Fabrication of Printed Substrate for Surface Enhanced Raman Spectroscopy

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FABRICATION OF PRINTED SUBSTRATE FOR SURFACE ENHANCED RAMAN SPECTROSCOPY

by

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A novel surface enhanced Raman spectroscopy (SERS) substrate was successfully fabricated on a silicon wafer using inkjet printing and on polyethylene terephthalate (PET) using gravure printing. Silver (Ag) nanoparticle (NP) based ink, was used for roughening of the surface of silicon and PET. A thickness of 400 nm was measured for the printed Ag NP printed film on silicon and the thickness of the single and double layered films on PET were measured as 340 nm and 680 nm, respectively by using vertical scanning interferometry. The Ag NP printed SERS substrate was tested for application with heavy metal compounds like cadmium sulfide (CdS), zinc oxide (ZnO) and mercury sulfide (HgS). An amplification of the SERS intensity by up to 5 orders of magnitude was observed for all test samples, due to the presence of hotspots between the metal nanoparticle aggregates. The responses demonstrated the feasibility of the novel SERS substrate to be used in applications for detection of heavy metal compounds.
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CHAPTER 1

INTRODUCTION

1.1 Background

In recent years, there has been an increase in efforts to gain a better understanding of the dynamics of printing flexible electronic devices. Printed Electronics (PE) employs traditional printing techniques for the deposition of electronically functional inks, including organic materials with semiconducting properties, for the manufacturing of electronic devices on flexible substrates [1-5]. The traditional printing methods used include gravure, inkjet, flexography and screen printing. Some examples of printed electronics devices that have been demonstrated and are showing varying degrees of commercial application and success are printed organic thin film transistors (OTFT) [6], flexible displays [7] and flexible printed solar cells [8].

While the performance of printed electronics does not currently match that of conventional manufacturing techniques, the advantages of printing, including lower-cost manufacturing processes, low manufacturing temperatures and minimal usage of resources during fabrication, have facilitated the production and manufacturing of PE at a commercial level [9]. In the next two decades, the growth of printed electronics will have a significant impact on the electronic market. According to IDTechEX, it is estimated that the market for printed electronics will increase up to $300 billion within the next 20 years [10].
Western Michigan University’s (WMU) Center for the Advancement of Printed Electronics (CAPE) in collaboration with the Center for Advanced Smart Sensors and Structures (CASSS) consists of a broad multidisciplinary group of faculty and staff, thus providing different research opportunities for the production of PE using various print methods and instrumentation technologies for material analysis. The laboratories are equipped with inkjet, screen, gravure, and flexographic presses as well as the apparatuses to completely characterize inks and substrates and evaluate printed results and a complete set of instrumentation for both passive and active electrical device and circuit characterization. Among all the techniques available to produce PE, gravure printing is renowned among these techniques to be a high speed, high quality method for the fabrication of PE [11]. Studies have shown the use of gravure printing as a method employed for the deposition of organic material on flexible substrates [12]. Inkjet printing has also been utilized for PE applications because it is a non-impact printing process which does not require any image carrier or mask [13]. The use of inkjet printing methods for manufacturing of electronics has been reported in many research studies [14, 15].

The detection of heavy metals, which are classified as a class of toxic pollutants in soil and water, has received increasing interest in the environmental, medical and food industries [16-18]. As a result of society’s evolution, the levels of toxic materials in use has augmented at a fast pace producing toxic pollutants that are not degradable and accumulate in the environment over time [19]. For example, toxic heavy metals such as mercury (Hg), cadmium (Cd) and zinc (Zn) are known to be
responsible for poisoning and fatal illnesses in living organisms, at concentration as low as micro molar or nano molar levels [20-22].

The ability to employ enhanced Raman spectroscopy (SERS) as a viable method for the detection of heavy metals has been reported [23]. SERS is best known for its capabilities to collect real-time molecular level vibrational information while providing a fast response as well as a high level of selectivity and sensitivity [24, 25]. The measurement process requires a prepared substrate for measurements. Many studies have shown a significant interest in fabricating an efficient and low-cost substrate for SERS [26, 27]. Studies have shown that the deposition of metallic nanoparticles (NP) such as silver (Ag) and gold (Au) on a substrate have a significant impact in the enhancement of Raman Spectra [14, 28]. The NP can be deposited on the substrates by using several different deposition methods such as lithography [29], chemical vapor deposition [30], and spin coating [31]. The disadvantages of these deposition techniques entail time consumption, expensive procedures and complex methods. These disadvantages could be overcome by employing the use of printing techniques. However, there are no reports on the use of inkjet printing NPs on silicon substrates for use as SERS sensors. Recently, there has been a growing interest in fabrication of flexible substrate for SERS [26]. Polyethylene terephthalate (PET), a flexible plastic, is a good substrate for deposition of NPs due to properties such as flexibility, transparency, and availability in terms of being wither coated or non-coated (resulting in deferent surface energy). Although one recent study shows the use of gravure printing for the deposition of NPs [32], there have been no studies to investigate the use of gravure printing for fabrication of printed SERS substrate.
Therefore, in this thesis work the author reports the development of printed flexible substrates and their application for detection of heavy metal compounds using SERS.

1.2 Author’s Contributions

A list of publications describing the work performed and the results of this research follow:


Outcomes of this research work were also presented in the following conferences:


1.3 Thesis Organization

The material that will be presented in this thesis is divided into seven chapters. Chapter 2 provides an introduction to sensors; their system and different forms of sensors. Chapter 3 introduces the theory behind the operation of Raman Spectroscopy as well as Surface Enhancement Raman Spectroscopy. Chapter 4 serves as an introduction to printing with emphasis on the importance of gravure and inkjet printing. Chapter 5 provides information on the design and fabrication of inkjet printed and gravure printed substrate for SERS. Chapter 6 presents the experimental materials, test setup and test results of the printed substrate fabricated for the detection
of heavy metal compounds. Chapter 7 provides a summary of the key project findings with conclusions and suggestions for future work.
CHAPTER 2

INTRODUCTION TO SENSORS

2.1 Introduction

The detection of physical, chemical or biological changes is measured through sensor devices. These devices cover a broad spectrum of projections which are composed of transmitting and receiving signals as a result of an impulse or change in a system at equilibrium. This means sensors can respond to physical phenomenon such as light, heat, pressure, magnetism or motion and send out resulting impulse.

According to Merriam-Webster’s Dictionary, "A sensor is a device that responds to a physical stimulus (as heat, light, sound, pressure, magnetism, or a particular motion) and transmits a resulting impulse (as for measurement or operating a control)” [33]. For example, the human system is composed of many sensors that provide us data and perceptions; the most common sensors found in a human being are the five traditional senses. Senses like sight, hearing, smell, taste and touch cover the majority of the signals coming toward a body from the environment.

The input to the human sensing system may be an optical signal, sound or light which warns the human about dangerous situation or some tastes and then makes the human body to react according to the situation. An example of human sensing system in terms of watching movies is presented in Figure 2.1 [34]. In this case, the eyes and ears are the optical and hearing sensors, respectively; these signals are transferred to brain to be recognized.
Figure 2.1. Human sensing system.

Temperature controllers, automated ignition car alarm systems, touch screen devices among others systems that are examples of sensors employed on a daily basis. Sensing devices are able to detect information at a point within a process, assist in decision making and generate an output signal. The signal is then analyzed through decisive patterns for corrective action and decision making. Some examples of input/output signals are shown in Figure 2.2.

Figure 2.2. Various sensors input/output relationships.

There are two main categories of sensors: natural sensors and artificial sensors. Artificial sensors are categorized as man-made and often transmit information in electrical form using the properties of movement of electrons. The
potential of man-made sensor in responding to different physical inputs and to convert
the information into an electrical form is significantly important. The simpler
definition of a sensor can be a unit which receives an input and responses by
generating an electrical signal. In contrast natural sensors are found in living organism
such as the human body, the environment, and the planet. In the natural sensors,
information received is transmitted in the form of electrochemical impulses [35, 36].

In more general terms, a sensor can be defined as a unit that receives a signal
or measurand and responds with an electrical signal. This signal can be categorized as
a property which is detected by a sensor, then transformed as an electrical output
signal. This electrical output signal is attuned to other electrical components such as
electronic circuits and electrical systems that embody an electrical mechanism. The
output signal is a quantifiable measurement that can be interpreted in terms of
electrical capacities such as voltage, current or charge which in return can be
modified, amplified and communicated.

Sensors can be categorized according to their functionality and level of
complexity. Sensors usually fall under two common categories: direct sensors or
complex sensors and either one can be categorized in terms of how they transduce the
input signal. A direct sensor allows the direct interaction and conversion of a signal or
measurand into electrical output signals without the use of an intermediary procedure.
A complex sensor is composed of one or more intermediate transduction procedures,
which are employed in the system before direct sensor can be used to generate an
electrical output signal [34].
The term transducer refers to the conversion of energy from one form to another. This term should be distinguished from sensors, which convert different types of energies to an electrical signal.

Sensors can be categorized as being passive sensors or active sensors. A passive sensor does not require an external energy source or excitation signal to generate an electrical signal; moreover, a passive sensor generates an electrical signal directly [37]. In contrast, an active sensor needs the aid of an external source of energy to produce an electrical signal.

In addition, it is known that most passive sensors are classified as direct sensors, these sensors range from photodiode, thermocouples and piezoelectric sensors among others. These examples are passive sensors that interact through dynamic or static characteristics.

A further classification of sensors is based on a selected reference in terms of relative sensors and or absolute sensors. A relative sensor is able to detect a measurand relative to a reference state and generates a signal related to the indicated state. An absolute sensor generates a signal respectively, to an absolute physical state.

Relative pressure sensors and absolute pressure sensors are fine examples of selected reference sensors. Relative pressure sensors function on the basis of referencing a baseline of nonzero pressure, for which an output signal is generated. An absolute pressure generates a signal with respect to a zero pressure or vacuum system [38].

