



**Development of Amine Group Modified Silicon  
Nanowire and Integrated with Microfluidic for Lead  
Ion Detection**

by

**NURI .A .KH. EHFAED  
(1541211932)**

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## LIST OF ABBREVIATIONS

°C	Degrees centigrade/Celsius
SiNW	Silicon nanowire
Silicon nanowires	SiNWs
UV	ultraviolet
DRIE	Direct reactive ion etching
DI H <sub>2</sub> O	Deionized water
EDS	Energy-dispersive X-ray spectroscopy
CVD	Chemical vapor deposition
T	Temperature in Kelvin
nm	nanometers
BOE	Buffered oxide etch
SEM	scanning electron microscope
Si	Silicon
d	diameter
M	meter
NWs	Nanowires
rpm	revolutions per minute
cm	centimeter
s	solid
Aq	Aqueous
PR	photoresist
1D	One dimensional
M	Molar, molarity, moles
μm	microns meter
Ω	Ohm
eV	Electron volts

## **Pengubahsuaian Permukaan dan Pencirian Struktur Nano Yang Sensitif dan Terpilih Untuk Pengesanan Logam Berat**

### **ABSTRAK**

Kajian ini meyumbang kepada pembangunan di dalam pengesanan kimia yang mudah alih, boleh dipercayai dan memberi pengesanan ion yang cepat. Sumbangan ini tertumpu kepada pengesanan silikon nanowire yang mampu membezakan ion plumbum dari kumpulan ion yang ada di dalam air dan ia disebabkan oleh pengubahsuaian pada permukaan pengesanan. Kajian ini merangkumi pelbagai aspek penting di dalam silikon nanowire dan peranti mikrofluid di dalam penghasilan pengesanan kimia yang lengkap. Khususnya, suhu bilik yang berkesan dan baru boleh menggabungkan mikrofluid polydimethylsiloxane (PDMS) kepada substrat yang berupaya kepada silikon nanowire, ia merupakan satu kaedah pengesanan kimia yang baru dan dilaksanakan untuk mengesan ketepatan plumbum ion di dalam air dengan mengubahsuaikan (3-aminopropyl) triethoxysilane (APTES) yang menghubungkan saluran mikrofluid, dimana saluran ini menghantar contoh kepada kawasan penderiaan untuk mengurangkan keupayaan ketara semasa tindak balas pengesanan bagi membolehkan bendalir melalui kapilari berbanding peresapan atau alir lintang. Teknik fotolitografi disediakan melalui nanostruktur silikon (Si). Peranti tersebut telah direka menggunakan oksida kering melalui pengawalan kadar aliran oksigen di dalam relau pengoksidaan dan rangkaian seragam silikon nanowire berjaya dihasilkan. Hasil menunjukkan plumbum boleh dikesan menggunakan ketepatan yang tinggi. Spektroskopi penyerapan atom telah menunjukkan pengesanan untuk menentukan kandungan plumbum di dalam sumber air yang telah dikumpulkan. Sumber air yang diuji meliputi: air paip, air sungai, air yang dirawat, air yang ternyahion, dengan kandungan 0.0859 mg/L, 0.0929 mg/L, 0.0052mg/L, 0.0023 mg/L dan 5.8pA, 7.2pA, 4.6pA, 3.3pA tindak balas semasa. Pengesanan logam berat yang berkesan oleh pengesanan mampu diperluaskan ke rangkaian pengesanan yang lebih besar iaitu di loji rawatan air. Berdasarkan SU8, bahan ikatan mikrofluid baru digunakan dalam pengesanan kimia nano elektrik untuk penderiaan ion dan menyiasat pengukuran elektrik yang dibenarkan untuk pengesanan label. Melalui kajian ini, pengesanan nano telah dibangun berdasarkan silikon nanowire dan mikrofluid polydimethylsiloxane (PDMS) untuk pengesanan ion tertentu. Hasil pengubahsuaian permukaan, sistem penyampaian contoh yang teratur dan Kajian telah menggunakan kaedah ikatan suhu bilik baru dengan menggunakan SU8 sebagai lapisan pelekat perantaraan. Ikatan telah dibandingkan di antara ikatan menggunakan SU8 yang diubahsuaikan dan tanpa diubahsuaikan. Oleh itu, ia mendapati ikatan SU8 yang diubahsuaikan lebih kuat berbanding ikatan plasma biasa melalui kaedah pengawetan yang sama. Pengawetan semalaman di dalam suhu bilik menghasilkan tekanan pecah purata iaitu 420 kPa dan mencukupi untuk alat peranti PDMS. Manakala, ikatan plasma yang disadur menggunakan SU8 menghasilkan tekanan pecah 174 kPa sahaja.

