminum on the substrate. The stylus is drawn at a constant speed across the sample under either constant or progressive loading at a fixed rate. “For progressive loading, the critical load is defined as the smallest load at which appreciable failure occurs on the sample; for the constant loading, the critical load corresponds to the load at which a regular occurrence of such failure is observed along the track. The scratch test is basically a comparison test and the critical load depends on the mechanical strength (adhesion and cohesion) of a coating to the substrate. The critical load depends on parameters that might be directly related to the test itself like the loading rate, scratching speed and indenter tip radius, indenter material. It also depends on the coating substrate parameters that include the substrate hardness and roughness, coating thickness and roughness, friction coefficient between coating and indenter, internal stresses in the coating. A scanning force microscopy is used to obtain high resolution images in three dimensions and the quantitative lateral and depth measurements can be obtained in the scratched portions. These images can be used to investigate the surface morphology and roughness before and after the tests. The tangential force recording enables the measurement of variations in force fluctuation along the scratch path. The pre scan recording on the sample is done to include the effects of non-uniformity in the flatness of the sample, where
the penetration depth is measured during the test. The post scan reveals the elastic recovery of the coating-substrate residue by providing the scratch path profile”. (Microphotonics)

Figure 3.6 gives the scratch test results of the alumina template on silicon. The two vertical lines indicate the occurrence of 1\textsuperscript{st} damage and delamination respectively. The intersection of these lines with various curves gives the value of critical load when 1\textsuperscript{st} damage occurs, value of critical load when delamination occurs, scratch length, penetration depth, friction coefficient and frictional force. A scratch of 1.1mm in length was made on the sample. The average critical force when 1\textsuperscript{st} damage is observed was found to be 40.49 mN. The delamination occurred at a force of 46.36 mN for the same sample. The penetration depth (Pd) was 2.5 \(\mu\)m and the value of coefficient of friction between alumina template and stylus is 0.5. Finally, the value of the frictional force is 20 mN.
Figure 3.6 Test results for alumina on silicon and, for comparison, aluminum on silicon.

<table>
<thead>
<tr>
<th>Structure</th>
<th>1st Damage (mN)</th>
<th>Delamination (mN)</th>
<th>Scratch Length (mm)</th>
<th>Pd (um)</th>
<th>Friction Coefficient</th>
<th>Frictional Force (mN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Alumina/Si</td>
<td>40.49</td>
<td>46.36</td>
<td>1.1</td>
<td>2.5</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>Al/Si</td>
<td>40.49</td>
<td>51.25</td>
<td>1.1</td>
<td>2.3</td>
<td>0.42</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 3. 7 Scratch test results for Cu-Alumina/Silicon structure
Chapter 4: Thin Film Nanoporous Alumina Membranes

One of the outcomes of the research on anodized alumina templates was the development of a new technique for the fabrication of nanoporous alumina membranes. Such membranes are of interest for various applications (Li, et al, 1999, Woo, et. al., 2006; Liu, et.al.2008). The membranes are fabricated by first creating thin film alumina templates on silicon substrates, and then by detaching them from the substrate through the use of a current pulse. Scanning electron microscope images of the membranes show regular hexagonal order of the nanoscale pores, which go all the way through the membranes. The membranes show excellent mechanical strength, flexibility and the ability to handle large bending stresses, which make them suitable for a variety of applications.

Typically, the pore structures in thin film alumina templates can be observed only from the top surface, and properties near the template/substrate interface can only be inferred from indirect measurements (Das, 2004). However, if the template can be removed from the substrate, valuable insight can be gained about template properties near the substrate. Such removable thin film templates, or membranes, also have the potential for interesting applications in the fields of electronic, photonic and biochemical devices. In fact, such an alumina membrane has been used as an etch mask to create antireflection structures on a silicon substrate (Kanamori, et al, 2001). In reference (Kenamori, et al, 2001), an alumina template was created on a bulk aluminum substrate, which was then removed by etching in a HgCl$_2$ solution for 50 minutes. The membrane was then placed on a silicon substrate and etched in phosphoric acid for 50 minutes to open the pores and adjust the pore diameters. The membrane was then used as an etch mask to etch the silicon substrate. The thin film template technology that we have developed makes
fabrication of such membrane masks much more straightforward and simpler. Instead of separately creating the membrane and attaching it to the substrate, the membrane (template) can be directly created on the substrate itself as described in our earlier paper Li. et al., 1999). In addition, our technique can also be used to form nanoporous alumina membranes by detaching the templates from the substrates.