2.2 Sensor Systems
The simplest sensor systems available are able to detect the measurand and display its output value. The generated output value from the system can be in any format. One example of such an output is the contraction and expansion of mercury inside of a glass thermometer. This change is due to the temperature difference taking place. Another instance is the strain gauge, which converts a strain to an electrical resistance; the electrical resistance can be measured with an ohm meter, which can be transferred into voltage or current forms. An example of an electrical sensing system is shown in Figure 2.3 [34-36].

The input measurand is converted into an electrical output by the sensor. The output value can be significantly small. These output values can be subjected to interface sources [34-36].

![Sensing system with electrical output](image)

*Figure 2.3. Sensing system with electrical output [34-36].*

One of the devices which can be used in the sensors system to reduce the noise is the signal conditioner. A signal conditioner adjusts the output signal into a stronger electrical signal which in return minimizes the noise level. The output of a signal
conditioner is compatible in terms of readout devices and displays. These signal conditioners can take on different forms, such as a multiple stage amplifiers, impedance matching devices, digital computation and storage following analog to digital converters. The output value is shown on the display devices corresponding to the input measurand. The signal conditioner, display device and the sensor are electrically powered by a power supply.

Complex sensing systems require one or more transducers in order to convert a measurand to an electrical signal as an output. For example, a chemical sensor consists of a heat sensor and transducer. The transducer is in charge of converting the energy from a chemical reaction to heat and the sensor converts the heat to an electrical signal. A complex sensing system that incorporates several transducers and a direct sensor is shown in Figure 2.4

![Diagram of complex sensing systems.](image)

*Figure 2.4. Diagram of complex sensing systems.*
Typically two or more sensors are used in a system to control and present the output of multiple sensors. These sensors can vary in the type of measurand. These sensors can be all from the same type such as a number of pressure sensors or different type of sensors such as temperature sensors and biosensors.

Standardizing the output of sensors helps to minimize the amount of signal conditioning required. It means the output of the whole sensors should be the same in electrical form to the processing system. A simple sensing system that can work with multiple sensors is shown in Figure 2.5 [34-36].

An output signal generated from each sensor goes to the signal conditioner then Multiplexer (MUX). By using a MUX, the feed signal is merged into a single composite signal. A modulator captures the signal and modulates the output of the carrier oscillator corresponding to the composite signal. The signal is then fed into an amplifier prior to being passed through a high directional antenna; the high directional antenna directs the signal toward a receiving antenna. Once the signal is received, it proceeds to an amplifier where it is then fed into a demodulator in order to access the time multiplexed composite signal. In the next step, a demultiplexer decodes the composite signal so that it can be displayed by a display device.
Figure 2.5. Simple telemetry sensing system employing multiple sensors [34-36].

In general man-made sensing systems are comparatively similar to the sensing systems of living organism. For instance, some of these resemblances include the acquisition and process mechanism of physical inputs, modifications in receptors due to environmental changes, amplification and processing of receptor signals by use of micro computer or central nervous system. Figure 2.6 demonstrates the similarity of the man-made sensing systems to a living organism.
Figure 2.6. Similarity of signal processing in living organisms and in intelligent machines.

2.3 Types of Sensors

The capability of sensing peripheral stimuli is identified by sensor detection modes. There are different categories of detection modes such as thermodynamic, mechanical, acoustic, chemical and biological stimuli, each of which has its own unique characteristics.

2.3.1 Thermal Sensors

A change in temperature or energy (heat) can be detected by a thermal sensor. A thermal sensor works on the basis of detecting the change in temperature with respect to a change in an input variable. A good example of this phenomenon is a thermometer [39]. Figure 2.7 represents a typical structure for a thermometer. The main components found in a liquid-in-glass thermometer are a bulb, stem,
temperature sensitive liquid and a scale from which the temperature changes can be
differentiated. The bulb in a thermometer is the temperature sensor in which
fluctuations due to temperature stimuli can be detected. The bulb is loaded with
temperature sensitive liquid, usually mercury. The scale is a representation of degrees
which are etched or printed in the glass of the thermometer as markings. As the
temperature fluctuates, the heat sensitive liquid increases or decreases due to capillary
action. As the temperature increases, the liquid inside the bulb increases and moves
up; as the temperature decreases, the liquid in the bulb decreases. This is due to the
expansion of the temperature sensitive liquid with respect to temperature fluctuations.

The level arrangement of the heat sensitive liquid within the bulb can be read
and examined by the etch marking on the glass stem. The mathematical expression
that dictates the volume of the temperature sensitivity after expansion is [39]

\[ V = V_0 \times \rho \] (1)

Where \( V_0 \) is the volume at 0°C temperature and \( \rho \) is

\[ \rho = 1 + \alpha t + \beta t^2 \] (2)

Where \( \alpha \) and \( \beta \) are coefficients of thermal expansion of mercury and \( t \) is the
temperature.

### 2.3.2 Mechanical Sensors

The electrical output of a mechanical sensor is generated by the mechanical
deformation or the deflection of the sensing material or membrane. Changes in
position, pressure, stress, acceleration and flow rate of the measurand are some of the
factors that deflect or deform the membrane to generate a change in the electrical
output signal. A schematic representation of a tactile sensor is shown in Figure 2.8 as
Figure 2.7. Liquid in thermometer [39].

one of the many examples of mechanical sensors. Mechanical sensors are composed of two foil conductors and a spacer; one of the foil conductors is grounded and the other is connected to a pull-up resistor. As an external pressure or force is applied to the conductor that is connected to the pull-up resistor, it forces it to move in the direction of the grounded conductor. The voltage yields zero only when enough force has been applied and both conductors have come in contact with each other. This phenomenon generates an electric contact between the grounded conductor and the pull-up conductor. If two or more sensing characteristics are desired, then a multiplexer can be applied.
For calculation of the applied force, the change between the deflected plate and the fixed ground plate can be measured, which shows the change in the capacitance of the configuration. The ratio of the capacitance of non-deflected structure and deflected structure can be used to calculate the deflection distance.

2.3.3 Acoustic Sensors

Acoustic sensors function on the basis of measuring modified acoustic signals which these modifications are the outcome of the wave propagating on or throughout of the sensors ‘surface. These modifications are determined by the amplitude or the velocity of the wave by monitoring the frequency or phase of the sensor. Piezoelectric crystals are widely employed in acoustic wave sensors in terms of generating the acoustic wave. When they are subjected to an electric field, a mechanical stress is generated by the piezoelectric crystals and vice versa. An acoustic temperature sensor is depicted in Figure 2.9.
Figure 2.9. Schematic of acoustic temperature sensor [40].

An acoustic temperature sensor is embodied by a transmitter, a receiver, and a gas filled sealed tube. Piezoelectric crystals make up piezoelectric plates which are the transmitter and receiver. The enclosed gas is dry air. An acoustic wave is generated when the electric field is applied to the transmitter. This acoustic wave propagates to the sealed tube where it is converted into an electrical signal by use of a receiver crystal; the electrical signal is then amplified and sent to the control circuit. The temperature of the tube can be determined by analyzing the change in frequency of the received signal with respect to the initial signal.

The velocity of the acoustic wave is proportional to the frequency of the electrical signal and its temperature. The mathematical relation depicting this occurrence is dictated by equation 3 [40].
2.3.4 Chemical Sensors and Biosensors

Chemical sensors and biosensors are complex sensors which transform the chemical information of a measurand by use of a transducer which results in the generation of an output electrical signal. A chemically sensitive film is found in both chemical sensors and biosensors. Biosensors can be realized from chemicals with its sensing layer on top of the film which is used for detection of biological materials. The film in chemical sensors detects chemical matter, in comparison to the biosensors film which detects biological material. For instance, a sensor with coating of an enzyme or antibodies is considered as a biosensor which can detects a measurand and provides an output signal for corresponding measurand. A fundamental diagram for biosensor or chemical sensor is represented in Figure 2.10 [41].

An ion-selective electrode (ISE) is an electrochemical sensor which is representative of chemical sensors. This electrochemical sensor consist of a silver (Ag) or silver chloride (AgCl) wire to function as a transducer, a membrane that produces chemo-electric signals and an internal electrolyte for coupling of the Ag electrode and membrane. The potential within the membrane can be detected on the silver wire based on the movements of the ions between the measurand and the membrane.

\[ v \approx 331.5 \frac{T}{\sqrt{273.15}} \text{ m/s} \]
2.3.5 Optical Sensors

The functionality of optical sensors is based on converting a measurand into an optical quantity after which time an optoelectronic transducer is used to generate a subsequent electrical signal. These optical sensors are categorized as being complex sensors. Optical sensors are comprised of optical waveguides and optical fibers. Optical fibers are made up of core and cladding. The refractive index of the core in the optical fibers ($n_1$) is always greater than the cladding’s ($n_p$), Figure 2.11 illustrates the basic structure of optical fibers utilized in optical sensors. To prevent light propagation losses into the fiber and accomplish complete internal reflection, the angel of incident light should be higher than a special value, called the critical angle. The critical angle ($\phi_r$) is obtained by the following equation, 4 [40]

$$\phi_r = \sin^{-1}\left(\frac{n_p}{n_j}\right)$$

As the light enters the optical fiber, if the angle of introduced light into the optical fiber is above the critical angle it will continue traveling through the fiber and
reflect in a long distance without propagation loss. On the other hand, if the angle of incidence above the critical angle contains a limit after which the light will not be inflicted to the optical fiber; this is determined as the angle of acceptance. Equation 5 presents the sine of the angle of acceptance, which is defined as the numerical aperture (NA) [42],

$$NA = \sqrt{\frac{n_j^2 - n_p^2}{n_p^2}}$$ (5)

Figure 2.11. Basic structure of optical fiber.

Glass and plastic are the main types of raw materials utilized to fabricate and develop optical fibers, which are used for wavelengths in the visible light region. Material such as glass and plastic along with reflective and polished coated hollow tubes are used for channeling light in near and far infrared regions.