## Development of Amine Group Modified Silicon Nanowire and Integrated with Microfluidic for Lead Ion Detection

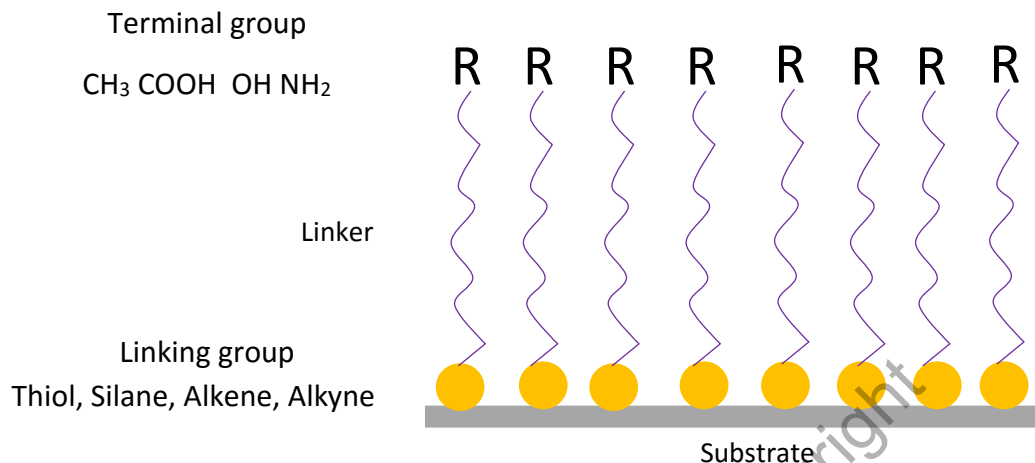
### ABSTRACT

This study describes the development of a chemical sensor that is portable, reliable, and rapid in the detection of lead ions. The developed sensor is based on silicon nanowire which distinguishes lead ions from ions present in water after the surface of the device was modified with 3-aminopropyl triethoxysilane (APTES) amino acid group which interacts with ions based on the mechanism of electronegativity of the element. This research broadly covers various important aspects of silicon nanowires and microfluidic devices for the creation of reliable chemical sensors. Also, this study created a new method of detecting lead ions by amine group modified silicon nanowire integrated with polydimethylsiloxane (PDMS) microfluidic. A new chemical sensor concept and implementation specifically developed to accurately detect lead ions in water through sensor modified with (3-aminopropyl) triethoxysilane (APTES) connected to microfluidic channel which send the sample to the sensing domain thereby decreasing the sensor response time by driving fluid through capillary phenomenon without undergoing diffusion or advection phenomenon. A silicon (Si) nanostructure was prepared using photolithography techniques, the device was fabricated via dry oxide etching approach with a controlled oxygen flow rate in oxidation furnace, network of uniform Si nanowires were successfully fabricated. Further, the device was functionalized with (3-aminopropyl) triethoxysilane (APTES) to serve as a sensor for heavy metal detection. The amino-functionalized Si nanowires were tested against the heavy metal lead ion ( $Pb^{+}$ ). The results indicated that Pb can be detected with high precision and selectivity, this was confirmed by atomic absorption spectroscopy in determining the level of lead content in water sample. The testing was carried with four (4) water samples, these include Tap water ( $H_2O$ ), River  $H_2O$ , Treated ( $H_2O$ ), DI (deionized)  $H_2O$  and found the levels of 0.0859 mg/L, 0.0929 mg/L, 0.0052mg/L, 0.0023 mg/L with 5.8pA, 7.2pA, 4.6pA, 3.3pA current responses, respectively. Thus, with this high response capabilities to the water samples, the sensor is effective for heavy metal detections and can be extended to a large sensor network in water treatment and monitoring plants. Further, new microfluidic bonding process based on SU8 cold pressed was implemented to achieve safe and reliable bonding. The requirement for a room temperature (cold pressed) process is particularly critical because the sensor must be functionalized with receptor molecules prior to bonding and cannot withstand significant heating after functionalization. Thus, the study developed new room temperature bonding method using SU8 as an intermediate adhesive layer. The SU8 modified bonding was compared with non-modified bonding. The bond strength of SU8 modified was found to be stronger than ordinary plasma bonding under the same curing conditions. Overnight room temperature curing and cold pressed yields an average burst pressure of 420 kPa, which is more than adequate for many PDMS sensor devices. In contrast, non SU8 coated plasma bonded resulted in a burst pressure of only 174 KPa.

