Optical and Raman characterization of ALD alumina coated multiwall carbon nanotubes and nanoporous gold film

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OPTICAL AND RAMAN CHARACTERIZATION OF ALD ALUMINA COATED
MULTIWALL CARBON NANOTUBES AND NANOPOROUS GOLD FILM

by

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Bachelor of Science in Electrical Engineering
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A thesis submitted in partial fulfillment of
the requirements for the

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May 2011
ABSTRACT

Optical and Raman Characterization of ALD Alumina Coated Multiwall Carbon Nanotubes and Nanoporous Gold Film

by

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Professor of Electrical and Computer Engineering
University of Nevada, Las Vegas

Due to their large surface to volume ratio nanostructures are inherently unstable. To insure long term stability of nano-devices, they have to be rendered inert to their environment. In this study, nanoporous gold films (NPGF) and multiwall carbon nanotubes were coated with ALD alumina of varying thicknesses. Subsequently, the plasmonic property of the former and electronic property of the latter was monitored by Transmittance and Raman Spectroscopy respectively. Transmittance spectra revealed that NPGF passivated by ALD-alumina maintains its plasmonic properties, i.e. its LSPR supporting properties remained intact. Raman spectra of ALD alumina passivated MWNTs show no coating induced changes in its characteristic Raman features. This led to the conclusion that ALD alumina is a benign and suitable technique for thin film passivation of NPGF and MWNTs. This result supports the expansion of ALD’s domain as a reliable thin film passivation technique in areas of SERS based biosensor research and the passivation of carbon nanotubes.
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I would like to dedicate this thesis to my family
# TABLE OF CONTENTS

ABSTRACT.......................................................................................................................... iii

ACKNOWLEDGEMENT ......................................................................................................... iv

LIST OF FIGURES ............................................................................................................... viii

CHAPTER 1 BACKGROUND .................................................................................................. 1
  1.1. Introduction .................................................................................................................. 1
  1.2. Carbon Nanotubes ...................................................................................................... 2
  1.3. Nanoporous Gold Film ............................................................................................... 4
  1.4. Stabilization of CNT and NPGF ................................................................................. 5
  1.5. Atomic Layer Deposition ........................................................................................... 6
  1.6. Passivation material ................................................................................................. 7
  1.7. Conclusion .................................................................................................................. 8

CHAPTER 2 SURFACE ENHANCED RAMAN SPECTROSCOPY ........................................... 9
  2.1. Introduction ................................................................................................................ 9
  2.2. Normal Raman Scattering ........................................................................................ 9
    2.2.1. Raman Effect-Quantum Mechanical Theory ....................................................... 9
    2.2.2. Raman Effect-Classical Theory ........................................................................... 10
    2.2.3. Raman Selection Rules ....................................................................................... 12
    2.2.4. Advantages of Raman Spectroscopy .................................................................. 14
    2.2.5. Disadvantages of Raman Spectroscopy ............................................................... 15
  2.3. Surface Enhanced Raman Scattering ....................................................................... 15
    2.3.1. Electromagnetic Enhancement Theory ............................................................... 16
    2.3.2. Chemical Enhancement Theory ......................................................................... 16
    2.3.3. Stability Issues with SERS Substrates ................................................................. 17
    2.3.4. Stabilization of NPGF SERS Substrate by ALD Alumina ..................................... 18
  2.4. Conclusion .................................................................................................................. 19

CHAPTER 3 RAMAN SPECTROSCOPY OF CARBON NANOTUBES ................................. 20
  3.1. Introduction ................................................................................................................ 20
  3.2. Radial Breathing Mode ............................................................................................ 20
  3.3. G-Mode ....................................................................................................................... 21
  3.4. Defect Induced Mode ............................................................................................... 22

CHAPTER 4 EXPERIMENT .................................................................................................... 24
  4.1. Introduction ................................................................................................................ 24
  4.2. Instruments Used ...................................................................................................... 24
  4.3. Sample Preparation .................................................................................................. 27
    4.3.1. Fabrication of Nanoporous Gold Film ............................................................... 27
    4.3.2. Alumina Coating of NPGF ................................................................................. 28
    4.3.3. Alumina Coating of MWNTs ............................................................................. 29
  4.4. Conclusion .................................................................................................................. 31
CHAPTER 5 RESULTS AND DISCUSSION ................................................................. 32
  5.1. Introduction ............................................................................................... 32
  5.2. Results of MWNT-Alumina Composite ...................................................... 32
  5.3. Discussion of MWNT-Alumina Composite .................................................. 34
  5.4. Results of NPGF-Alumina Composite ......................................................... 36
    5.4.1. Structure Characterization of NPG-Alumina Composite ......................... 36
    5.4.2. Optical property of NPGF-Alumina Composite ..................................... 37
  5.5. Discussion-Alumina-NPGF Composite ....................................................... 38
  5.6. Conclusion ................................................................................................. 38
  5.7. Future Work ............................................................................................... 39

REFERENCES ........................................................................................................ 40

VITA ...................................................................................................................... 42
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Graphene to carbon nanotube transformation</td>
<td>3</td>
</tr>
<tr>
<td>1-2</td>
<td>Schematic representation of multiwall carbon nanotube</td>
<td>4</td>
</tr>
<tr>
<td>2-1</td>
<td>Raman Transitional schemes</td>
<td>10</td>
</tr>
<tr>
<td>2-2</td>
<td>Carbon Tetrachloride (CCl₄)</td>
<td>13</td>
</tr>
<tr>
<td>2-3</td>
<td>Raman and IR spectra of CCl₄ [19]</td>
<td>14</td>
</tr>
<tr>
<td>3-1</td>
<td>First Order Raman Spectrum for Graphite</td>
<td>23</td>
</tr>
<tr>
<td>4-1</td>
<td>Savannah S100 ALD system</td>
<td>24</td>
</tr>
<tr>
<td>4-2</td>
<td>Lab-VIEW based GUI for Controlling ALD Parameters</td>
<td>25</td>
</tr>
<tr>
<td>4-3</td>
<td>Tecnai G2 F30 S-Twin TEM</td>
<td>26</td>
</tr>
<tr>
<td>4-4</td>
<td>LabRAM HR Raman System</td>
<td>27</td>
</tr>
<tr>
<td>4-5</td>
<td>ALD deposition - TMA cycle</td>
<td>29</td>
</tr>
<tr>
<td>4-6</td>
<td>MWNT samples after ALD deposition of Alumina</td>
<td>31</td>
</tr>
<tr>
<td>5-1</td>
<td>Raman spectra of MWNTs after deposition of ALD alumina films</td>
<td>33</td>
</tr>
<tr>
<td>5-2</td>
<td>Result of Lorentzian line shape analysis of the Raman spectrum</td>
<td>34</td>
</tr>
<tr>
<td>5-3</td>
<td>TEM image of NPGF</td>
<td>36</td>
</tr>
<tr>
<td>5-4</td>
<td>Transmittance Spectra of Alumina-NPGF</td>
<td>37</td>
</tr>
</tbody>
</table>
CHAPTER 1
BACKGROUN