Fiber Bragg Grating (FBG) is the most appropriate example that describes an optical fiber sensor [43]. The FGB sensor observes the shift in wavelength produced by the returned Bragg signal, as a function of the measurand. Figure 2.12 represents the main principle of the Fiber Bragg Grating strain sensor. Sources with spectra
broadband are applied to introduce a beam of light into the sensor system involving gratings. Furthermore, the gratings mirror for narrow spectra of light wavelengths is known as the Bragg's Wavelength [43]

\[ \lambda_B = 2n_{eff}\Lambda \]  

(6)

Where,

\( \lambda_B \) is the Bragg’s wavelength

\( n_{eff} \) is the refractive index

\( \Lambda \) is the grating period

\[ \text{Figure 2.12 Fiber Bragg Grating sensor [43].} \]

2.4 Sensors Specifications

2.4.1 Sensitivity

The change of output electrical quantity over the small change in input variable is a ratio defined as sensitivity [41]. The slope of the sensor response curve yields the sensitivity with respect to the sensor’s output which is represented as a
function of the input variable. In addition it can be defined in terms of the transfer function with respect to the input variable. The derivative expression of sensitivity is represented as [44],

$$\frac{\partial X}{\partial M} = \text{sensitivity}$$

(7)

Where,

$X$ is the output of the sensitive material property

$M$ is the input variable

### 2.4.2 Selectivity

The entire types of sensors described above are fabricated to be purposely selective of variables that can be biological, chemical or physical in nature. The selectivity in a sensor is determined by the level of responses of responses outputted by the sensor towards the desired or undesired variable [41].

An Array of sensors can be used for selective detection of desired variable from collection of desired and non-desired variables. For example, if a set of a number of $m$ sensors, are sensitive to the identical $n$ number of quantities, then by considering ($n \geq m$). the sensor’s response is dictated by the vector following form [41],

$$(r_1 = f_1(x_1 \ldots x_m))
\quad (r_n = f_n(x_1 \ldots x_m))$$

(8)

Where,

$x_1$ through $x_m$ are manifold of variables

$f_1$ is the function of the manifolds

$r_1$ through $r_m$ are the vectors
This vector representation computes the sensitivities of the sensors with respect to the involved qualities through the use of a Jacobian matrix [45].

\[
S = \left( \begin{array}{cccc}
\frac{\partial f_1}{\partial x_1} & \cdots & \frac{\partial f_1}{\partial x_m} \\
\vdots & \ddots & \vdots \\
\frac{\partial f_n}{\partial x_1} & \cdots & \frac{\partial f_n}{\partial x_n}
\end{array} \right)
\]  

(9)

A Jacobian matrix will show the maximum selectivity of the array of sensors when the matrix is rank \(n\) and it can be diagonalized. This is possible when the array has at least \(m=n\) particular sensors.

### 2.4.3 Noise

Any sensor, no matter how well designed or constructed produces undesired irregularities and disturbances in the signal. These irregularities distort the output electrical signal causing errors while affecting the sensor. There exist two types of noise; systematic noise and stochastic noise. Systematic noise is caused by the design of the sensor where tolerance, quality of material and calibration are the basis of such irregularities in the sensor’s signal. Stochastic noise is caused by unpredictable and sporadic disturbances within the sensor. There are occurrences where a sensor’s noise is not considered a major predicament and can have little to no impact on the output signal, since the noise within this sensor is very small in comparison to the fluctuation of the physical elements. Noise affects the overall performance and presents errors within the sensor, causing intolerances in the sensor over the entire range of frequency spectrum. The equivalent power spectral density in all frequencies is defined as white noise. One of the examples of white noise is Johnson noise, also called thermal noise,
which exists in a resistor. In every physical, biological or chemical sensor, noise is substantial; it cannot be eliminated just prevented [41].

2.4.4 Accuracy

Accuracy is an imperative factor in any sensor. Characteristically, the measurement of the inaccuracy of a sensor is used to describe the accuracy of the sensor. Inaccuracy describes the highest deviation point from the ideal input-output variable value; this deviation can also be defined by taking the difference between the actual output and computed output for a given input. In reality, every sensor executes its functionality with some type of deficiency, which as a result, present a substantial source of alterations in the transfer function of the sensor system. These alterations may come from workmanship, design errors, manufacturing tolerances along with other limitations. Although it is preferable that a sensor perform with little inaccuracy, it is virtually impossible to have sensor with broad transfer functions not be limited to a specified accuracy.

2.4.5 Calibration

Calibration is the rectification of a specific variable to a certain position or value for an overall transfer function. The sensor needs to be calibrated to prevent inaccuracy or error that may cause any variation in the sensor’s functionality. Calibration in sensors relieves some of the tolerances imposed by the manufacturer and decreases the interface (readout circuit and signal conditioning). An illustration of this concept is presented when a conductometric sensor has to be calibrated with a given accuracy of ±1 μS/cm for measurement of humidity test equipment of higher accuracy (an accuracy of ±0.5 RH).
During the calibration process, a new transfer function will be described for a sensing system. A mathematical relationship with specific variables is developed in order to account for the overall transfer function system. An overall system includes the entire circuit and its components (which contains the sensor). Equation 10 shows the mathematical form for the linear systems and Equation 11 for the exponential models. These variables should be determined in terms of the calibration of the system.

\[ Y = a + bt \]  \hspace{1cm} (10)
\[ Y = ce^{kt} \]  \hspace{1cm} (11)

Where Y is the output electric signal.

Variable a and b are used for the linear model and c and k for the exponential.

### 2.4.6 Hysteresis

Prior conditions or measurements may affect the current sensor value. As a result, the same measurement conditions arrived at from different paths may have different values. When the paths are defined and predictable, a hysteresis error can be defined [46].

The main causes of hysteresis are friction and construction disfiguration. A good example of hysteresis is when for a temperature sensor, the temperature increases from 0 °C to 24 °C the output voltage is 8 mV at 12 °C, but if the temperature decreases from 24°C to 0°C the output voltage is 4mV at 12°C. In this case the sensor has hysteresis of 4 mV at 12°C. This example is shown in Figure 2.13.
2.4.7 Nonlinearity

Nonlinearity is the maximum divergence in a sensor that occurs when a real transfer function deviates away from an ideal transfer function. Nonlinearity is estimated by drawing a straight line representing the ideal transfer function and superimposing it onto the real non-linear transfer function over a dynamic range.

A graphical representation evaluates the deviation and span between the real transfer function represented by the straight line that lies on the graph. This straight line lies diagonally across the graph in between equidistant lines where the real transfer function is graphed over the dynamic range of the device. Figure 2.14 represents the nonlinearity curves. Calibration can eliminate the sensor nonlinearity when it is larger than an acceptable linear tolerance.
2.4.8 Resolution

Traces of miniscule and incremental changes influence the input variable which can be detected or sensed over the range of the sensor; this is known as resolution of the sensor. The resolution of a sensor is dependant on the type of quantity being measured. Noise affects the resolution of the sensor and does not allow the sensor to work properly. Therefore, narrow bandwidth filters are often utilized to reduce the noise within the sensor. Yielded outputs from the sensor can be summed and the signal power of the measurements can be computed by the square of the summed elements. The noise power increments linearly and are assumed to be
independent. As the rapid changes of the measured values are modified, the application of the system becomes more restricted and limited.

2.4.9 Saturation

The output of each sensor does not change in respect to the change in the input due to some working limitations. Figure 2.15 demonstrates the incensement of input measurand after the point of saturation for the output. After this point, the sensor does not respond to a change in the input.

![Saturation Diagram](image)

*Figure 2.15. Saturation of the sensor.*

2.4.10 Dead Band

The unresponsiveness given by a range of input variables in a sensor as the output signal of the sensor remains in close proximity to an invariable value or a value...
of zero is defined as the dead band. Figure 2.16 shows a representation of dead band taken from a sensor system. As it is observed from the graph, the unresponsiveness or insensitiveness to change in the sensor is denoted by a constant band as the input variables are subjected to the system.

![Dead Band Diagram](image)

**Figure 2.16.** Dead band of the sensor.

### 2.5 Summary

Sensors work on the basis of producing an output variable as a responsive measure to the input stimuli and range of variables within the sensor. Complex sensors along with electronic circuits in a sensing system are considered a complete system which displays the output values of a measurand. Sensors convert physical, thermal, mechanical, acoustic, optical, chemical and biosensing quantities into
electric signals depending on the method detection. An introduction to the sensing systems functionality and components has been presented and discussed. In the next chapter Raman scattering will be presented as a method for detection of toxic heavy metals.
CHAPTER 3

RAMAN SCATTERING

3.1 Introduction

Raman spectroscopy can be described based on inelastic scattering of light which happens because of the interaction between the laser source and the vibration modes or states of the test molecules. This interaction causes a frequency shift between the incident and scattered photons and is known as the molecular vibration energy. As a result, the spectrum from the excited molecule provides a structural fingerprint of the molecule which has interacted with incident light. An enhancement in the Raman signal can be achieved by Plasmon resonance which occurs due to the interaction between light and a metal surface. Metallic materials which have good optical properties can provide a high plasmonic resonance. Silver (Ag) and gold (Au) are an example of these materials. There is no limit how small can be the structure for fabrication of SERS substrate but there is a need to have a much smaller dimensions rather than wavelength of light which connects SERS to the nano technology. Normal flat metallic structures can be used as a SERS substrate but the resulting enhancement from these structures is much lower than nano-structures. Surface areas of these substrates play an important role in the SERS. Roughened metallic surface which can provides a large electromagnetic field is a suitable substrate for obtaining a high intensity Raman signal. Properties of analyte and its interaction with substrate are another important aspects of process. If the molecule does not have a high intensity Raman signal, some modifications such as using larger area or using a substrate with
high enhancement is needed. To obtain the enhancement in the intensity of Raman spectra the molecule should be very close or on the nanoparticles (NPs). The optical frequency built these NPs creates an electromagnetic field which enhances the Raman spectra. The advantages of SERS include the acquisition of the Raman spectra in a very short period of time and its ability to analyze analytes without any sample modification. The unique fingerprint and label free usage of Raman spectroscopy has made it a very favorable method for identification of different type of materials. In this chapter the theory of Raman scattering will be presented. Mechanism of SERS and important parameters such as Substrate, analyte and enhancement factor will be introduced.