## CHAPTER 1: INTRODUCTION

### 1.1 Background of Study

Functionalization of silicon nanowire surfaces with 3-Aminopropyl) triethoxysilane (APTES) for the detection of lead ion is an important approach to introduce a new surface chemistry to be employed for heavy metal ions detection (Rashid et al, 2013). The surface chemistry is becoming more valuable and interesting when dealing with Nano-devices such as silicon nanowire devices because of the high surface to volume ratio of these structures and the possibility of variation of the characteristic of the device by surface amendments to various applications (Abdul Rashid et al., 2013). Figure 1.1 shows the illustration of surface modification scheme where substrate, linking group, linker, and terminal group (R) are shown. Figure 1.1 shows a typical surface modification scheme illustrating the reaction mechanism of the sensor with the target analyte. The reaction is possible due the nanotechnology which allows the manipulation of interaction between the sensor and the target element. Generally, the nanotechnology is a very exciting and emerging field to integrate atomic based solid-state inorganic structures with chemically active interfaces that could response to target species such as heavy metals ions (Ahmed & Fekry, 2013).



**Figure 1. 1:** an illustration of surface modification scheme

### 1.1.1 Nanotechnology

Because of the advancement of nanotechnology, scientists and engineers are taking control of atoms and molecules individually, manipulating them and putting them to use with an extraordinary degree of precision. Nanotechnology is spreading rapidly in various applications. Governments and businesses around the world are investing billions of dollars in nanotechnology research and development (R&D). The nanotechnology-based devices are on the rise and have been used in many applications particularly in the area of sensing such as, bio-sensing, chemical sensing among others. Recently, Nano based sensors have been used as environmental sensor and humidity sensor. Thus, these generate considerable interest today. The recent progress on the development of sensors based on nanowire and its application to environmental monitoring have increased and the use of nanowires in the detection of environmental pollutants especially heavy metals in water have been proposed by several research community (Tarasov, 2012; Wang & Yu, 2013). Over the past decade,

advances in nanowires and fabrication have led to the increase in the use of nanowires in many applications (Tarasov, 2012; Wang & Yu, 2013). Significant progress has been made in creating novel nano-sized sensors for chemical and biological sensing applications (Zeng et al., 2011; Zhang & Fang, 2010).

Silicon nanowires-based sensors provide promising approaches for selective and sensitive analysis and have advantages over the traditional instrumental analysis as they are compatible with portable devices that can be deployed into portable application and be used in screening and testing (Zeng et al., 2011; Zhang & Fang, 2010). The sensor can be coupled with microfluidic to serve as a lab on chip device. With the advance of microfluidic sample manipulation, a portable device can be developed for multiplexing, quantitative and rapid analysis that can bring about a measurement with high sensitivity (Screen & Carbon, 2016; Paul & Tiwari, 2015). High-throughput screening and ultrasensitive detection technology, based on silicon nanowires, offer effective screening methods for many environmental analysis (Screen & Carbon, 2016; Paul & Tiwari, 2015).