In this research, the membranes were fabricated on silicon substrates. P-type <100> 0.1-0.3 ohm-cm silicon wafers were first cleaned using a standard technique and etched in a 1% hydrofluoric acid solution to remove any native oxide. Next, a 0.5 μm thick aluminum layer was deposited on the back of the wafers and annealed at 450°C for 30 minutes to form a good electrical contact. Following this, a 0.5 μm thick aluminum layer was deposited by electron beam evaporation on the top surface. Unlike our previous work, the top aluminum layer was not annealed in these studies. The top aluminum layer was then anodized in 20% sulfuric acid using a two-step anodization process; the two-step process has been demonstrated to improve pore size distribution and pore periodicity. (Li, et al. 1999) The acid solution was chilled and circulated during anodization to prevent heat buildup at the aluminum/electrolyte interface. In the first step, around 0.25 micron of aluminum was anodized at a constant potential of 40V, and the resulting alumina was then completely etched using a chromic acid solution. This step is believed to leave behind ‘footprints’ that act as seeds for pore initiation for the next anodization step. The wafer was then anodized at a constant current of 30 mA/cm² until the potential starts to rise indicating that the pores have reached the silicon surface (explained below). At this point, a short current pulse (80 mA/cm² for 2 seconds) was applied to detach the template from the silicon substrate.
The samples were then rinsed in DI water and imaged by field emission scanning electron microscope.

As described previously, the anodization process was monitored by observing the voltage-time characteristics for constant current anodizations, and current-time characteristics for constant voltage anodizations.

Figures 4.1a and 4.1b show scanning electron microscope images of two membranes created by the above procedure; the images were taken at an angle to show both top and cross-sectional views. The membranes are partially suspended in air, with an edge connected to the silicon substrate from which it was detached. The membranes are approximately 300 nm thick with an approximate average pore diameter of 20 nm. It can be seen that the pores go vertically down to the bottom of the membranes. Figure 4.2a shows an alumina membrane that was bent over itself after detachment from the silicon substrate; this provides an opportunity to simultaneously view the porous top layer as well as the bottom surface of the membrane. The top layer shows the expected honeycomb regular porous structure. In addition, there is also indication of porous structure at the bottom of the membrane. Figure 4.2b shows a higher magnification image of the membrane bottom surface, which clearly shows the presence of the pores, confirming that pores go all the way through the membrane. These results are significant for applications of membranes as etching masks and as nanofilters. A remarkable feature, observed in Figure 4.2a, is the high degree of flexibility and mechanical integrity of the membranes, which allow them to be bent to such an extent without fracturing. Close-up views of the membrane edges illustrating in more details the bending of the nanoscale channels are shown in Figures 4.3a and 4.3b. These
images confirm the high degree of bending stresses the membranes can handle. This mechanical integrity of the membranes, together with their porous nature, makes them suitable for a variety of photonic, electronic and sensing applications.
Figure 4.1

(a) top and (b) bottom Scanning electron microscope images of two different alumina membranes created in these experiments.
Figure 4.2 (a) top. Folded alumina membrane showing both top and bottom surfaces. Membrane top surface shows regular hexagonal array of pores. (b) bottom. Higher magnification image of membrane bottom surface showing presence of pores confirming that the pores go all the through the membrane.
Figure 4.3 Scanning electron microscope images of membrane edges at two different angles (a) top and (b) bottom showing high degree of bending of the nanochannels.
The definitions of Mobility, Conductivity, for basics of heat transfer are provided below:

Electron mobility

The electron mobility is defined by the equation:

\[ \text{Vd} = \mu \cdot E \]

Where:

- \( E \) is the magnitude of the electric field applied to a material,
- \( v_d \) is the magnitude of the electron drift velocity (in other words, the electron drift speed) caused by the electric field, and
- \( \mu \) is the electron mobility.

The hole mobility is defined by the same equation. Both electron and hole mobilities are positive by definition.

Usually, the electron drift velocity in a material is directly proportional to the electric field, which means that the electron mobility is a constant (independent of electric field). When this is not true (for example, in very large electric fields), the mobility depends on the electric field.