1.1. Introduction

The properties of materials change drastically as it is miniaturized to the nanoscale (below 100nm). When matter is confined or structured on the nanometer scale, some physics that matters little in bulk systems dominates important properties. Additionally, as the surface to volume ratio for a metal cluster becomes very large, the thermodynamically stable cluster crystal structure can change dramatically. Quantum mechanical effects, typically relevant at very short length scales, may become dominant when system sizes approach the nanometer regime. These size dependent properties can be exploited for various novel applications ranging from biomedicine to nano-electronics. There are numerous engineered nanostructures with enormous potential for applications. Here we take two of these nanostructures and discuss their potential and the challenges that must be overcome to exploit their novel properties.

Carbon nanotubes and nanoporous gold (NPG) are of particular importance in the field of biological and chemical sensing [1], [2]. The conductance of carbon nanotubes is very sensitive to adsorption of analytes [3]. This makes it suitable for the implementation of electronic biosensor. In this context a biosensor is a device that transduces the adsorption of analytes via change in its conductance. Similarly, NPG has potential application for diagnostic applications. Its thermal stability, chemical inactivity, and large surface area, ease of preparation makes it a candidate for SERS-based bio-sensing applications [4], [5].
Despite these successes, the stability of carbon nanotubes and nanoporous gold film remain an issue. Because of their inherent high surface area, they are reactive to their environment. Reaction with the environment can potentially compromise their useful properties [3]. To prevent long term device reliability problems, we need to stabilize these nanostructures against their local chemical and electrical conditions.

One way of passivating nanostructure surface is via thin film deposition technique, in which a nanometer size thin dielectric film is deposited to physically isolate the nanostructure from potential reactants in the environment. For this purpose a number of thin film deposition methods are available. Chemical vapor deposition (CVD) is one possible technique; however, it lacks precise thickness control. Atomic layer deposition (ALD) is more suitable as its self limiting process allows precise thickness control of the deposited film. Thus, using ALD we coated the two nanostructures with thin layers of alumina. Subsequent transmittance and Raman characterization of the coated samples show ALD process did not affect the properties of MWNTs and NPG leading to the conclusion that ALD is a benign coating method for the passivation of NPG and MWNTs.

1.2. Carbon Nanotubes

Carbon nanotubes (CNT) are cylindrical structures made from graphene rolled into a cylinder as shown in Figure 1-1. The manner in which the graphene layer is rolled in to cylindrical shape is specified by a pair of indices, (n, m), which determine the CNT’s chirality. Depending on the chirality vector, carbon nanotubes can be metallic (conducting) or semiconducting [6]. A general rule for determining the electronic property of CNTs is that; if (n-m) is a multiple of 3, then the CNT structure is armchair,
therefore conducting, otherwise either it is zigzag and exhibits semiconducting behavior or chiral [7]. Although it is desirable to be able to grow CNTs with specific chirality, current growth mechanisms are not chirality specific; therefore large scale synthesis results in inhomogeneous tubes [8]; both metallic and semiconducting tubes are found in any given sample.

![Graphene to carbon nanotube transformation](image)

Figure 1-1 Graphene to carbon nanotube transformation

Carbon nanotubes are also categorized by type as SWNT and MWNT. A MWNT is formed when SWNTs of varying diameter slide into each other to form concentric shells as illustrated in Figure 1-2. The tubes are held in place by weak van-der-waal forces. Unlike SWNTs, MWNTs are zero band gap structures, therefore conducting. Due to the contribution from delocalized electrons in each tube, the conductivity in MWNTs is
thought to be multiplicative. It has also been reported that MWCNTs are able to sustain high current density up to $10^9$ A cm$^{-2}$; a desirable property for application in molecular electronics. Although much of the properties of MWNTs are less understood than SWNTs due to the complex interlayer interaction, their high current carrying capacity makes them promising potential for application in electronics.

![Schematic representation of multiwall carbon nanotube](image)

Figure 1-2 Schematic representation of multiwall carbon nanotube

1.3. Nanoporous Gold Film

Nanoporous materials have many potential applications due to their very high surface area to volume ratio. NPG is of particular interest because of its resistance to corrosion as well as the ability to tailor the gold surface to be sensitive to various chemical and biological species. Nanoporous gold can be synthesized by subjecting an alloy of gold
and silver to a process known as dealloying, during which the silver is selectively removed from the alloy. This is commonly accomplished by immersion of the alloy into concentrated nitric acid. In the process, the silver is selectively etched away leaving behind nanoscale pores in the range of 5-100 nm depending on process parameters; length of etching time and concentration of nitric acid. The ratio of the volume of gold to the overall volume is between 25% and 35% [9]. The resulting high surface area gold nanostructure is exploited for its plasmonic property in applications such as surface enhanced Raman spectroscopy among others [1].

SERS based biological and chemicals sensing technology puts much emphasis on sensitivity and limit of detection. This requirement is met by SERS substrates with optimal plasmonic properties. Recent studies show promising plasmonic properties of NPG that indicate the potential of this nanostructure in biosensing applications [2]. NPG films prepared by a chemical dealloying method have distinctive plasmonic properties in that they can simultaneously support localized and propagating surface plasmon resonance [11]. As we will see in later sections, the ability to support localized surface plasmon resonance is important aspect of the SERS substrate.