This technology will certainly find widespread applications in water quality and safety monitoring in the near future (Cui et al, 2015; Dielacher et al., 2015). Researchers worldwide are actively exploring studies on new materials, such as fabrication of anisotropic-shaped silicon nanowires with new theories and models (Screen & Carbon, 2016; Paul & Tiwari, 2015). New sensing instruments are being designed and exploited to provide better sensitivity and resolution for chemical and biological sensing (Cui et al,

2015; Dielacher et al, 2015). Microfluidic and nanosensor, these two lines of researches are being merged to produce next-generation nano sensors. However, it should be noted that a number of critical issues still need to be addressed before these become the realistic tools for environmental monitoring ( Cui et al, 2015; Dielacher et al, 2015).

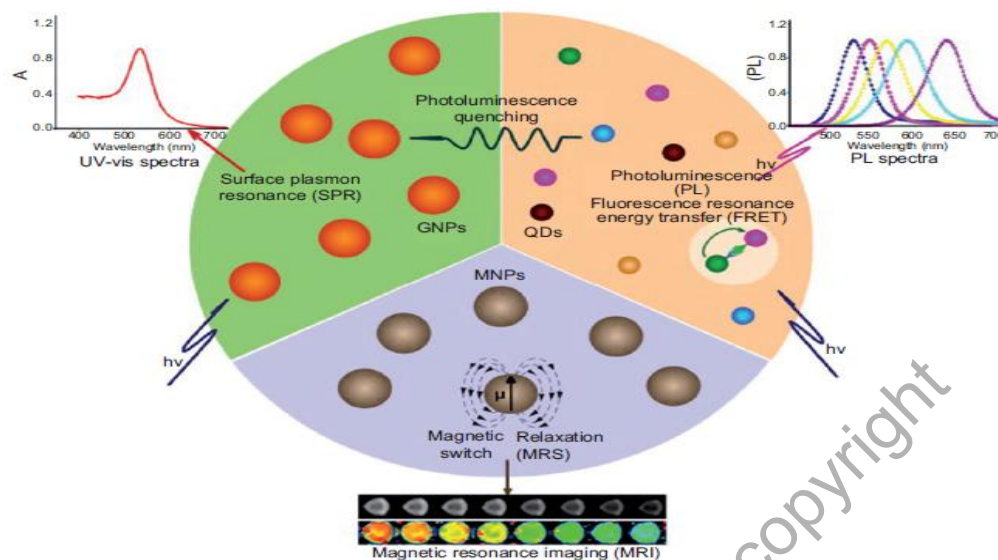
Therefore, the study proposed reliable sensing mechanism based on robust characterization method with good reproducibility, this will eliminate uncertainties especially for silicon nanowires devices fabrication (Zeng et al., 2011; Zhang & Fang, 2010). The repeated and different nanostructures still need to be characterized to have high throughput assay, which is very important for environmental applications and procedures needs to be developed in field-deployable platforms (Zeng et al., 2011; Zhang & Fang, 2010). Nevertheless, with these results obtained, they provide new fundamental insights into the silicon nanowires-based nanotechnology and resulted in more powerful nano sensors for ions detection (Zeng et al., 2011; Zhang & Fang, 2010).

Chemical pollution in water is one of the major environmental problems in today's world, therefore, polluted water poses a threat to human health, welfare, and hinders the sustainable development of both society and the economy (Tarasov, 2012; Wang & Yu, 2013). The presence of chemical toxins, heavy metals, inorganic, and organic pollutants in water due to either natural or artificial processes are needed to be monitored constantly to safeguard the supply of clean drinking water for the public, and to control the impact on the environment and ecosystem (Tarasov, 2012; Wang & Yu, 2013). In recent years, the

combination of nanotechnology, chemistry, physics and biology have created avenues in the development of ultrasensitive detection and imaging methods, including applications in electronic, magnetic, environmental, pharmaceutical, cosmetic, energy, optoelectronic, catalytic, and material fields (Tarasov, 2012; Wang & Yu, 2013).

