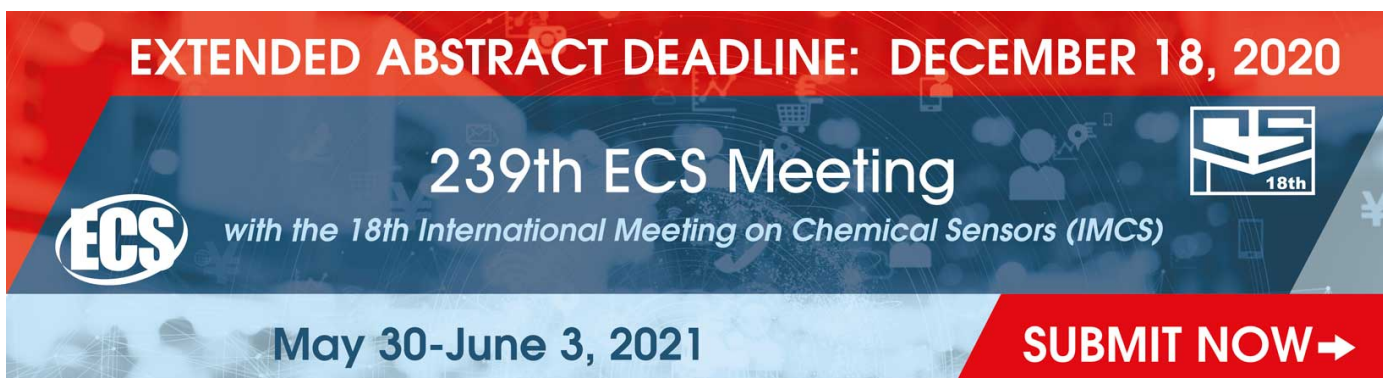


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Amino-propyltriethoxysilane Modified Heavy Metal Sensor Based on Silicon Nanowire Arrays

Nuri. A.KH. Ehfaed¹, Shillan Bathmanathan¹, Tijjani Adam¹, Mohammed Mohammed², Aeshah M. Mohammed³, Omar S. Dahham¹, U. Hashim⁴, Nik Z. Noriman¹

¹Faculty of Engineering Technology, Kampus Uniciti Alam Sg. Chuchuh, 02100 Padang Besar, Universiti Malaysia Perlis (UniMAP)

²Center of Excellence Geopolymer and Green Technology, School of Materials Engineering, Universiti Malaysia Perlis, 01007, P.O. Box 77, D/A Pejabat Pos Besar, Kangar, Perlis, Malaysia

³University of Bagdad college of education for pure science Ibn-Alhatham

⁴Institute of Nano Electronic Engineering (INEE), 2Department of Electronic Engineering 01000 Kangar, Perlis, Malaysia

Abstract. Safety of consuming water from various resources can be questioned nowadays due to high content of material that is highly possible to have toxic content and cause permanent damage to human itself. Possible toxic content includes heavy metal such as lead, arsenic, cadmium and mercury. A highly sensitive or selective heavy metal sensor needed to aid in detection of these metal species. In this paper, the manipulation of silicon nanowire to detect heavy metal content in liquid sample is explained. Device is fabricated into two main elements which is the detecting part which is the nanowire and probes on the both sides. Next, the characterizations of the device are discussed as well as the discussion on the detections capabilities. The APTES surface modified integrated electrochemical nano-sensor was subjected to various concentration of lead ions, the responses were monitored assessed for the detection ion chemical activities, this response were observed using semiconductor parametric analyzer (SPA). The surface modified nano-sensor show a linear behavior with current response between 2-140pA, the detection limit for the lead ions was 0.1µm/l. The water samples which were collected in Taman Tasik Damam in Malaysia show similar characterization for area of around 20 square meters. Thus, the excellent and reliable behavior shown by this device, it can be adopted as detection device for various heavy metal detection in near future.

1. Introduction

Heavy metal has no real defining factor but usually related to metallic material that has the density more than 5 g/cm³. Heavy metal could bring a really big impact on the quality of human health [1]. Indirect or unintentional consumption of heavy metal could happen through simply drinking untreated water from unknown water supply. Water supply could be accumulated with heavy metal from agriculture waste, discarding waste into water or mining. Thus ability to analyze the metal species in water supply is important hence reducing of risk being harmed. Among various metal ions arsenic, cadmium, lead, mercury are considered to be highly toxic because of their toxicity, they are also listed in the National Primary Drinking Water Regulations. Long term exposure to inorganic arsenic causes skin pigmentation change and lesions and eventually leads to cancer. Cadmium targets mainly the kidneys to cause renal diseases and stays in our body with a half-life of 10 to 35 years. Children