1.4. Stabilization of CNT and NPGF

Electronic devices that integrate nanoscale components as their active device are susceptible to instability. This is due the fact that the large surface area to volume ratio of nanomaterials, which means the constituent atoms are exposed to the environment. If a chemical reaction takes place between the surface atoms and environmental reagents, then bond is formed. This leads to altered electronic property of the nanostructures. Even physical adsorption can contaminate and degrade device performance in some
cases. Unfortunately, air molecules, humidity, and other adsorbents in the environment want to adsorb on the pores of gold NPGF. Simple physical adsorption of dust particles can alter LSPR conditions due to its dependence on dielectric surrounding. This renders the NPGF unstable SERS substrate incapable of reproducing results. Later we will see how this problem of device instability arising from interaction with environmental chemical species can be resolved by applying a thin layer of passivation coating via thin film deposition methods [12].

1.5. Atomic Layer Deposition

Atomic Layer deposition (ALD) is a thin film deposition technique characterized by its ability to coat surfaces with atomically precise, conformal, and pinhole free layers. The self limiting process of ALD means that once the surface saturates the coating ends. The excess precursors are purged out by purge gas (typically nitrogen or argon) to prevent parasitic CVD deposition on the substrate. This limits one ALD cycle to be precisely one atom thick, approximately 0.1 nm per monolayer. The overall thickness depends on the number of cycles, which makes it easier to control the film thickness.

One thing that makes ALD suitable for passivation of SERS substrates is its precise control of thickness. Since surface enhanced Raman scattering is distance dependent, the molecule of interest has to be within specified distance in order to couple with the LSPR on the NPGF. Making the separation distance between the target molecule and the hot spot where the LSPR is excited can undermine the enhancement factor. In consideration of this, the thickness of the passivation layer has to be thick enough to insure perfect passivation of the device against the environment and thin enough so the molecule is within range of SERs enhancement.
According to theoretical analysis, SERS enhancement can be expected from molecules within the decay length of electromagnetic fields, i.e. 0-4 nm [13]. The characteristic distance, at which SERS signals decrease by half is generally about 0.7 nm [14]. This type of thin spacer layer films can only be achieved by a deposition method that allows precise control of film thickness. ALD satisfies this requirement. By contrast CVD and PVD are not capable of conformal deposition in this range.

Another advantage of ALD is that it is better at step coverage in high surface area to volume ratio structures than CVD and PVD. Although Chemical vapor deposition and Physical vapor deposition are broadly used in IC industry for deposition of gate dielectric and interconnect coating, they are limited to coating thickness above 10 nm [15]. Additionally, high aspect ratio structures present a huge challenge for CVD and PVD. The highest aspect ratio that can be coated with 100% step coverage is 10:1. PVD is even worse; it can only guarantee 50% step coverage at 10:1 aspect ratio. By contrast, ALD can deposit conformal coating in high aspect ratio nanostructures, such as carbon nanotubes [16]. Thus ALD is better suited for deposition of thin passivation dielectric layers on high surface to volume ratio materials.

1.6. Passivation material

A material for passivation of NPGF and CNTs has to have certain characteristics. In the current context, NPGF is to be developed as a SERS active substrate for single molecule detection. To this end, a material with high affinity for bio-molecules and good adhesion to the substrate is preferred. Secondly, it has to be robust and inert as to withstand chemically corrosive environments. It must prevent diffusion of impurity atoms through it. ALD satisfies all these conditions, additionally, ALD Al$_2$O$_3$ has been
shown to be free of defects and pinholes which enable them to be used to passivate semiconductor surfaces in electronic device fabrication [17].

1.7. Conclusion

In this chapter we introduced carbon nanotubes and nanoporous gold film. The unique properties of carbon nanotubes such as chirality dependent electronic property and ballistic transport are briefly mentioned. Brief introductory description of nanoporous gold synthesis and its plasmonic properties was given. The role of NPGF in SERS-based biosensing is also introduced. Atomic Layer Deposition is introduced as the most suitable thin film deposition technique for passivation of the nanostructures against environmental exposure.
CHAPTER 2
SURFACE ENHANCED RAMAN SPECTROSCOPY

2.1. Introduction

In this Chapter, we discuss theoretical background to Raman Effect and the selection rules governing Raman emission. This is followed by a discussion of the techniques developed to enhance the inherent weakness in normal scattering, mainly, surface enhanced Raman scattering. Problems with lack of reproducibility with SERS substrates (NPGF) followed by a solution to remedy such problems is presented (ALD passivation) is presented.

2.2. Normal Raman Scattering

2.2.1. Raman Effect-Quantum Mechanical Theory

From Quantum mechanical consideration, Raman Effect is the inelastic scattering of incident photon by matter resulting in exchange of energy between the photon and the scattering molecule. If the molecule was initially in the ground state, then the interaction with the photon would excite it to an intermediate electron state known as virtual level as shown in. In this case, the photon loses energy upon scattering by the molecular system. This is called stokes Raman scattering. On the other hand, if the molecule were initially in excited state, the interaction would excite it to a virtual level as shown in Figure 2-1 and when it relaxes back to ground state, it emits a photon of higher frequency than that it absorbed. The difference in frequency of the absorbed and emitted photons is plotted as anti-stokes Raman scattering. According to Boltzmann’s distribution, molecules are more likely to be in the lower energy states under thermal equilibrium. Therefore the
interaction is more likely to result in the loss of energy by the photon upon scattering. As a result, stokes Raman lines are of higher intensity than anti-stokes.

2.2.2. Raman Effect-Classical Theory

The classical description is more intuitive and models the Raman Effect as the inelastic scattering of light due to exchange of energy between an induced dipole in the molecule and the vibrational modes of the molecule. When light interacts with matter, the electric field component of the Electromagnetic (EM) radiation induces an oscillating dipole in the molecules of the sample. This induced dipole (polarized molecule) starts to radiate, during which it may interact with the vibrations of the molecule, which at times, results in energy exchange with the vibrational modes of the molecule. When this is the
case, the resulting radiation is of lower or higher frequency, and the applied field is said to be Raman scattered by the molecules in the sample. The shifts in frequency are characteristic of the scattering molecule; and it is this ability to extract information that earns Raman scattering its place in analytical technique for the elucidation of molecular structure.