3.2 Raman Scattering Theory

3.2.1 Theory of Scattering

Scattering can be described as an interaction between molecules and the photons from incident light which provides an emitted or scattered photon in all directions [49]. If the absorbed photon and emitted photon have the same energy level and same wavelength this scattering is called elastic scattering or Rayleigh scattering [49]. Even though these photons have the same level of energy they might have different directions and polarization. But if the scattering process causes a change in the energy level of the absorbed and emitted photon, the scattering is called inelastic scattering [50]. There are two different class of inelastic scattering: 1) Stokes scattering and 2) Anti-Stokes Scattering. In the case of stokes scattering, both the frequency and the energy level of emitted photon are shifted. The incident photon has an interaction with the molecule at the ground mode and the molecule moves to a higher vibrational
excited state. For this case, the scattered photon has less energy compared to the incident photon [49, 50]. In Anti-Stokes scattering, the emitted photon is shifted in frequency and energy level, but the incident photon interacts with the molecule at the excited state, which causes the molecule to move to a lower vibrational state [49]. In the Anti-Stokes case, the scattered photon has a higher energy rather than the incident photon. Figure 3.1 shows the different scattering types energy levels.

\[ \begin{array}{c}
\text{Excited energy state} \\
\text{Virtual energy state} \\
\text{Ground energy state} \\
\text{Incident light}
\end{array} \]

\[ \begin{array}{c}
\text{Rayleigh scattering} \\
\text{Stokes scattering} \\
\text{Anti-Stokes scattering}
\end{array} \]

*Figure 3.1. Rayleigh scattering vs. Stokes and anti-Stokes scattering [49].*
3.2.2 Raman Scattering

Raman scattering can be described based on theory of inelastic scattering of light. This scattering happens because of the interaction between laser source and vibrational modes or states of a molecule. This interesting phenomenon was discovered by Chandrasekhara Venkata Raman in 1928 and resulted in him being awarded a noble prize in 1930.

The frequency shift between an incident and scattered photon can be described as molecular vibration energy [48, 49]. As a result, the spectrum of the emitted molecule provides a structural fingerprint of that molecule which has interacted with incident light [48-50]. During Raman scattering, there is always a higher possibility for Stokes Raman scattering in comparison to Anti-Stokes Raman scattering. This can be due to the higher intensity of the Stokes Raman band rather than the Anti-stokes at room temperature. Because of the nature of molecules; there are more molecules in the ground energy state than in the excited vibrational state at room temperature. This by increasing the temperature the number of molecules in the first excitation state will increase and it is anticipated that of more molecules will exist in this state rather than the ground state.

3.2.3 Resonance Raman Scattering

If the energy level of incident or scattered photon is close to the level of electronic transitions of the molecule, the virtual state will resonant with one of the electronic levels in the molecule. This phenomenon causes an enhancement in the effectiveness of the amount of Raman scattering up to several order of magnitudes.
This phenomenon, which is shown in Figure 3.2, is called Resonance Raman Scattering (RRS) [49, 50].

3.2.4 Raman Spectrum and Raman Shift

The energy difference between photons during scattering is called Raman shift and it is positive for Stokes scattering and negative for Anti-Stokes scattering [49, 50]. The Raman shifts are shown with cm$^{-1}$ and the intensity of Raman shift is dependant on the incident wavelength. In most case, a Raman shift is shown as a function of Raman intensity. Figure 3.3 shows an example of SERS for Carbon Nanotubes (CNT) to illustrate the concept of SERS. Those peaks shown in this figure correspond to the vibrational modes of the molecule, which are based on the group theory and vibrational motion of the molecules [48-50]. This vibrational energy of each mode determines the Raman shift of a peak corresponding to that mode; these peaks are unique for each material. The Raman intensity varies from each mode to another due to the fact that the total intensity integrated for each peak is relative to the corresponding mode.

3.2.5 Raman Cross-Section

A cross-section is an important parameter in determining the efficiency of Raman spectroscopy. By definition, the linear relationship between the signals produced by the Raman process to the intensity of incident light in respect to molecule position is called a Raman cross-section [49, 50]. This definition relates the intensity of scattered photons to the intensity (power) of incident light, but it does not consider the direction of the profile of the scattered photon.
Figure 3.2. Resonance Raman Scattering.

3.3 Surface Enhancement Raman Spectroscopy (SERS)

Having reviewed the theory behind Raman scattering the discovery and background of SERS can now be discussed. The mechanism of SERS and related topics will be presented as well as the definition of the Raman enhancement factor and different types of enhancement found in a Raman peak. In 1974 Fleischmann, Hendra and McQuillan reported the observation of a huge amplification in the Raman spectrum of pyridine in the presence of silver electrodes, which were roughened electrochemically [49, 52].
Figure 3.3. Example of Raman peaks for CNT [51].

At first they thought that this large enhancement is due to larger amount of target molecule which covered bigger surface area but in a later report by JeanMaire and Van Duyne and Albrecht and Creighton [49, 50] this high enhancement in intensity of Raman signal was presented as being the result of the formation of hot spots on the boundaries of NP leading to the observed enhancement of the electromagnetic field.

The important issue associated with Raman scattering is the weakness of the Raman Spectrum. Basically SERS is an enhancement of the Raman signal up to several orders of magnitude. This enhancement is mainly due to the interaction between light and metal surface which is related to the effect of Plasmon resonance. Plasmon resonance will be explained in section 3.3.1.3 [49].

A SERS effect happens when the molecule is very close to or on a metallic surface. Only in this situation does Plasmon resonance enhances the Raman spectrum
Due to the dependence of enhancement in Raman to Plasmon resonance and optical properties of a metallic surface, this feature requires an in depth understanding of different fields of study, particularly chemistry, physics and electrical engineering.

3.3.1 Important Parameters for SERS

Substrate and analyte play very important roles in SERS measurements. The importance of these two parameters will be explained in following sections. Also, the plasmonic resonance, which is the main reason for enhancement in SERS, will also be discussed.

3.3.1.1 Substrate

In a simple definition, a good SERS substrate is one, which provides high Plasmon resonance and enhances a weak Raman spectrum. These substrates provide a high amplification of Raman spectrum. It has to be mentioned that the enhancement from these substrates can be uniform or there might be a huge variation in enhancement. This enhancement usually comes from a metallic surface such as gold or silver, which are both very commonly used in the fabrication of SERS substrates due to their optical properties [53] which makes them able to provide a good Plasmon resonance in the visible or near infrared range. SERS measurements have been reported on different metallic surfaces such as copper and platinum, although with lower enhancement than gold and silver.

SERS substrates can be classified into three types based on the following forms of materials:

- Metallic particles in solution such as a colloidal solution
• A planar metallic structure which is array of nanoparticle that are supported by a planar structure such as glass and silicon

• Metallic electrodes.

Metallic electrodes had an important role in the SERS process and even its discovery, but because of their low enhancement factor they are not being used as much as before. One of the good examples of metallic particles in solution can be the tracing of the molecule in water where Au and Ag colloidal can exist and amplify the Raman spectra. The same colloids can be attached or dried on the appropriate substrate to fabricate the planar metallic structure [49, 50]. In this work, the author used a planar metallic structure as the substrate for SERS.

3.3.1.2 SERS analyte (probe)

The intensity of Raman scattering is one of the most important factors in selecting appropriate probes for SERS. Orientation of the molecule on the substrate and toward to the incident light play a major role in the intensity of Raman spectrum. Also, the intensity of Raman Spectra is dependant on the power of laser source. Molecules having the electromagnetic field close to exciting laser energy are considered as a good candidate to be used as a SERS analyte [54]. In addition the probe should be able to absorb on the SERS substrate. Most of the molecule can be attached to the metallic surface; however some of them might need a chemical process and treatment. Figure 3.4 shows the comparison between Raman and SERS
Figure 3.4. Compression of Raman peaks for CNT in the Raman and SERS. The red line shows the Raman picks for CNT in the absence of Metallic Surface and the Blue line demonstrates the Raman picks for CNT under SERS.

For the same molecule, there might be some slight differences between SERS and Raman spectrum due to the SERS process. Enhancement in the Raman signal is mainly the result of Plasmon resonance [49] which happens due to hot spots. These hot spots occur due to plasmonic resonance which is wavelength dependent, so the amplification of the peaks can be different [49]. Also, the amplifications might differ because of the Raman mode symmetry of the molecule and orientation of the molecule on the surface.

The Raman spectrum from molecules provides a unique fingerprint for that specific molecule and makes it a very efficient method to be used in the detection of heavy metals. For many applications, if we can amplify the Raman spectrum, it can be useful. Thus, it can be used for the detection or identification of molecules, drugs, and explosives.
SERS is commonly used in various applications which are related to usage of metal surfaces [49]. The light scattered from the analyte can show some effect of metallic surface and also can be used for the study of Plasmon resonance. It can show the effect of plasmonic resonance on electromagnetic field built from the interaction of light with a metallic surface [55]. SERS can also be used as a tool for detection and identification of a single DNA molecule [56]. Figure 3.5 shows the history of publication about Raman and it shows that Raman spectroscopy has been gaining much interest.