For the past decade, the field of environmental monitoring has seen the application of nanowires being utilized as functional probes for analyzing toxins, metal ions, and inorganic and organic pollutants nano structures, usually with the size between 1 and 100 nm, displayed unique properties that were not found in bulk-sized materials, mainly due to the strong physical confinement of electrons or holes in the nanowires at the nanoscale (Tarasov, 2012; Wang & Yu, 2013). From a sensing perspective, the small size of nanowires gives them large surface-to-volume ratios which lead to rapid responses and high sensitivity (Tarasov, 2012; Wang & Yu, 2013).

In addition, the physical properties of silicon nanowires (i.e., optical, electronic, magnetic properties) can be enhanced by controlling the size, composition, shape, and surface chemistry to generate highly functional molecular probes such as quantum dots (QDs), magnetic, and carbon nanotubes that can have specific target-binding properties which allow highly selective and sensitive target detection. As shown in Figure 1.2, different types of nanostructures demonstrate different optical, fluorescence and magnetic properties, and interactions between these properties make nanowires great potential for environmental screening.



**Figure 1.2:** different nanostructures with different mechanism (Wang & Yu, 2013)

Nanotechnology is the technology that concern with design, fabrication, and applications of nanostructures (Tarasov, 2012; Wang & Yu, 2013). Which also includes fundamental understanding of physical properties and phenomena of nanomaterial and nanostructures (Abdul Rashid et al., 2013; Ahmed & Fekry, 2013; Boken & Kumar, 2014). Study on the fundamental relationships between physical properties and material dimensions in the nanometer scale, is also referred to as Nano science (Abdul Rashid et al., 2013; Ahmed & Fekry, 2013; Boken & Kumar, 2014). In the general sense, nanotechnology has been defined as being “concerned with materials and systems whose structures and components operate at nanoscale level. These exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their Nano scale size (Abdul Rashid et al., 2013; Ahmed and Fekry, 2013; Boken and Kumar, 2014).

### 1.1.2 Nanostructures

Decreasing dimensions to smaller pieces with 0.1  $\mu\text{m}$  (100 nm) average length will not only influence the electrical properties, but also further decreases the dimensions to even smaller pieces with average dimensions less than 10 nm will allow new properties such as visible light or enough catalytic activity for a specific reaction to be achieved (Abdul Rashid et al., 2013; Ahmed & Fekry, 2013; Boken & Kumar, 2014). These new properties are related to the “size effect,” and 100 nm is approximately the border: nanostructures with dimensions lower than this amount generally behave entirely different with bulk materials (Abdul Rashid et al., 2013; Ahmed & Fekry, 2013; Boken & Kumar, 2014). The reasons for the different properties of materials on the nanometric scale or their nanometric size effect have created many industrial applications (Abdul Rashid et al., 2013; Chen, Li, & Chen, 2011 ; Cui et al, 2015; Chua et al, 2009).

The abilities to fabricate and surface modify are consider the first corner stone in nanotechnology and are the most challenging parts (Abdul Rashid et al., 2013; Chen, Li, & Chen, 2011 ; Cui et al, 2015; Chua et al, 2009). The challenge as a results of tiny nature of the device and nanostructured materials have at least one dimension falling in the nanometer scale, and include nanoparticles (including quantum dots, when exhibiting quantum effects), nanowires and nanorods, thin films, and bulk materials made of up nanoscale building blocks or consisting of nanoscale structures. However, working on this scale have greater challenges.

The synthesis and fabrication are the only way to obtain nano structure, based on the two several nanostructures been obtained (Abdul Rashid et al., 2013; Chen, Li, & Chen, 2011 ; Cui et al, 2015; Chua et al, 2009). The following are the summary of nano structure realization techniques:

Vapor phase growth, where laser reaction pyrolysis for nanoparticle synthesis while atomic layer deposition (ALD) for thin film deposition.