Starting from the simple fact that the magnitude of the induced polarization \( P \) is directly proportional to the molecular polarizability \( \alpha \) and the incident electric field \( E \), one can easily derive equation 1.1. The actual derivation is left out and it is found in [18]. The classical treatment results in equation 1.1 for the polarization of the molecule in which the presence of inelastically scattered fields is evident.

\[
P = E_0 \alpha_0 \cos 2\pi v_0 t + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \frac{\cos 2\pi (v_0 + v_j) t}{2} + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \frac{\cos 2\pi (v_0 - v_j) t}{2} \tag{1.1}
\]

where \( P \) is the polarization of the molecule, \( \alpha_0 \) the polarizability at equilibrium position, \( \left( \frac{\partial \alpha}{\partial q} \right)_0 \) is the rate of change of \( \alpha \) with respect to the change in \( q \), evaluated at the equilibrium position; \( q \) is the nuclear displacement as the molecule vibrates with frequency, \( v_j \).

From equation 1.1, we can clearly see that the induced polarization contains three terms. The first term represents the Rayleigh scattered light, which carries the same frequency as the incident electric field with its intensity scaled by the factor, \( \alpha_0 \). The second and third terms are frequency shifted scattering and they represent the anti-stokes and stokes Raman lines. Looking at the last two terms reveal the effect of molecular vibrations (\( q \)) on the induced dipole.
2.2.3. Raman Selection Rules

Conservation of energy dictates that during the interaction of a photon with a molecule the angular momentum must be conserved. Any vibrational transition that violates this rule is not allowed. A rule that specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation is known as selection rule.

Like any vibrational technique, Raman transition from one state to another is subject to selection rule as well. Any vibrational mode in a molecule cannot be Raman active unless the angular momentum of the molecule is conserved during transition from one quantum level to another. From classical model of the Raman Effect, one can see this rule in effect as well. A quick look at equation 1.1 reveals that for the stokes and anti-stokes terms to survive, the molecule must show a change in its polarizability with respect to the normal coordinate, q, i.e. $\frac{\partial \alpha}{\partial q} \neq 0$, which is essentially Raman selection rule stated classically. Thus, not all vibrational modes of a molecule can be probed by Raman Spectroscopy. Fortunately, the selection rules of Infrared Spectroscopy are complementary to that of Raman, so vibrational modes of a molecule that are not Raman active can be probed using IR.

To appreciate how the shortcoming of Raman is complemented by IR, let us see how both techniques work to probe all modes of vibrations in Carbon tetrachloride (CCl₄). CCl₄ molecule consists of four chlorine and one carbon atoms with a total of five atoms in the molecule as shown Figure 2-2. Therefore, the number of normal modes, excluding translational and rotational are $3(5)-6 = 9$. “Due to high symmetry of the molecule, doublets and triplets of identical types of vibration (transformed into one another by
symmetry operations), with evidently are indistinguishable frequencies. This is called degeneracy [19]. Thus, in reality, only four out of nine vibrations are different (unique). Out of these four unique vibrations of CCl₄, v₃ is not Raman active (very weak) because its polarizability remains constant (\( \partial \alpha / \partial q = 0 \)) during vibration. Raman spectrum of CCl₄ is shown in Figure 2-3. v₁₋₄ are the normal vibrations of CCl₄. Notice that v₁ is missing in the IR, but strong in Raman. By contrast, v₃ is weak in Raman, but strong in IR. This example illustrates how the use of IR and Raman together can elucidate molecular structure of a material.
2.2.4. Advantages of Raman Spectroscopy

There are several advantages in using Raman spectroscopy over other spectroscopy methods. 1) Raman spectrum can be obtained from aqueous solution with little interference from water, which accounts for 50 % of the contents of biological samples [20]. 2) Minimal sample preparation is required. 3) Raman spectroscopy is nondestructive method in that spectra can be obtained without opening the container in which the probed substance is placed.

Figure 2-3 Raman and IR spectra of CCl₄ [19]
2.2.5. Disadvantages of Raman Spectroscopy

The biggest disadvantage of Raman Spectroscopy is the low scattering cross section. Only one in a million incident photons undergo Raman Scattering. This necessitates long acquisition time in order to obtain sufficient number of Raman scattered photons. This causes a problem as long exposure of the sample can result in photo degradation of the sample. Additionally, Raman scattering is susceptible to interference from fluorescence emission. This is because normal Raman scattering has a very low cross section, $10^{-30}$ cm$^2$ per molecule, which is few orders of magnitude lower than fluorescence cross section [13]. This makes it too weak to be used for the detection of low concentration analyte without enhancement. In the early days, these disadvantages coupled with lack of instrumentation and source of monochromatic light proved Raman impractical. All these changed in 1974, when a routine lab experiment unraveled enhanced Raman signal from Pyridine molecules adsorbed on electrochemically roughened silver electrodes [21]. The finding came to be known as Surface Enhanced Raman Scattering (SERS).

2.3. Surface Enhanced Raman Scattering

Surface enhanced Raman scattering (SERS) is a phenomenon where Raman-active molecule spatially confined on rough metallic surface show enhanced Raman scattering intensity of several orders of magnitude. The researchers who observed this extraordinary enhancement attributed it to the large surface area provided by the electrochemically roughened silver electrodes, which in turn increased adsorption of scattering molecules [21]. This explanation did not satisfy fellow researchers, therefore the search for better explanation continued. It was not long before more acceptable
models emerged to explain this extraordinary increase in Raman emission. These models are formally known as Electromagnetic and chemical enhancement mechanisms.

The electromagnetic model is based on resonant coupling of incident light with the localized surface plasmons on rough metallic nanostructures. EM enhancement is responsible for most of the Raman field enhancement. The chemical enhancement is due to charge transfer interaction between the metal and adsobate molecule. Its contribution is minimal 10-100.