3.3.1.3 Plasmonic

Plasmonics is the study of the properties of metals and their interaction with light results in an electromagnetic field from this interaction [49, 50]. Recently, due to progresses in nano science, it has been possible to design and fabricate metallic structures in the scale of nano meters. This development has opened another window to the study of the characterization of metallic NPs, which is also sometimes referred to nano plasmonics. There is a strong overlap between plasmonic and SERS. It is

Metals have the ability to reflect light very well. This ability along with the conductive properties of metal come from the existence of free electrons in the conduction layers. These unique properties enable the optical characterization of metals to be analyzed by their dielectric function [49, 50]. The Plasmon resonance of metal cannot be explained before analyzing the electromagnetic mode that can be
identified by dielectric function. The dielectric function describes the electromagnetic modes of molecule which resonate with the incident light. This possible to use SERS as a tool for plasmonic studies of different materials and in fact, the plasmonic effect is the main reason behind enhancement in SERS.

interaction between light and molecule produces a local electromagnetic field which locally enhances the Raman spectrum. It means that the optical resonance resulting from interaction between light and metal which is due to presence of free electrons in conduction layer of metals release energy and enhances the Raman spectrum [49, 50]. The appropriate metal to be used in SERS should have these two properties:

1. The real part of dielectric function should be large in magnitude and negative.
2. The imaginary part of dielectric should be small.

The dielectric function can be explained based on dielectric permittivity of material. Some of the materials have a large dielectric constant and they are not known as a conductive material. It means this kind of materials cannot provide huge electromagnetic field which can amplify the Intensity of Raman spectrum so they cannot be used as proper substrate for SERS. More understanding of this theory is presented in reference [49].

For instance, if a small metallic sphere is considered to interact with an electromagnetic field from incident light, the electromagnetic field inside of the sphere can be described as [49]

\[
E_{ln} = \frac{3e_m}{e(\omega) + 2e_m} E_o
\]

(12)

Where \(e_m\) is the relative dielectric constant and \(e(\omega)\) represents dielectric function. The electromagnetic field inside of the sphere \(E_{ln}\) is dependent on the electromagnetic field of incident light \(E_o\). In this case, if the denominator of the formula is very small, close to zero, the fraction will be very large. This is not possible for dielectric materials which have a high dielectric constant. By using metallic particle due having very small imaginary part of the dielectric function and a negative real part, the denominator of fraction can be very small. At the point of having a real part of the dielectric function close to \(-2e_m\) this fraction will be very large. It means the electromagnetic field of the sphere is enhanced. This enhancement is due to the large optical resonance. This resonance will result in enhancement of the intensity of Raman spectrum peaks [49].

### 3.3.2 Enhancement Factor
The Enhancement Factor (EF) of a target molecule can be defined as a comparison between the intensities of the Raman peaks obtained with and without the use of metallic NPs, under similar test conditions [50].

There are different definitions for enhancement factor based on dependence of SERS on different parameters such as characteristics of incident light, calculation of numbers of molecule which are contributing in the process, orientation of the analyte on the substrate, analyte absorption properties, different form of substrate (liquid and planner) and set up for spectroscopy. There are four methods for calculation of enhancement factor and their properties and the mostly common used method is introduced in this section.

3.3.2.1 Single Molecule Enhancement Factor

A Single Molecule Enhancement Factor (SMEF) is the amplification of a molecule at a specific point [49, 57, 58]. This enhancement is dependent on the localization of the target molecule on the metallic NP surface as well as the orientation of the NPs to the direction of the incident laser [49, 50, 57]. This definition of the SMEF is mathematically shown below:

\[\text{SMEF} = \frac{I_{\text{SERS}}^{SM}}{\langle I_{\text{RS}}^{SM} \rangle}\]  \hspace{1cm} (13)

Where \(I_{\text{SERS}}^{SM}\) is the intensity of the spectrum under SERS and \(I_{\text{RS}}^{SM}\) is the average of the intensity of the Raman spectrum per molecule for the same analyte. The main problem associated with this definition is that in the Raman process many molecules contribute in producing a Raman signal and usually many molecules are measured to
obtain a Raman signal. Therefore it is very complicated to make sure the obtained Raman signal is not from the contribution of group of molecules.

### 3.3.2.2 SERS Substrate Enhancement Factor

This definition provides a comparison between enhancement factors of different substrates and looks at the average of the enhancement of substrates which is mathematically shown below:

\[
EF = \frac{I_{\text{SERS}}/N_{\text{Surf}}}{I_{\text{RS}}/N_{\text{Vol}}}
\]

Where \(N_{\text{Vol}}\) is the average number of scattered molecules for Raman Spectrum and \(N_{\text{surf}}\) is the average number of adsorbed molecule under SERS measurement.

This definition of EF has been often used by many researchers and authors in different works [49, 59]. This method has been used as a representative of enhancement for substrate. Determining the number of molecules which contribute in the production of a SERS spectrum is not an easy task and we usually use an estimate for the number of molecules in SERS [49].

If the substrate properties are known completely it is possible to have an accurate definition of \(N_{\text{surf}}\) and \(N_{\text{Vol}}\) and identify the SERS Substrate Enhancement Factor (SSEF) in terms of the experimentally measured spectrum [49, 57].

\[
SSEF = \frac{I_{\text{SERS}}/\mu_M \mu_S A_M}{I_{\text{RS}}/c_{\text{RS}}H_{\text{eff}}}
\]
Where \( c_{RS} \) is the concentration of the target molecules in the non-SERS measurement and \( H_{eff} \) is the height of the scattered volume [1]. \( \mu_M \) (m\(^2\)) is the density of the surface of the structure and \( \mu_S \) (m\(^2\)) is the density of the molecule on the metallic surface.

Because of the difficulty in estimating of \( \mu_S \) and \( \mu_M \) this formula is not often used.

### 3.3.2.3 Analytical Enhancement Factor

For some of the application the concern is how much enhancement can be predicted from SERS comparing with the signal from non-SERS condition. In this case base on concentration of analyte the analytical enhancement factor (AEF) is used. The AEF can be explained mathematically as [49, 57, 58]:

\[
AEF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}}
\]  

(16)

Where \( C_{SERS} \) is the concentration of target molecule under SERS measurement and \( C_{RS} \) is the concentration of the same molecule in the same condition of experiment in the absence of metallic surface. This definition is depended on many factors such as adsorption properties and coverage of substrate and also the number of adsorbed molecules. So, sample preparation has an important role in this definition of EF. Since AEF strongly dependant on the preparation of analyte this method cannot be applied for representation of different substrates.

### 3.3.2.4 Enhancement Factor Estimation Based on Cross-Section Measurement
The direct measurement of the cross-section is very time consuming and require the use of special instruments. The alternative method is measurement of cross-section with respect to reported cross-section of standard reference. In this case the cross-section can be calculated mathematically as [49, 57]:

\[
\left(\frac{d\delta RS}{d\Omega}\right)_{sample} = \left(\frac{d\delta RS}{d\Omega}\right)_{Ref} \frac{I_{Sample}}{I_{Ref}} \frac{C_{Ref}}{C_{Sample}}
\]  

(17)

Where the C is the concentration of target molecule and I is the intensity of measured peak under SERS and in the absence of metallic surface. The Raman spectrum is measured under SERS and non-SERS, then the cross-section can be calculated under SERS and in the absence of metallic surface. By comparing these two values, EF will be calculated. This method is used for the case where the SERS substrate is in the form of nanoparticles in solutions [49].

In this work, we used the Substrate EF formula due to having employed a planar structure as the substrate for SERS. This method is a representative of the substrate and shows the efficiency of different substrate. There are many reports on using this method in this case for the calculation of EF [59].

3.3.3 Principle of Enhancement

Enhancement in SERS includes two terms, electromagnetic enhancement and chemical enhancement. It has been reported that electromagnetic enhancement has a much higher effect on the enhancement of a Raman spectrum [49-52].

3.3.3.1 Electromagnetic Enhancement

The basic working principle of Raman spectroscopy lies in the fact that a tiny fraction of the incident photons undergo inelastic scattering which causes a change in
frequency of the electromagnetic field [60]. The intensity of the Raman signal is proportional to the electromagnetic field of an analyte, which is mathematically given as [61]

\[ I \propto E_a^2 \]  

(18)

Where \( I \) is the intensity of the Raman field and \( E_a \) is electromagnetic field of the analyte.

An enhancement in the Raman signal can be achieved by electromagnetic interaction between light and metal which is due to the Plasmon resonances [62-64]. The closeness of the molecules to the metallic surface is a very important requirement to obtain this enhancement. Plasmon resonances of these metal NP builds the optical frequency field, which creates the electromagnetic field that results is the enhancement of Raman spectrum. The deposited metal NP on the substrate in the molecular scale is not uniform and this causes a different electromagnetic field on the surface based on the location of NP. A very high enhancement can be achieved at some points. These points, called hot spots, are shown in Figure 3.6 [62-64].

![Figure 3.6. A schematic illustration of SERS “hotspots” between adjacent silver nanoparticles. These hotspots generate strong electromagnetic fields that cause the enhancement of Raman scattering.](image)
When an analyte is loaded onto the substrate, the molecules settle in the hotspots. This causes spatially localized surface plasmon resonances where the electric field of the laser enables an enhancement in the intensity of the Raman field which is given mathematically as [65]

\[ I \propto (E_a + E_p)^2 \]  \hspace{1cm} (19)

Where \( E_p \) is the electromagnetic field because of the added metallic NP.

The vibrational transitions in RS, that happen during the scattering of light by molecules, almost always start from the lowest vibrational energy levels (with quantum number \( n = 0 \)) [49, 66]. The vibrational transition normally occurs at the next highest level (\( n = 1 \)), which causes strong infrared (IR) or Raman modes, that are called "fundamental bands" [66]. Transitions to higher levels (\( n = >2 \)) cause much weaker IR and Raman "overtone bands" [66]. The group theory thus makes it possible to predict which of the bands will be IR, Raman or IR-Raman active. It has to be mentioned that not all of the vibrational modes in the molecule are Raman active. Group theory based on symmetry of molecule can explain why some of these modes are not Raman active. Because of the symmetry the incident light might not be able to induce transition between different levels of vibrational modes, those modes are Raman inactive. In addition some of the active modes have the same arrangement between their vibrational levels. These modes preset the same Raman peaks [67].