The SI unit of velocity is \( \text{m/s} \), and the SI unit of electric field is \( \text{V/m} \). Therefore the SI unit of mobility is \( \text{m}^2/\text{(V·s)} \). However, mobility is much more commonly expressed in \( \text{cm}^2/(\text{V·s}) = 10^{-4} \; \text{m}^2/(\text{V·s}) \).

Mobility is usually a strong function of material impurities and temperature, and is determined empirically, mobility values are typically presented in table or chart form. Mobility is also different for electrons and holes in a given semiconductor.

Electrical conductivity

There is a simple relation between mobility and electrical conductivity. Let \( n \) be the number density of electrons, and let \( \mu_e \) be their mobility. In the electric field \( \mathbf{E} \), each of these electrons will move with the velocity vector \( -\mu_e \mathbf{E} \), for a total
current density of ne u(e)E (where e is the elementary charge). Therefore, the
electrical conductivity \( \sigma \) satisfies:
\[
\sigma = ne u(e)
\]
This formula is valid when the conductivity is due entirely to electrons. In a p-type
semiconductor, the conductivity is due to holes instead, but the formula is
essentially the same: If \( p \) is the density of holes and \( u(h) \) is the hole mobility, then
the conductivity is
\[
\sigma = p u(h)
\]
If a semiconductor has both electrons and holes, the total conductivity is
\[
\sigma = e \{n u(e) + p u(h)\}
\]
Photons are associated with electromagnetic waves; whereas phonons
are associated with vibrations of atoms in a crystal or lattice.

**Photon** is a unit of quantum of light and a carrier of electromagnetic
energy. It has no mass has no electric charge. Photons in general do not
collide with one another and thermal transport by electromagnetic radiation
is not regarded as conduction of heat. Photons are defined through
electromagnetic wavelengths which range from: gamma rays (wavelength 10-
12 meters) to ELF (extremely low frequency) radio waves (wavelength
100000 kilometers). Visible light ranges from 390 to 750 nm (nanometers, or
10-9 meters). References to this report provide additional details regarding
electromagnetic radiation frequencies, wavelengths.

Photons move at speed of light.

Energy of a photon = \( E = \frac{hc}{\lambda} = \hbar \omega = hv \)

Where \( E \) can be in Joules or Electron Volt (eV)
\( h \) = Planck’s constant = \( 6.626 \times 10^{-34} \) joule sec = \( 6.626\times10^{-34}m^2kg/sec\)
\( c \) = speed of light= \( 2.98 \times 10^8 \) m/sec
\( \lambda = \text{wavelength} \)

\( \omega = 2\pi \nu \)

\( \nu = \text{photon frequency} \)

The equation for photon energy in eV can be expressed as:

\[
E (\text{eV}) = \frac{1.24}{\lambda (\mu m)}
\]

1 eV = 1.6x10\(^{-6}\) j

Photon momentum = \(\hbar k = \frac{h}{c} = \frac{h}{\lambda}\)

Where \(\hbar = \frac{h}{2\pi}\)

**Electron**

\[
E = \frac{p^2}{2m}
\]

Where

\(P = \text{momentum} = mv = 9.1 \times 10^{-24} \text{ kg m/sec}\)

Mass of electron = 9.1x10\(^{-31}\)kg

\(V = \text{velocity} = \text{approx.} \frac{1}{10} \text{ of velocity of light}\)

\(\lambda_e = \frac{h}{p} = 0.728 \times 10^{-10} \text{ m} = 0.0728 \text{ nm}^\text{iii}\)

\(K = \text{Boltzmann's constant} = 8.617 \times 10^{-5} \text{ eV/K} = 1.381 \times 10^{-23} \text{ J/K}\)

\[= 1.3806503 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}\]
Term \( hc = \left( 1.99 \times 10^{-29} \text{ joules} - m \right) \frac{1 \text{ ev}}{1.602 \times 10^{-19} \text{ joules}} = 1.24 \times 10^{-6} \text{ eV} - m \)

1. micrometer (\( m \)) = \( 10^{-6} \) \( m \) also called micron

1. nanometer (\( nm \)) = \( 10^{-9} \) \( m \) = \( 10^{-3} \mu m \)