2.3.1. Electromagnetic Enhancement Theory

The Electromagnetic mechanism model of SERS is based on resonant coupling of the incident light with localized surface plasmons on the surface of metallic nanoparticles. When light is incident on a molecule adsorbed on metallic nanostructure, Raman scattering by the molecule is greatly enhanced. The signal is enhanced in two ways: first the incident electric field is enhanced by resonant coupling with the LSPR. The enhancement is as $E^2$. The second enhancement is due resonant coupling between the LSPR field and the Raman scattered signal. This enhancement is also as $E^2$. The total enhancement due to resonant excitation of localized surface plasmons is $E^4$. Thus, it is the overall enhancement associated with the incident and scattered fields that we call Electromagnetic contribution to SERS [22]. This modeling enabled experimental research to continue with a primary objective of optimizing the enhancement.

2.3.2. Chemical Enhancement Theory

In addition to the EM enhancement discussed above, evidence exist that attest the existence of a second enhancement mechanism, which is believed to operate independent of the EM enhancement. In order to prove the existence of this second mechanism,
consider the SERS intensities of two molecules with nearly identical polarizability. Under the same experimental conditions, the EM enhancement of these two molecules should not show a large difference due to the fact that EM mechanism is nonselective Raman amplifier. But this was not the case; CO and N\textsubscript{2} differ by a factor of 200 in their SERS intensities despite their nearly identical polarizability and the same experimental conditions. This difference which is unaccounted by EM enhancement is attributed to chemical enhancement by inference. The contribution from chemical enhancement varies greatly, but often the gain is in the range between 10-100 [18].

The combined SERS enhancement factor of up to $10^{14}$ has propelled Raman spectroscopy to the forefront once again. Surface enhanced Raman spectroscopy is one of the actively researched areas with promising potential for sensitive biological sensors. Under suitable conditions, sensitivity of SERS can be sufficient for detection of a single molecule [23].

2.3.3. Stability Issues with SERS Substrates

Despite the promising analytical applications of SERS, stable SERS substrates capable of reproducible enhancement have been elusive [24]. This is due to the fact that the EM enhancement is based on nanoscale geometries with high surface to volume ratio. Such structures are highly unstable, therefore exhibit signal fluctuations in response to minute environmental variations. Thus, despite SERS enhancement factor reaching single molecule level, until stable SERS substrates capable of operating under various environment are fabricated, SERS based biological sensors cannot be implemented.
2.3.4. Stabilization of NPGF SERS Substrate by ALD Alumina

Atomic Layer deposition (ALD) is a thin film deposition technique characterized by its ability to coat surfaces with atomically precise, conformal, and pinhole free layers. The self limiting process of ALD means that once the surface saturates the coating ends. The excess precursors are purged out by purge gas (typically nitrogen or argon) to prevent parasitic CVD deposition on the substrate. This limits one ALD cycle to be precisely one atom thick, approximately 0.1 nm per monolayer. The overall thickness depends on the number of cycles, which makes it easier to control the film thickness.

One thing that makes ALD suitable for passivation of SERS substrates is its precise control of thickness. Since surface Enhanced Raman Scattering is distance dependent, the molecule of interest has to be within specified distance from the SERS substrate for effective electromagnetic coupling to occur. Separating the hot spot from the probed molecule by a thick passivation film can undermine the enhancement factor tremendously. In consideration of this, the thickness of the passivation layer has to be thick enough to insure perfect passivation of the device against the environment and thin enough so the molecule is within range of SERs enhancement. Thus, ALD’s precision control of film thickness proves invaluable in the optimization process of SERS substrates.

Another advantage of ALD is that it is better at step coverage in high surface area to volume ratio structures than CVD and PVD. Although Chemical vapor deposition and Physical vapor deposition are broadly used in IC industry for deposition of gate dielectric and interconnect coating, they are limited to coating thickness above 10nm [15]. Additionally, high aspect ratio structures present a huge challenge for CVD and PVD.
The highest aspect ratio that can be coated with 100% step coverage is 10:1. PVD is even worse; it can only guarantee 50% step coverage at 10:1 aspect ratio. By contrast, ALD can deposit conformal coating in high aspect ratio nanostructures, such as carbon nanotubes [16]. Thus ALD is better suited for deposition of thin passivation dielectric layers on high surface to volume ratio materials.

2.4. Conclusion

In this chapter basic background information about Raman Effect was presented. Surface Enhanced Raman scattering and models that explain it were discussed. The fact that SERS enhancement is characterized by signal fluctuation and lack of reproducibility was briefly discussed. Passivation using ALD is suggested as a solution to the instability of NPGF SERS substrates. To this end SERS substrates will be coated with ALD alumina of various thicknesses and will be characterized by optical method to see if the structure can still be preserved post-deposition.
CHAPTER 3

RAMAN SPECTROSCOPY OF CARBON NANOTUBES

3.1. Introduction

Raman spectroscopy provides a wealth of information about the properties of carbon nanotubes. Each band in the Raman spectrum of CNT, the Radial Breathing Mode (RBM), the disorder induced mode (D-band), and the high energy mode (HEM or G-band) all capture different properties of carbon nanotubes. For example, the peak position of the RBM is dependent on the diameter of the tubes, which is useful for determining the diameter of the tubes present in the sample. The spectral line shape and peak positions of the G-band contain information about the SWNT electronic property allowing us to distinguish between semiconducting and metallic CNTs. The G band spectrum also captures doping effects resulting from different charge transfer interactions with local chemical environments. Furthermore, the relative intensity of the G band to the D band is also an indicator of SWNT quality. All these rich information content embedded in the Raman spectrum of carbon nanotubes puts Raman Spectroscopy as the leading characterization technique for studying CNT properties, charge transfer interactions, structural evolution of carbon nanotubes when embedded in a matrix. In this Chapter we review the information content of RBM, D, and G Raman bands of SWNTs and MWNTs in detail.