3.3.3.2 The \( E^4 \) Approximation Method

\( E^4 \) approximation method is one of the methods which has been used for the prediction of enhancement in SERS. In this method, it hypothesized that the Raman
Spectroscopy is happening on or close to the metallic surface. This enhancement is divided into two terms including a local field intensity enhancement \( M_{\text{Loc}}(L) \) and directional enhancement factor \( M_{\text{Rad}}^d(R) \). In the case for a single molecule, the enhancement factor will be presented as below [49]:

\[
SMEF = M_{\text{Loc}}(L)M_{\text{Rad}}^d(R) \tag{20}
\]

In this formula \( M_{\text{Loc}}(L) \) shows the field intensity with respect to the intensity in absence of the metallic surface and \( M_{\text{Rad}}^d(R) \) demonstrates the enhancement achieved by Raman emitted dipole. Calculation of \( M_{\text{Rad}}^d(R) \) is very difficult and for simplicity it is usually assumed that \( M_{\text{Loc}}(L) \approx M_{\text{Rad}}^d(R) \). Based on this definition of \( M_{\text{Loc}}(L) \) SMEF is described as: [49]

\[
SMEF \approx M_{\text{Loc}}(L)M_{\text{Loc}}(R) \approx \frac{|E_{\text{Loc}}(L)|^2 |E_{\text{Loc}}(R)|^2}{|E_{\text{Loc}}|^2 |E_{\text{Loc}}|^2} \tag{21}
\]

When this is taken at (L=R) it demonstrates \(|E|^4\) as:

\[
\frac{|E_{\text{Loc}}(L)|^4}{|E_{\text{Loc}}|^4} \tag{22}
\]

This model only predicts the radiation enhancement and does not estimate any enhancement based on substrate and surface [49].

3.3.3.3 Chemical Enhancement

Chemical enhancement is another form of enhancement which occurs in the SERS. In this type of enhancement the probe has to attach chemically to the metallic surface. The chemical enhancement in the Raman spectrum can be explained as a charge transfer mechanism [49, 50].

This effect involves the transition to empty orbital of a molecule from the Fermi level of metal and on the other hand formation of substrate and target molecule
changes the properties of molecule such as becoming resonance Raman scattering [49, 50]. The amount of contribution of the chemical effect to Raman enhancement is still of much controversy. Most of the studies have shown a much higher contribution due to the electromagnetic effect rather than the chemical effect. In some cases, the difference between calculated enhancement factors and measured enhancement factor is referred to as the chemical enhancement factor.

3.4 Applications of SERS

Surface enhancement Raman Spectroscopy can be used in different fields such as; biomedical applications, nanotechnology, gemology, drug industry applications, and detection of heavy metal compounds, semiconductors and bioscience [55].

3.4.1 Application of SERS in Detection of Heavy Metal Compounds

There has been an increasing interest in the development of highly sensitive and selective systems for the detection of minute quantities of toxic heavy metals that have been responsible for environmental pollution [17]. Existence of heavy metal compounds, even at concentrations as low as micro molar, have a harmful effect on the human body, animal life and nature [18]. These common pollutants which can be found in water and soil cause dangerous effects on the brain and nervous system as well as several types of bone diseases [68]. Different techniques such as UV-vis spectroscopy [69], plasma mass spectrometry [70] and colorimetric analysis [71] have been reported for the detection of heavy metals but these methods need sample treatment which makes the detection process time consuming and expensive. These disadvantages can be surpassed using surface enhanced Raman spectroscopy (SERS) which is an analytical tool that has been used for the detection of heavy metals due to
its high sensitivity, selectivity and capability of providing molecular level vibrational information [72-74].

3.5 Summary

Theory of Raman scattering as well as SERS was introduced. Mechanism of enhancement and different methods for calculation of enhancement factor were discussed. There are different methods for fabrication of SERS substrate. Recently there has been an effort for employing of traditional printing techniques the for manufacture of these substrates. In the next chapter different printing techniques and their ability to deposit materials onto substrate will be presented.
CHAPTER 4

INTRODUCTION TO PRINTING TECHNIQUES

4.1 Introduction

Ongoing research and development in the area of printed flexible electronic devices and its research and development has led to the incorporation of traditional printing techniques in the development and manufacturing of electronics [75, 76]. Printed electronics has the capability of being fabricated in big masses without the intricate processes of electronics that involve conventional silicon manufacturing technology, which require complicated photolithographic patterning procedures, high temperature and high vacuum deposition methods [77]. The advantages of printed electronics such as cost efficiency, flexibility and lightweight products are contributing factors of this new technology which utilizes resourceful materials and provide mechanical flexibility during their fabrication.

4.2 Types of Printing Techniques

Printed techniques can be characterized by the four traditional methods of printed techniques employed in the fabrication of printed electronics. These are screen printing, inkjet printing, offset printing and gravure printing. Flexography and gravure printing techniques are defined as roll-to-roll printing, mainly because a film or web passes through numerous rolls. Inkjet printing is considered for its thin film printing; while screen printing is known for printing thick film layers. A more elaborate
explanation of the printing techniques discussed thus far is found within the context of this thesis.

4.2.1 Screen Printing

Screen printing is considered a pressure like process; in which the image carrier (mask) is not in direct or physical contact with the substrate. Figure 4.1 shows a schematic configuration of the screen printing method.

Screen printing is comprised of a screen printing plate or mesh and a fill blade or squeegee and a screen printing plate or mesh. Generally squeegees are fabricated from rubber or polymeric raw materials. The screen printing plate consists of a frame which holds the screen mesh and the stencil which is the image carrier. A common material that makes up the frame is steel or aluminum for their hardiness and ease of cleaning. The screen or mesh is composed of screen fabric which is a veil like material composed of metal, fabric, plastic or other type of material depending on the ink and screen’s functionality. The stencil can be made of many types of materials depending on its purpose. The screen mesh and stencil materials highly depend on the type of solvents and cleaning agents to be used during printing. A dollop of ink is deposited on top of the screen mesh and it is swept with the squeegee on top of the screen with an applied force and high pressure. The ink passes through the screen mesh and is transferred onto the substrate when the ink is stroked across the mesh [78].
4.2.2 Inkjet Printing

A non-impact printing process such as inkjet does not employ the use of a stencil (image carrier) or mask which is ultimately dependable on the type of transfer methods utilized. Inkjet printing is characterized by two types of printing techniques as continuous inkjet or drop on demand inkjet. Drop on demand inkjet printing can be based on thermal on piezoelectric actuation. Figure 4.2a, b and c illustrate the difference between these classifications.
A continuous or consistent stream of ink is generated during printing process which is electronically controlled in continuous inkjet printing. Through the use of high voltage an electrostatic field is formed and the ink droplets are subjected to it by charging an electrode and the ink droplets begin to form. The charged ink droplets are deflected through electrostatic plates where droplets that are non-deflected are transferred onto the substrate. The deflected ink droplets are recycled through the system. In comparison, a drop on demand inkjet printing produces ink droplets where they are deposited onto image areas without the assistance of an electronic field. Drop on demand inkjet printing techniques use thermal and piezoelectric techniques to generate drops of ink [79].
4.2.3 Flexographic Printing

Flexographic printing is a roll-to-roll printing technique that became popular in the 20\textsuperscript{th} century. The science behind flexographic printing involves a plate cylinder which is made of rubber or photopolymers, an impression cylinder, an anilox roll and an inking unit. The image is transferred from plate cylinder which contains raised image areas that are inked through the use of an inking unit. The inking unit transports the ink particles onto the anilox roll which is metered with the assistance of a built in doctor blade that wipes the excess ink from the surface of the anilox roll. The doctoring of the ink leaves ink only in the engraved cells of the anilox roll. This ink is then transferred to the plate cylinder. The imaged areas on the plate cylinder are elevated with respect to the overall surface of the plate cylinder. Thus, the non-image areas are recessed with respect to the surface of the cylinder and do not receive the ink. Once the ink has been deposited onto the imaged areas of the plate, it is carried by the plate cylinder to the substrate, which passes in between the plate cylinder and the impression roller. Upon contact with the substrate the image carried by the plate cylinder is impressed onto the substrate with the help of the impression roller as back support [79]. Figure 4.3 shows the Flexographic printing process.
4.2.4 Gravure Printing

The gravure printing process includes an image carrier which is the gravure cylinder, an ink fountain, doctor blade and an impression cylinder as demonstrated in Figure 4.4. Copper coated steel is the main raw material from which the gravure cylinder is made. The cylinder has small recessed cells that are engraved onto the surface of the copper coated steel to form the desired image. These cells can be electromechanically engraved, electrochemically etched or laser engraved. The image carrying cells hold the ink when the cylinder is submerged into the ink fountain. The
impression cylinder is manufactured with materials like rubber. These ink containing
cells get filled with the ink in the ink fountain where doctor blade wipes off the
remaining ink on the surface of the cylinder. The ink in the cells impressed onto the
substrate where an impression cylinder supports the back of the substrate for
impression [80].

![Diagram of gravure printing process](image)

*Figure 4.4. Gravure printing [80].*

### 4.3 Why Gravure and Inkjet printing?

High quality, high velocity printing, numerous ink film thicknesses, low
viscosity inks and simple processes are just some of the characteristics that contribute
to gravure printing [79]. These characteristics offer a significant number of
advantages over other conventional printing processes. The undemanding and
effortless process of gravure printing offers the simplistic procedure of transferring
the ink onto the substrate [79]. Whereas, flexographic printed images obtain an
appearance of dense ink in the exterior edges of the printed designs giving the images
a halo appearance. Screen printing is facing limited image resolution. Gravure printing has many attributes that allow the ink to be transferred to the substrate in a very efficient and high speed manner covering a broad range of printing area without alterations [79]. Table 4.1 summarizes resolution, film thickness and printing speed of different printing techniques. This table describes the resolutions along with the ink film thicknesses and printing speeds of the most common printing processes. In comparison with the rest of the printing techniques, gravure is by far the highest when it comes to speed and posses the highest resolution (smallest features) of them all. This table is based on Employing of these printing methods for deposition of graphic inks on the substrate. In case of fabrication of printed electronics the feature sizes will be different.