1. Angstrom (\( Å \)) = \( 10^{-10} \) \( m \)

Pressure units:
- 14.7 psia = 0 psig = 29.92 in Hg = 760 Torr = 33.95 ft H2O = 2116.8 lbs/sq.ft
- 1 atm = 1.013 bar = 14.696 psi = 33.9 ft of H2O
- 1 inch of Hg = 12.8 mm of H2O
References


Das, Biswajit) Source: Physica E: Low-Dimensional Systems and Nanostructures, v 23, n 1-2, p 141-146, June 2004


Horiba Labram HR800 Software and Hardware manual

Horiba Labram HR 800 LabRam HR Raman Microscope User’s Operating Notes


Curriculum Vitae

ASHOK EM SUDHAKAR ESQ., P.E., D.E.E., C.G.C.

SUMMARY: Pursue projects that utilize my knowledge in business, law, construction, multi-disciplinary engineering, environmental law, procurement process for private and governmental entities, policy, legislative process, domestic and international business, patents, contracts administration, negotiations and analyses.

QUALIFICATIONS: A proven experienced and knowledgeable team player focused on costs, budgets, schedule, quality and increasing the bottom line of the company/entity and implementing the company’s/ entity’s goals and objectives. Possess a thorough understanding of commercial general conditions, liability provisions, indemnity provisions, insurance requirements and policy implications; incorporates background in legal, engineering, construction and financial aspects of a business.

PROFICIENCIES:

- Excellent oral/written communication skills
- Strong decision making/problem solving skills
- Effective Planner / prioritizing
- Exemplary Interpersonal skills/ team player
- Effectively work with government agencies and regulators.

PATENTS AND TRADE MARKS

Granted U.S. Patent for a Green product for maintenance of road and highways infrastructures. Granted U.S. Patent for protection of digital identity and personal and corporate data stored on a mobile phone in the event the mobile phone is lost or stolen. Granted two U.S design patents for a children’s electronic tablet and automatic napkin roller machine Three (3) patents pending

Granted five (5) US Trade Marks

Four (4) Trademarks pending
EDUCATION

B.TECH, Indian Institute of Technology, Delhi, India
M.S., Engineering, University of California, Berkeley, California, USA
J.D., Law Degree - Golden Gate University, San Francisco, California, USA
Certificate, Spanish 1, 2 - Dartmouth College, New Hampshire, Rassias Foundation, Hanover, USA
Certificate, Credit Analysis, Equity Valuation, and Financial Reporting - North Western University Kellogg Graduate School of Management, Evanston, Illinois, USA
Ph.D. candidate, Department of Electrical and Computer Engineering, University Of Nevada, Las Vegas, USA
Ph.D. candidate School of Environmental and Public Affairs, Workforce development and organization Leadership, University Of Nevada, Las Vegas, USA

HONOR SOCIETIES

PHI KAPPA PHI
TAU BETA PI NVB

AWARDS & HONORS

National Society/ California Society of Professional Engineers.
Trial Lawyers Association of America.
Bechtel Corporation, San Francisco, California
University of Las Vegas- outstanding graduate assistant teaching award.

CERTIFICATIONS AND PROFESSIONAL LICENSES

Admitted to United States Supreme Court
Admitted to Supreme Court of Commonwealth of Pennsylvania
Admitted to United States Court of Appeals for the Third Circuit
Admitted to United States District Court for Eastern District
Diplomate, the American Academy of Environmental Engineers
Licensed Professional Engineer in the State of California
Licensed Professional Engineer in State of Pennsylvania
Licensed General Contractor in State of Florida (Certified General Contractor)
Licensed General Contractor in the Commonwealth of Virginia
Licensed General Contractor in the State of California (Heavy construction, Electrical, Low Voltage, Building, Environmental Remediation, Asbestos, Traffic Controls, Masonry, Concrete and Landscaping)

SPECIAL EXPERTISE

- Past Pennsylvania DER Certified Host Municipality Inspector (Hazardous Waste Facilities)
- Established the First Civilian UXO (Unexploded Ordnance) School in United States in conjunction with TEEX (Texas A&M University, College Station) and Sudhakar Company Inc. to train civilians for removal of UXO (Unexploded Ordnance). UXO removal has been and is traditionally performed by EOD US Government trained personnel. School approved and certified by United States Department of Defense (DDSB). Copyrighted Course materials prepared.