3.2. Radial Breathing Mode

The Radial Breathing Mode (RBM) is one of the three main first order Raman active modes of carbon nanotubes with analytical value. Its Raman peak is generally observed in the range of wavenumber 150 cm$^{-1}$ to 300 cm$^{-2}$ relative to the excitation laser line. The
exact peak location is dependent on the diameter of the nanotube according to the following empirical relationship:

$$\omega_{\text{RBM}} = \frac{A}{d} + B$$  \hspace{1cm} (3.1)

where A and B are constants and their values depend on environmental variations. This relationship between the RBM frequency and tube diameter is useful for determining the diameter of the tubes present in the probed carbon nanotube samples.

3.3. G-Mode

The G band is common to all sp$^2$ hybridized carbon forms, yet each carbon form modulates the G band spectral features in a characteristic manner and clearly shows its Raman signature through it. The most basic G band spectrum is that of graphene, in which a sharp and strong G band associated with planar vibrations of C atoms is observed at around 1582 cm$^{-1}$. In CNTs the G band gets modified by curvature effects. It splits into two dominant peaks (G$^-$ and G$^+$). This splitting of the G band, which is attributed to the curvature induced phonon confinement effect, distinguishes CNTs from graphite. Thus even though, the G band is common to all sp$^2$ hybridized C forms, its spectral profile is characteristic of the probed carbon structure; a single narrow peak in the case of graphene and two superimposed double peak structure in the case of SWNTs.

Additionally, the split of the G band (G$^-$ and G$^+$) in CNTs has a wide range of analytical value. Their peak position and line width is known to carry information about the electronic structure of the CNTs. Any perturbation to the CNT electronic structure; such as charge transfer interaction, doping, etc. modulates the G-mode and is reflected in
the G-band spectral features. Therefore one can probe structural evolution of carbon nanotubes as they interact with local chemical environment.

The Splitting of the G band is also observed in MWNTs, however, it is not pronounced. Because the splitting is curvature induced effect, it is more pronounced in small diameter CNTs. Contrary to SWNTs in which small diameter tubes are accessible, small diameter tubes are buried under larger diameter tubes of the MWNTs. Therefore the G band represents the large diameter tubes. The splitting of the G band is smeared out as the tubes responsible for the G band gets larger in diameter. As the two peaks of the G-band merge, it is no longer possible to differentiate between MWNT samples and graphite. The exception to this is to establish resonance condition in which case it is possible to see Raman features associated with small diameter tubes. Therefore, it is possible to probe MWNTs spectral features completely only when resonance condition is satisfied.

3.4. Defect Induced Mode

The D-mode is a defect induced Raman mode that is observed in all carbon forms that are not perfectly crystalline. The main defect mode is observed around 1355 cm$^{-1}$ as shown in the Raman spectrum of graphite in Figure 3-1. A second defect mode (D2) at around 1620 cm$^{-1}$ also occurs as a shoulder to the G band. The D2 band is absent in highly crystalline graphite.
Figure 3-1 First Order Raman Spectrum for Graphite
CHAPTER 4
EXPERIMENT

4.1. Introduction

In this chapter, we introduce the methodology employed in addressing the research question. Nanoporous gold film and carbon nanotubes are used for studying the effect of ALD coating on the properties of nanostructures. In order to study the effect of ALD on the structural and electronic properties of these nanomaterials they are coated with ALD alumina of various thicknesses. The resulting Alumina-NPG and Alumina-MWNT composites are characterized using TEM, UV-VIS and Raman spectroscopy.

4.2. Instruments Used

The instrument used for depositing aluminum oxide on MWNTs and NPG substrates is the Savannah ALD system, S100 model manufactured by Cambridge NanoTech is shown in Figure 4-1 Savannah S100 ALD system. The sample chamber can hold

Figure 4-1 Savannah S100 ALD system
substrates up to 100 mm in size. It is equipped with two heated precursor lines capable of handling gas, liquid or solid precursors. The Savannah is capable of deposition on Ultra High Aspect Ratio substrates. With exposure mode option selected conformal and uniform deposition of films is achieved on substrates with aspect ratios of greater than 2000:1 [25].

The Savannah ALD-100 is easy to use. It allows a real time monitoring of the deposition process through a user friendly GUI. The user is able to control key system parameters such as substrate temperature and precursor dose with easy to use LabVIEW-based GUI as shown in Figure 4-2. Deposition parameters such as substrate temperature, pressure, precursor flow rate, precursor pulsing time, purge time, and the number of cycles are all set with the LabVIEW program. The deposition parameters are recorded and saved.

Figure 4-2 Lab-VIEW based GUI for Controlling ALD Parameters
Transmission electron microscopy (TEM) images were obtained using a Tecnai G2 F30 S-Twin TEM instrument shown in Figure 4-3. The TEM operates at 300 kV using a field emission gun in Schottky mode as an electron source. It allows characterization of materials at resolution down to atomic scale, point-to-point resolution equal to 2Å, and magnification of 1,000,000 times can easily be achieved.

LabRAM HR Raman System we used for characterization of MWNT-alumina composites is shown in Figure 4-4 LabRAM HR Raman System. The spectrometer is equipped with 795 nm wavelength light source. This Raman spectrometer is particularly suitable as it offers very high performance Raman microscope for analyzing the composition of the sample at high resolution [26].
4.3. Sample Preparation

Preparing nanoporous gold film (NPG) samples involved dealloying and alumina coating using ALD. MWNTs needed to be sonicated before ALD coating in order to achieve uniform dispersion.

4.3.1. Fabrication of Nanoporous Gold Film

Au film Alloy (Ag$_{70}$Au$_{30}$) and Nitric acid (NHO$_3$ 70%) was purchased from Sigma Aldridge (Milwaukee, WI). Preparation of nanoporous gold was achieved by selective electrochemical etching (dealloying) of the Ag$_{70}$Au$_{30}$ in 70 % Nitric Acid. The result was a gold film having pore dimensions of 5-30nm. Five Plastic containers were rinsed with regular water. Then they were filled with distilled water up to half capacity. The 100 nm thick Gold alloy (Ag$_{70}$Au$_{30}$) was placed on the plastic containers with DI water. Subsequently, the gold alloy was transferred to the container containing nitric acid.
in order to etch away the silver particles so that the pores can be created. Five gold alloy film samples were exposed for 5, 30, and 90 minutes. Different sizes of pores were produced depending on the time of exposure to the nitric acid. The longer the exposure time to Nitric acid the wider was the pore size. The resulting substrates were stored at room temperature.