Table 4.1. Comparison of conventional printing techniques [78, 79].

<table>
<thead>
<tr>
<th></th>
<th>Resolution</th>
<th>Inkfilm thickness</th>
<th>Printing speeds*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Screen</strong></td>
<td>50 µm</td>
<td>3-60 µm</td>
<td>8 m/s</td>
</tr>
<tr>
<td><strong>Inkjet</strong></td>
<td>20 µm</td>
<td>0.05-0.50 µm</td>
<td>2.5 m/s**</td>
</tr>
<tr>
<td><strong>Flexography</strong></td>
<td>20 µm</td>
<td>0.5-2 µm</td>
<td>5 m/s</td>
</tr>
<tr>
<td><strong>Gravure</strong></td>
<td>15 µm</td>
<td>0.5-8 µm</td>
<td>15 m/s</td>
</tr>
</tbody>
</table>

*Maximum speed based on what is used in traditional printing applications, **for 600 x 600 dpi.

On the another hand, for deposition of material on silicon, inkjet printing has a high ability because inkjet printing is a non-impact printing process which does not require any image carrier or mask, operates in continuous or drop-on-demand (DOD) modes
The DOD mode, due to its smaller drop size and higher placement accuracy, is suitable for NP deposition applications. In the DOD mode, an acoustic pulse, generated thermally or piezoelectrically, ejects the ink through the inkjet nozzles onto the substrates. A piezoelectric DOD inkjet printer uses electrical energy whereas a thermal DOD inkjet printer uses heat energy to initiate the ink transfer. A high evaporation rate of the ink solvents and the use of water based solvents restrict the use of a thermal printer thereby making the piezoelectric printer more suitable for a wider variety of printing inks and solvents.

In this study, we have used a DOD piezoelectric inkjet printer and gravure printer to develop a novel SERS substrate. Ag NP ink was deposited on top of a silicon wafer and PET to fabricate the SERS substrate.

4.4 Summary

Printing techniques such as screen printing, inkjet printing, flexographic printing and gravure printing processes which are used in the field of printed electronics have been discussed in chapter five. These printing techniques are efficient and offer many advantages in comparison with the other conventional type of printing, such as CMOS fabrication. As demonstrated in the text, gravure printing has number of advantages for printed electronics such as high quality printing, high printing speeds and simple process. Also Inkjet printing due to non-impact printing process is an ideal method for some of the fabrications. In upcoming chapters the discussion of fabrication of inkjet printed substrate as well as gravure will be presented.
CHAPTER 5

SUBSTRATE FABRICATION

5.1 Introduction to Printed Sensors

The recent development of printed electronics as well as flexible electronics leads to utilizing of traditional printing techniques for fabrication of sensors and electronic devices on the flexible substrates such as paper, plastic, and textiles [83, 84]. There are many reports on using conventional printing techniques for various applications in the fabrication of electronic devices such as radio frequency identification (RFID) tags and solar cells and displays [3, 7, 85]. Studies have also reported the use of different methods such as electron beam lithography [86] and electrochemical etching [87] for roughening the surface of silicon (Si) substrates to enhance Raman spectra by several orders of magnitude but there is no report on the deposition of NPs on silicon as a substrate for SERS.

In recent years there have been increasing interests for the fabrication of flexible substrates for SERS. Fabrication of printed substrate for SERS using inkjet printing methods was reported [26]. However, there have been no reports on a gravure printed flexible substrate for SERS.

Printed sensors and substrates for SERS have several advantages when compared to conventional sensors and substrates. The NPs can be deposited on the substrates using different methods such as spin coating [31] lithography [29], and chemical vapor deposition [30]. The disadvantages of these deposition techniques
include time consumption, expensive procedures and complex methods. These limitations could be overcome by employing the use of traditional printing techniques. Printed sensors or substrates have the benefits of low manufacturing temperatures, less waste of material during fabrication and higher productivity through continuous processing. All of these benefits lead to a more cost efficient manufacturing process.

5.2 Fabrication of Inkjet Printed SERS Substrate

A 400 nm thick film of Ag NP ink was inkjet printed on a silicon wafer, using a DIMATIX inkjet printer (DMP 2831), as an array of 21 squares each having an area of 1 cm². The ink was loaded into a DIMATIX DMC-11610 cartridge (10 pL) through a 25 mm disposable Whatman syringe filter, with a Poly vinylidene difluoride filter (PVDF) filter membrane of 0.45 μm pore size, which was used to sieve the larger particles in order to achieve smooth printing. The printed substrate was then cured in a VWR 1320 temperature controlled oven for 30 min at 100 °C. Figure 5.1 shows a photograph of the inkjet printed silicon wafer.

Films thickness was measured using vertical scanning interferometry with a WYKO RST-plus optical profiler. Fig. 5.2 shows the 3D profile of the printed silver ink with the thickness of 400nm. The profilometry image shows that even though the edges of the inkjet printed NP film were not uniform, the section of the film was more uniform further away from the edges where the measurement was performed.

Atomic force microscope (AFM) topography measurements of the printed substrate was performed to obtain the roughness of printed film. Fig. 5.3 Shows the AFM image taken with the AFM microscope Autoprobe CP (Thermomicroscopes, USA), with Proscan version 1.3 software operating in tapping
Figure 5.1. An Inkjet printed SERS substrate: The SERS substrate, consisting of an array of 21 squares (1 cm ×1 cm), was fabricated by inkjet printing silver nanoparticles on a silicon wafer and cured at 100 °C for 30 minutes in an oven.

mode. The root mean square (RMS) value of roughness for the sample was found to be 12 nm.

5.3 Fabrication of Flexible Gravure Printed SERS Substrate

A laboratory gravure press K-Printing Proofer from Testing Machines Inc was employed to gravure print single and double layered thin films of Ag NP ink, with a NP size of 20–50 nm on PET to fabricate the SERS substrate.

The thickness of the single and double layered films was measured as 340 nm and 680 nm, respectively. The printed substrate consisted of a row of 1 cm by 1 cm squares. After depositing the Ag NP, the substrate was cured in a VWR 1320
**Figure 5.2.** Profilometry scan of the printed SERS substrate illustrating silver nanoparticle film thickness of 400 nm along the Y profile.

temperature controlled oven for 20 min at 130°C. Figure 5.4 shows the gravure printed SERS substrates.
Figure 5.3. AFM image of nanoparticles on silicon wafer. Measured roughness was 12 nm.
Figure 5.4. Single and double layered gravure printed silver nano ink on PET substrate.

5.4 Summary

This chapter presents the fabrication of inkjet printed substrate for SERS as well as flexible gravure printed. It starts with an explanation about printed sensors and common methods for fabrication of SERS substrate. Fabrication and characterization of printed substrates was presented. The next chapter presents the printed substrate as a well functional substrate for SERS in which details of the materials, instruments, experiment setup and discussion on results is presented.
CHAPTER 6

DETECTION OF HEAVY METAL COMPOUNDS USING PRINTED SERS SUBSTRATE

6.1 Introduction

Capability of SERS to be used as a tool for detection of heavy metal compound has been reported [23, 49]. The detection principle is based on ability of Raman spectroscopy to provide a unique structural finger print of different materials. The effect of metallic NP on the enhancement in the intensity of Raman signal has been covered in the previous chapters. This effect makes SERS very sensitive and selective in detecting target molecules. The light from the laser source excites the molecule and the spectrum from the excited molecule is collected and delivered to the software to provide a specific Raman spectrum for the target probe. Figure 6.1 shows a schematic of the working setup of SERS for the detection of heavy metals.

6.2 Materials and Chemicals

CdS, HgS and ZnO, all in crystalline form, were purchased from Sigma–Aldrich Chemical Company. An Ag NP ink, with particle size of 150 nm, was also purchased from Sigma–Aldrich Chemical Company. An Ag NP ink (in aqueous form) from Inktec was used for the metallization of the PET A 4 inch P-type [100] silicon wafer was used as the SERS substrate. 25 mM, 45 mM 75 mM, concentrations of CdS, HgS and ZnO were prepared by mixing 25 mg of the heavy metals in 5 ml of deionized (DI) water. For the gravure substrate a 50 mM concentration of HgS and
CdS for Raman measurement and 10µM of CdS and HgS for SERS measurement, were prepared.

### 6.3 Experiment Setup and Discussion

The experiment setup is shown in Figure 6.2. The toxic heavy metal analytes were spray coated onto the bare silicon wafer as well as the Ag NP printed area.

A laser source in the near infrared region with a wavelength of 785 nm was used to excite the sample using a Raman probe (Inphotonics Inc.), with an integration time of 3 seconds at 300 mW. A spectrometer (QE 65000 Ocean Optics, 780 nm - 1100 nm) was employed to obtain the Raman spectra through the collection fiber of the Raman probe. The Raman spectra were then analyzed using Spectra Suite software (Ocean Optics) for the Raman signature spectra of the target molecules.
Integration time is defined as the period of time during which the spectrometer collects photons. By having a longer integration time it is possible to have a higher intensity, however if this time is too long then there is a possibility of saturating the spectrometer. This is because the amount of light that is striking the detector is more than what it is capable of measuring. The saturation point of the spectrometer is calculated mathematically using:

\[ \text{Saturation point} = 2^n - 1 \tag{23} \]

Where, \( n \) is the number of bits in the analog to digital convertor of the spectrometer (\( n=16 \) for QE 65000 spectrometer). Based on this calculation, the saturation point of the QE65000 spectrometer is at 65535. The optimum signal is
achieved around 85% of the spectrometers’ maximum ability. In this case it will be around 55705. The integration time was then varied and set to 3 seconds to stabilize the output signal at this optimum range.