TEACHING AND INSTRUCTION

Lead Program Instructor - Environmental Law and Regulatory Compliance, Penn State University, Berks campus, Pennsylvania.
Instructor- Real Estate Investments- Temple University, Pennsylvania.
Graduate Instructor -UNLV- EGG 101, Engineering Experience. Developed and implemented a unique four component course for first year engineering students.

PUBLICATIONS/TECHNICAL PRESENTATIONS (selected)

- Penn State University, Berks Campus, Lead Instructor environmental engineering and environmental law
- Residual Waste lectures
- Environmental Laws & Regulatory Compliance Instructor,
- Temple University, Pennsylvania, (1985-1987), Real Estate Investments, Instructor
- Developed and provided instruction to about 50 students per quarter in real estate investment techniques; aspects included tax implications, financing, contracts, and real estate management
- Manufacturer’s Association – Clean Air Act
- Paper presentation -American Society of Civil Engineers, What are Hazardous Substances, Materials, Wastes Toxics and Pollutants?
- Committee reports for ACI (American 315 Concrete Details Committee)
• California Society of Professional Engineers – Nuclear Issues and Answers.
• Authored paper in Soils Magazine: What your mother never told you about petroleum exclusions.
• Guest Speaker at LIUNA (AFLCIO) conferences.
• Speaker Annual Berks County Bench Bar conference-Environmental Law.
• Reviewer of The Small Business Owner’s Guide to a Good Night’s Sleep, Preventing and solving chronic and costly problems, by Debra Koontz Traverso, Bloomberg Press
• Presenter at conferences and invited speaker at several organizations.
• Authored and presented peer reviewed paper “Collision of Technology and Privacy” at international conference in November 2013, Riyadh Saudi Arabia
• Co-Authored and presented a peer reviewed paper” Under Representation of Women in Stem- Do Early Childhood Experiences Matter? At First Year Engineering Experience conference.

WORK HISTORY

2008-2010 EAS Investment and Development; Chief of Operations
2008- Present Chandra Maurya Corporation, Chief of Operations

Developed and analyzed international markets for procurement of technology, equipment and services with an emphasis on developing long-term client relationships. Areas of emphasis includes, but not limited to, solar systems, water, and power and transportation infrastructures and security technologies including installation of ballistic resistant materials and ballistic resistant vehicles UAS and UAV’s. Interact with governmental agencies. Reviewed contracts, conducted proactive environmental compliance reviews, oversaw financial analysis, negotiations and resolution of possible contract conflicts and liabilities prior to execution. Responsible for several International projects in various stages of execution.
Developed and commercialized software (Granted US patent) for Android OS based mobile devices. Inventor developed and manufactured unique products for advertising industry and special equipment for special operations of Law Enforcement.

1989 - 2009 Sudhakar Company International; COO

Lead for increasing sales from USD 1 million to 24 million dollars in10 years. Captured 35 % of market share of infrastructure markings. Developed and instituted procedures, policies, controls and methodologies and environmental compliance that established the company as the market leader in transportation infrastructure markings. Developed workflow processes, office and project controls from contract award through execution and final payment. Review and oversaw the preparation and execution of contracts and purchase orders resulting in proper use/management of finances. Provided training to personnel in establishing priorities, planning,
communications, documentation and contract provisions with special emphasis on insurance, indemnity liability and payment provisions. Created, developed a unique labor leasing program with agreements by labor unions to assist employers and potential employees.

1985 – 1990 Sudhakar Company Inc.; Owner

Executed, and managed engineering and construction contracts predominantly for the Department of Defense, and other US Federal agencies. Effectively managed and supervised all staff members and administrative office functions; and processed funds; screened and scheduled applicant appointments; successfully resolved client complaints /concerns which significantly increased revenue by 25% over a 19 month period.

1973 – 1985 Bechtel Corporation, Contracts Manager/Engineer

Lead Contracts Manager as a part of Bechtel Business Development team for L-48 for Alaska Standard Oil project proposal. Prior positions in Bechtel Corporation included senior engineer, supervising engineer, procurement manager, senior construction engineer staff and project operations positions, Legal Assistant, for nuclear plants and fossil fuel plants, tasks and assignments in multi-disciplinary fields.