4.3.2. Alumina Coating of NPGF

Nanoporous gold substrates were coated with Alumina thin film by ALD technique using the following pre-cursors; Tri-methyl aluminum [Al (CH₃)₃] (TMA) and water (H₂O). Film deposition was made under the following settings of the ALD reactor; temperature at 80 °C (353 K), pressure gauge of 0.2 Torr and a mass flow of N₂ at 100 sccm. (TMA and deionized water vapor were pumped alternately through the reaction chamber using Nitrogen as a carrier gas at a mass (volume) flow rate of 100 sccm (standard Cubic Centimeter per minute), a pressure of 1 torr, and a growth temperature of 80 °C. In the first cycle, TMA is introduced to the ALD reactor for an exposure time of 0.1 second, and chemical reaction starts between the TAM (Al(CH₃)₃) and the Hydroxyl group (-OH) on the substrate surface. Once the reaction is complete the non reacted gaseous bi-products are purged out by exposing the reactor to N₂ for 10 seconds. The second half of the cycle begins by introducing water (H₂O) vapor into the reactor for an exposure time of 0.1 second. The H₂O vapor reacts with the Methyl group (-CH₃) on the surface of the substrate until all –OH groups are formed again. This regeneration of –OH activates the surface for the whole process to be repeated (i.e. TMA exposure). The reactor is exposed to N₂ once again to purge out the remaining bi-products. This way deposition of a single alumina layer (one complete cycle) takes about 42 seconds.
According to previous studies, a layer of alumina deposition is approximately 0.1nm. Thus, the resulting layer is determined to be 0.1nm multiplied by the number of cycles.

4.3.3. Alumina Coating of MWNTs

MWNTs were bought from Sigma Aldridge. The sample was poured into ethanol solution in a test tube. The mixture is then placed in a sonication machine for ten minutes during which it is subjected to sonar frequency in order to achieve uniform dispersion of the CNTs in ethanol solution. Subsequently, the CNT is poured on microscopic glass strips and allowed to air-dry. Seven samples were prepared in this manner. A special care is taken to achieve uniform density of the samples on the glass strip.

The MWNT samples were coated with alumina using atomic layer deposition technique according to the following procedure. The MWNTs were placed in the ALD reactor which was set at temperature of 80 ºC. Once the temperature was stabilized,

![Figure 4-5 ALD deposition - TMA cycle](image)
TMA [Al(CH₃)₃] and de-ionized water were alternately pulsed through the reaction chamber, using N₂ as the carrier gas, at a mass flow rate of 20 sccm, a pressure of 1 Torr, and a growth temperature of 80 ºC.

In the first cycle, TMA is introduced to the ALD reactor for an exposure time of 0.1 second, and chemical reaction starts between the TMA (Al(CH₃)₃) and the substrate surface as illustrated in Figure 4-5 ALD deposition - TMA cycle. Once the reaction is complete the non-reacted gaseous bi-products are purged out by exposing the reactor to N₂ for 10 seconds. The second half of the cycle begins by introducing water (H₂O) vapor into the reactor for an exposure time of 0.1 second. The H₂O vapor reacts with the Methyl group (-CH₃) on the surface of the substrate until all –OH groups are formed again. This regeneration of –OH activates the surface for the whole process to be repeated. The reactor is exposed to N₂ once again to purge out the remaining bi-products. This way deposition of a single alumina layer (one complete cycle) takes about 42 seconds. According to previous studies, the rate of alumina deposition is approximately 0.1 nm per cycle [1]. Thus, the resulting layer is determined to be 0.1 nm multiplied by the number of cycles. Figure 4-6 shows the resulting MWNT-Alumina composite after ALD deposition.
In this chapter we introduced the methodology and instruments used. We prepared nanoporous gold films by dealloying (selective etching of silver from the gold film using Nitric acid) followed by deposition of alumina using ALD. Next we dispersed MWNTs by sonication, deposited ALD alumina passivation layers of three different sub-wavelength thickness layers. Consequently, we performed TEM characterization of NPGF. Finally we obtained transmittance spectra of NPGF and Raman spectra of MWNTs. In the next chapter the results are analyzed and results are discussed.
CHAPTER 5
RESULTS AND DISCUSSION

5.1. Introduction

Here in this chapter we present and discuss the optical response of NPG and MWNTs to various coatings of ALD Alumina passivation layer. Raman spectra of Alumina-MWNTs composites show that the G-band peak positions, the intensity of the G\textsuperscript{+} band and its FWHM is sensitive to Alumina adsorption. However, the shift in Raman emission frequency and the FWHM broadening are not significant enough to cause us concern that the property of MWNTs may have been compromised. Similarly, TEM characterization of NPGF shows successful alumina coating. Transmittance spectra obtained shows that the plasmonic properties of NPGF were intact after ALD alumina deposition. We observed a red shift in LSPR wavelength as a function of alumina thickness, which is attributed to the change in dielectric environment of the NPGF cause by the coating.

5.2. Results of MWNT-Alumina Composite

Raman spectra obtained from MWNTs coated with ALD alumina of three different thicknesses is shown in Figure 5-1. A general evaluation of the spectra shows no difference between the three spectra except for small intensity variation. After lorentzian de-convolution of the bands, however, a slight variation in the peak position of the G band is revealed.
The disorder induced (D-band) is observed around 1309 cm$^{-1}$ for all Alumina-MWNT composite samples. Its intensity, however, attenuated with increasing ALD cycles of alumina. Similar response was observed on the second order D band (D2) which was observed around 2650 cm$^{-1}$.

Figure 5-1 Raman spectra of MWNTs after deposition of ALD alumina films
The peak position of the G band showed sensitivity to an increase in ALD alumina thickness. Figure 5-2 shows Lorentz fit to the G-band region corresponding to ALD alumina coating of A) 0.2 nm B) 0.4 nm C) 0.7 nm. The fitting reveals the following frequencies; spectrum A, 1574.9 [22.2] cm$^{-1}$ and 1608 [17.1] cm$^{-1}$; spectrum B, 1574.3 [22.9] cm$^{-1}$ and 1608.4 [18.1] cm$^{-1}$; spectrum C, 1573.9 [23.8] cm$^{-1}$, 1608 [25.7] cm$^{-1}$. The number in parenthesis is the FWHM of the peaks.