- 1) Liquid phase growth, including colloidal processing for the formation of nanoparticles and self-assembly of monolayers
- 2) Solid phase formation, including phase segregation to make metallic particles in glass matrix and two-photon-induced polymerization for the fabrication of three-dimensional photonic crystals.
- 3) Hybrid growth, including vapor–liquid–solid (VLS) growth of nanowires.

Another way of techniques classification depends on the form of products:

Nanoparticles by means of colloidal processing, flame combustion, and phase segregation.

- 1) Nanorods or nanowires by template-based electroplating, solution liquid–solid growth (SLS), and spontaneous anisotropic growth.
- 2) Thin films by molecular beam epitaxy (MBE) and atomic layer deposition (ALD).

- 3) Nanostructured bulk materials, for example photonic bandgap crystals by self-assembly of nanosized particles (with photonic crystals the structure sizes may be well above 100 nm; the nano aspect there is more on the fabrication and less on the properties).

These techniques are grouped based on two major approach (Top-down and bottom-up). Top-down and bottom-up approaches, spontaneous and forced processes are other ways to classified fabrication and processing techniques ( Cui et al, 2015; Dielacher et al, 2015; Lieber, et al, 2001). Top-down can be considered as an extension of lithography (Abdul Rashid et al., 2013; Chen, Li, & Chen, 2011 ; Cui et al, 2015; Chua et al, 2009). The bottom-up approach concept and practice in material science and chemistry is not new either ( Cui et al, 2015; Dielacher et al, 2015; Lieber, et al, 2001). Synthesis of large polymer molecules is a bottom-up approach, where individual building blocks (monomers) are assembled to form a polymerized or large molecule into bulk material. Another example for bottom-up approach is crystal growth, where growth species are atoms, or ions, or molecules, which orderly assembled into the desired crystal structure on the growth surface (Cui et al, 2015; Dielacher et al, 2015; Lieber, et al, 2001).

### **1.1.3 Types of Nanostructures**

Nanostructures are classified according to their geometrical properties which usually consist of Nano cages, Nano needles, Nano belts ( Cui et al, 2015; Dielacher et al,

2015; Lieber, et al, 2001), Nano crystallites, Nano composites, Nano fabrics, Nano fibres, Nano flakes, Nano flowers, Nano foams, nanoparticles, Nano pillars, Nano meshes, Nano pin films, Nano rings, Nano rods, Nano powders, nanowires, Nano clusters, Nano shells, nanotubes, quantum dots, quantum heterogeneous structures and sculptured thin films ( Cui et al, 2015; Dielacher et al, 2015; Lieber, et al, 2001). The most popular mode of nanostructures classification is based on their dimensions where nanostructures can be described as zero- (0-D), one- (1-D), two- (2-D), and three-dimensional (3-D) nanomaterial's. Amorphous materials were added as another branch for this classification where the dimensions of nanostructure are not located in the nanometre size range <100 nm. In 0-D nanostructures, all dimensions are in the nanometre size range (such as well-separated Nano powders or nanoparticles). Whereas in 1-D nanostructures, they have one dimension above the nanometre size range and has a shape like a rod, and consist of nanotubes, Nano rods, nanowires and Nano needles ( Cui et al, 2015; Dielacher et al, 2015; Lieber, et al, 2001).

The 2-D nanostructures have two dimensions beyond the nanometre size range which display plane-like structures, and consist of thin films, Nano layers and Nano coatings. Whereas the 3-D nanostructures have three dimensions outside the nanometre size range (Dhahi, Hashim, & Ahmed, 2011; Zhong et al, 2003). These bulk 3-D nanostructures consist of various kind and commonly which comprise of Nano crystalline units that show the affected properties of Nano scale due to the size effect. A 3-D nanostructure can include different distributions of nanoparticles or Nano crystallites, groups of nanowires and