It is also possible to minimize the amount of noise by increasing the average scanning number. In this thesis work no difference in noise was observed when the average scanning number was varied. Hence all measurements were performed with an average scanning number of 1.

6.4 Results and Discussion

6.4.1 Inkjet Printed Substrate

The Raman spectrum obtained for CdS on the Ag NP printed substrate is shown in Figure 6.3. CdS has $C_{6v}$ hexagonal symmetry with 4 atoms per unit cell [88]. According to the group theory there is one $A_1$ and one doubly degenerate $E_1$ branch which is Raman active, two doubly degenerate $E_2$ branches and two inactive $B_1$ branches [88]. The Raman spectrum yielded peaks for Ag NP at 918 cm$^{-1}$ and 1391.81 cm$^{-1}$; and for CdS at 291.91 cm$^{-1}$, 244.07 cm$^{-1}$ and 259.23 cm$^{-1}$ which are related to the Raman active $A_1$, $E_1$ and $E_2$ branches [88]. Comparing the peaks obtained on bare silicon substrates and Ag NP printed silicon substrate, an enhancement factor of 3 for CdS was observed.

Figure 6.4 shows the Raman spectrum of ZnO on Ag NP printed substrate versus ZnO on bare silicon wafer. ZnO has a Wurtzite crystal structure where all atoms are present in the $C_{3v}$ sites of space group $C_{6v}^d$, with two formula units per primitive cell [89]. Group theory predicts the Raman active optical phonons as $A_1 + 2E_2 + E_1$ [89]. The SERS response of the ZnO spectrum on Ag NP printed
substrate exhibited peaks at 381.08 cm\(^{-1}\), 410.25 cm\(^{-1}\) and 439.47 cm\(^{-1}\) which correspond to \(A_1\) (TO), \(E_1\) (TO) and \(E_2\) (High), respectively that have been reported in the Raman scattering of bulk ZnO \([90]\). Peaks at 918 cm\(^{-1}\) and 1391.81 cm\(^{-1}\) were also observed for Ag NP. An enhancement factor of 4 was observed in the Raman spectrum of ZnO on inkjet printed Ag NP when compared to that of Raman spectrum on bare silicon wafer.

\[\text{Cadmium Sulfide (CdS)}\]

\[\text{Cadmium Sulfide on Silicon Wafer}\]

\[\text{Cadmium Sulfide on Nano Silver Ink}\]

\[\text{Figure 6.3. Comparison of the Raman spectrum of cadmium sulfide on the Ag printed surface vs. cadmium sulfide on bare silicon substrate. The picture shows an enhancement factor of 3 for the spectrum obtained from the printed SERS substrate.}\]

The SERS response of the Ag NP printed substrate towards HgS is shown in Figure 6.5. The structure of HgS consists of helical spirals and is classified under the spatial symmetrical group \([91]\). The group theory predicts the Raman optical phonons.
as $2A_1 + 3A_2 + 5E$; where two $A_1$ mode symmetrical vibrations are active only in the Raman spectra; three $A_2$ mode antisymmetrical vibrations are inactive in Raman spectra and twice degenerate five E-mode vibrations that are active in RS spectra [91].

Raman peaks at 249.13 cm$^{-1}$ for the $A_1$ mode and 203.36 cm$^{-1}$ for the E mode were observed for HgS on the Ag NP printed silicon substrate and peaks at 918.49 cm$^{-1}$ and 1391.81 cm$^{-1}$ were also observed for Ag NP. The Raman spectrum of HgS on Ag NP printed substrate was 5 times higher than the spectrum obtained for HgS on bare silicon wafer.

![Graph](image)

*Figure 6.4*. Comparison of the Raman spectrum of zinc oxide on the Ag printed surface vs. Zinc Oxide on bare silicon substrate. The picture shows an enhancement factor of 4 for the spectrum obtained from the printed SERS substrate.

The enhancement of the SERS response obtained can be attributed to the electromagnetic enhancement mechanism which is a direct consequence of hot spots
created by the agglomeration of the printed nanoparticles [92]. In the hot spots or the region between the nanoparticles, which are also called as “nanogaps”, the electromagnetic field is known to be very intense [93, 94]. The electromagnetic field is thus dependent on the hotspot or nanogap size which is directly related to the nanoparticle dimension. Research studies on silver and gold nanoparticles have shown that as the gap between the particles decreases, as a result of decreasing the nanoparticle size, there is an increase in the electromagnetic intensity which leads to enhancement of Raman signals [95-97].

Figure 6.5. Comparison of the Raman spectrum of mercury sulfide on the Ag printed surface vs. mercury sulfide on bare silicon substrate. The picture shows an enhancement factor of 5 for the spectrum obtained from the printed SERS substrate.

6.4.2 Gravure Printed Substrate
The response of the single and double layered gravure printed SERS substrate toward HgS is shown in Fig. 6.6. Raman peaks at 249.13 cm\(^{-1}\), 279.37 cm\(^{-1}\) and 339.21 cm\(^{-1}\) were attributed to HgS on the Ag NP printed substrate. The peaks detected at 856.16 cm\(^{-1}\), 1131.50 cm\(^{-1}\) and 1605.30 cm\(^{-1}\) were related to the Ag NP.

Figure 6.7 shows the Raman spectrum for CdS. The peaks at 856.16 cm\(^{-1}\), 1131.50 cm\(^{-1}\) and 1605.30 cm\(^{-1}\) were related to Ag NP and the peak at detected at 259.23 cm\(^{-1}\) is from CdS.

![Mercury Sulfide (HgS)](image)

*Figure 6.6. Comparison of the Raman spectrum of mercury sulfide on single and double layered SERS substrate vs. mercury sulfide on bare PET substrate.*
Figure 6.7. Comparison of the Raman spectrum of cadmium sulfide on single and double layered SERS substrate vs. mercury sulfide on bare PET substrate.

The Raman spectra of the test analyte that was spray coated on bare PET and Ag NP printed PET are overlaid for comparison. The intensities of the Raman spectra for the test analytes on the Ag NP printed substrate was compared with the Raman spectra for the test analytes on bare PET. This comparison demonstrated an enhancement factor of 5 orders of magnitude for the peaks at 294.13 cm\(^{-1}\) for HgS and at 259.23 cm\(^{-1}\) for CdS on the single and double layered Ag NP printed substrate, respectively. These peaks are due to the group theory which has been explained previously. The obtained enhancement factor was by using substrate EF method which is shown below [49]:
The enhancement factors obtained can be attributed to the effect of plasmonic resonance, which is a phenomenon that is caused mainly due to interaction between light and metallic NP [98], in SERS. The weak Raman spectrum is enhanced by several orders of magnitude due to the introduction of strong electromagnetic fields at locations known as hotspots on the printed SERS substrate [99]. Hotspots or nanogaps, are regions created between the NPs due to the agglomeration and non-uniformity of NPs, in the molecular scale [100].

### 6.5 Reproducibility of Substrate

All the measurements were repeated after storing substrates for three months. A enhancement factor of 5 orders of magnitude were successfully obtained. In addition after running the SERS measurement the substrate was washed with water several times and the efficiency of the substrate was still in the 80% range of the first measurement. Figure 6.8 Shows the Raman measurement after rinsing the substrate three times. Reproducibility is not reported for inkjet printed substrate. After washing the inkjet printed substrate it was observed that NPs were washed away from the substrate so, each printed substrate was used for one time SERS measurement.
6.6 Summary

This chapter explains the response of printed substrate using silver NP ink having 150 nm particles as a reporter for SERS. This substrate was fabricated on the silicon wafer by means of inkjet printing. Also a gravure printed substrate was fabricated on PET using a silver NP ink containing 20–50 nm sized particle. The response of the printed substrates towards different heavy metal compounds exhibited a 5 orders of magnitude enhancement in the Raman peaks. The reproducibility of the substrate was tested by rinsing the substrate and repeating the measurement. Using this method it was determined that the enhancement remained in a reasonable range. The next chapter concludes the thesis and contains suggestions for future research.
CHAPTER 7

CONCLUSION AND FUTURE WORK

7.1 Conclusion

In this thesis work the author presented the fabrication of an efficient printed substrate using inkjet and gravure printing processes. Ag NP based ink with average particle size of 150 nm was used for metalizing the silicon wafer to enhance the detection of heavy metal compounds. Also gravure printed substrate using Ag NP having 20–50 nm particle size was fabricated. PET was used as the substrate. Response of this substrate toward detection of heavy metal compound was demonstrated.

Outcomes of this research are summarized as follows:

1. In this work, a novel SERS substrate by inkjet printing a Ag NP based ink on a silicon wafer was fabricated. The capability of the SERS substrate to produce an enhanced Raman effect was demonstrated by testing heavy metal compounds such as HgS, CdS and ZnO. The SERS based response of the Ag NP printed substrate towards 25 mM of CdS, 75 mM of ZnO and 45 mM of HgS showed an enhancement factor of 3, 4 and 5, respectively when compared to the response of HgS, CdS and ZnO immobilized on a bare silicon wafer.

2. A novel SERS substrate was successfully designed and fabricated using gravure printing of Ag NP ink on PET. The capability of the printed sensor to be used as a SERS substrate for the detection of toxic heavy metals was demonstrated in this
paper. While detecting HgS and CdS immobilized on the SERS substrate, an amplification factor of 5 orders of magnitude was detected as compared to that produced by HgS and CdS immobilized on plain PET.

### 7.2 Future Work

Future work includes:

1. Further studies toward improving the selectivity of the printed SERS substrates towards a wider range of biochemical.

2. Further research to develop a gravure printed substrate that is suitable for being used in a hand-held SERS (considering the need for minimization of the size of instruments) based system for the detection of a wide range of biochemical sensing applications.

3. Further enhancement is expected by bending the substrate therefore a study on the effect of degree of substrate bend on the enhancement factor is warranted.

4. Utilizing different printing techniques such as screen printing on different substrates such as different papers for fabrication of high efficiency SERS substrate.
REFERENCES