5.3. Discussion of MWNT-Alumina Composite

The G-band is sensitive to surface modification of CNTs through interaction with chemical species or through charge transfer interactions [27], [28]. Information such as electronic structure, strain, and oxidation state of the CNT is encoded in the line shape of the G mode. Shift in peak position relative to the graphitic peak location around 1580 cm$^{-1}$ indicates doping. Thus in monitoring the MWCNT for any change in its features we focused on the G band. Any change in structural or electronic property of the MWNTs induced by the coating is reflected in the G band intensity, peak position, or line shape.
The G band is inherent to sp² hybridized carbon structures, as such its appearance in all of the spectra in the vicinity of 1575 cm⁻¹ indicates the preservation of the structural integrity of the sp²-hybridized carbon atoms of the sidewall nanotubes [29]. In regards to the shift in peak position of the G band, it is a well known doping effect. A frequency downshift is associated with acceptor doping (The down shift is associated with bond length expansion following charge injection as observed in alkali metal doping of nanotubes and graphite [30] and an up-shift is linked to donor doping. However, the down-shift observed in our result is relatively small ($\Delta \omega^-=0.6$ cm⁻¹ and $\Delta \omega^+=1$ cm⁻¹) compared to doping induced shift in the G band peak position reported in some of the studies. For example, the G band frequency shift associated with polyethylenimine (PEI) adsorption and electrochemical doping by alkali metals is $5$ cm⁻¹ $< \Delta \omega < 10$ cm⁻¹, which corresponds to change in charge of $\Delta Q=0.02$ [30]. This change in charge is considered low level doping [30]. Therefore, the ALD alumina induced G-band shift of $0.4$ cm⁻¹ $< \Delta \omega < 0.6$ cm⁻¹ in our case, by comparison, is not significant enough to affect the electrical property of the MWNTs.

This leads us to conclude that the effect of sub-nanometer ALD alumina on the electrical property of MWNTs is insignificant. The fact that there was no significant change in line shape is also another indicator that the doping was not of any significance. Thus ALD coating of sub-nanometer alumina layer is benign, therefore can safely be used for passivation of MWNTs against local chemical and electrical environments.
5.4. Results of NPGF-Alumina Composite

5.4.1. Structure Characterization of NPG-Alumina Composite

TEM image of alumina-coated Nanoporous gold were observed with TECNAI G2 F30 S-TWIN TEM and recorded as shown in Figure 5-3. The gray area is the gold ligament and the white region is pores. As can be seen, pores and ligaments have random morphology with different longitudinal and transverse dimensions. From the TEM image, we observe the pore size distribution range 5-30 nm in diameter. The alumina coating deposited by ALD is visible on the edges of the pores and its thickness is determined to be 0.5 nm from the deposition conditions (5 ALD cycles and 0.1 nm per ALD cycle).

Figure 5-3 TEM image of NPGF-Alumina Composite
5.4.2. Optical property of NPGF-Alumina Composite

Transmittance spectra obtained from NPGF-alumina samples that are coated with 0nm, 12 nm, and 17 nm of alumina is shown in Figure 5-4. The peak associated with the uncoated NPGF occurs at 520 nm. The peaks associated with 12nm alumina coated NPGF shows a red shift to 560 nm. Its intensity also increases. Additional increase in alumina thickness coating red-shifts the peak position as it does 17nm coating. In short, a consistent red shift and intensity increase of the transmittance peak as a function of alumina thickness is observed.

![Transmittance Spectra of Alumina-NPGF](image-url)

Figure 5-4 Transmittance Spectra of Alumina-NPGF
5.5. Discussion-Alumina-NPGF Composite

The shift in the wavelength of maximum transmittance observed in the alumina-coated NPGF medium indicates the sensitivity of localized surface plasmon excitation wavelength to the local dielectric environment. It is due to the dielectric increase in the environment of the NPGF introduced by the thicker alumina. Of interest to us here is that the NPGF capability to support LSPR after being subjected to ALD process during alumina coating. The fact that the LSPR could be excited is evidence that NPGF still satisfies the conditions for SERS activity. This is significant because the in order for EM enhancement to occur LSPR must be excited. As discussed in chapter 3, the electromagnetic enhancement in SERS is due to resonant coupling of the induced dipole in the molecule and the localized surface plasmon excitation. For this reason the preservation of plasmonic property on SERS substrates is necessary.

5.6. Conclusion

Using optical characterization techniques; mainly Transmittance and Raman spectroscopy, we demonstrated Atomic Layer Deposition of alumina film to be a benign coating technique for passivation of nanoporous gold (NPG) and multiwall carbon nanotubes (MWNTs). NPG and MWNTs coated with varying ALD alumina using TMA and H\textsubscript{2}O as ALD precursors showed no change in their characteristic optical spectra indicating that ALD alumina is a benign coating method. The LSPR supporting capability of NPG was intact after alumina was deposited indicating its plasmonic property is unaffected by the ALD process. Raman characterization of MWNTs coated with sub-nanometer ALD alumina showed no significant change in its characteristic spectral features. The G-band frequency, which is known to be sensitive to charge
transfer interactions with external chemical species remained unchanged indicating that the coating did not induce change in electronic property of the MWNTs. Thus we conclude that ALD alumina is a benign passivation technique for both NPG and MWNTs and can safely be used to stabilize these nanostructures.

5.7. Future Work

The experiments we conducted focused on answering whether atomic layer deposition affects the electronic and plasmonic properties of MWNTs and NPGF respectively. To this end, we characterized the ALD alumina coated MWNTs and NPGFs samples and found out that ALD is a benign thin film deposition. It would also be of interest to characterize the samples periodically to determine their life time. Using probe molecules, the SERS activity level of NPG can be recorded periodically. Such data can tell us the life time of the SERS substrate. The life time of CNTs may be determined in a similar fashion.
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