absorb four to five times as much lead as adult; children who ingest lead may suffer from neural diseases and anemia. Lastly, both elemental mercury and methyl mercury are toxic, coal-fired power plants and methyl mercury from fish and shellfish are two important sources of mercury. Mercury stays in the air for one year, but can be stable in ocean sediments for millions of years. Nanotechnology is manipulation of scale of one to hundredth to be integrated or made into a device to aid the human work. In another words the ratio of the length to the surface of the structure is outstandingly high [2]. Nanotechnology has vast range of applications such as in medical, military, electronics as well as textiles [3-6]. A semiconductor nanowire is a strong pole with a width under 100–200 nm made out of one or a few semiconductor materials [7]. A lower point of confinement is difficult to characterize – wires of 5 nm in distance across are reasonable alternatives for this innovation. Nanowire wire can be grown in various ways such as vapor-liquid-solid (VLS) growth mechanism and vapor-solid-solid (VSS) mechanism [8]. Nanowires can likewise be developed without a metal seed, for instance within the sight of an oxide or by masking a substrate. In order to produce nanowires, molecular or chemical beam epitaxy, vapor phase epitaxy or chemical vapor deposition, and ion implantation. Nanowire has a great detecting capability of a small electrical changes is a sample. Fabrication process will be started by cleaning a clear wafer surface with chemical combination of RCA1 and RCA2

2. Methods and Materials

Mask pattern is designed in many variations to test for the best specification for the device. AutoCAD is used create the two terminal and both are connected by nanowire that has different length as well as number of nanowire strips. After completion of the design it is the printed on the chrome mask and will be later used during exposure process. Silicon layer will be washed by using mixed chemical combination of RCA1 and RCA2. Wafer is first rinsed with RCA1 mixture which composes of pure water, 200ml of NH₄OH and 400ml of H₂O₂. RCA2 is used next to remove residual metal contaminations by rinsing combinations of pure water, 300 ml of concentrated HCl, and 300 ml H₂O₂, Alcohol chemical bath done by combination of acetone, methanol and isopropanol that will remove any impurities sticking on the wafer surface. Wafer is then placed spin machine vacuum sucker and set to spin in a constant velocity until the wafer is fully coated with photoresist. The time will be set around 30 to 60 seconds depending on the resist viscosity. Type of mask that will be used is a chrome type which has two main base materials, soda lime glass high optical exposing agent. Coated wafer will be exposed to UV ray. As negative photoresist will be used the photoresist in which the bit of the photoresist that is presented to light gets to be distinctly insoluble to the photoresist designer. The unexposed segment of the photoresist is broken down. Exposure will be done in yellow room. Oxidation is done by implanting an oxide layer onto the wafer surface. Dry oxidation is chosen to provide a thin coating layer. Wafer will be inserted into the chamber and heated with oxygen gas. Oxide layer thickness can be varied by adjusting the oxide concentration, pressure, temperature and time in the chamber. The unmasked material can be expelled either by wet (synthetic) or dry (physical) carving. Wet drawing is unequivocally isotropic which restricts its application and the carving time can be controlled troublesomely. As a result of the purported under-engraving impact, wet scratching is not suited to exchange designs with sub-micron include measure. Be that as it may, wet carving has a high selectivity (the engraving rate firmly relies on upon the material) and it doesn't harm the material. On the opposite side dry drawing is exceptionally anisotropic however less specific. Be that as it may, it is more skilled for transferring little structures. It is impossible to directly fabricate a device in a nano scale because it is too small to transfer imprints to the wafer surface. Thus scale miniaturization is required to reduce its scale. Etching is done in a slower process and measured under high performance microscope. This process is repeated again and again to go to the smallest scale possible without affecting the device performance. Scale of the device will be miniaturized into nano scale by constantly etching the surface and observing under optical characterization method. This critical process is simultaneously repeated to get smallest possible dimension of the device without affecting the sensitivity and selectivity of detection capabilities. Wet etching has a fast reaction time, but might cause the nanowire to be uneven and might be disconnected. Characterization is divided into several classes where optical characterization, surface characterization, and electrical characterization.

Optical characterization gives the viewer knowledge on the physical composition on structure generally of the device. Surface characterization will provide specific and accurate structural view of the device [9]. Semiconductor electron microscopy (SEM) produces results at higher resolution. This microscopy method is important due to the size of the device itself in nano scale. Equipment used to produce the result is Atomic Force Microscopy (AFM). AFM uses a lever and cantilever to detect the surface change and producing a 3-dimensional image. Electrical characterization is the most important to prove the detection capability of the sensor. Early findings obtained will be the fundamentals to work on the device. Early characterizations will be displayed to prove that there is heavy metal in the water samples and after the device has been fabricated, it is possible to validate the result as well as the surface morphology to understand the possible error that will be interfered during the and after the fabrication process. This could bring us to the understanding of the fabrication outcome from various methods and choosing the best possible steps.

3. Results and Discussion

The figure1 below shows the surface topography of the nanowire sensor using atomic force microscope (AFM). The device coupled with arrays of it clearly observed that with smooth structure is on the silicon substrate. Structural imaging produced under atomic force microscopy. This characterization could give the information on the surface dimensions and physical defects. This smooth structure was obtained as result of careful processing and fabrication process that is adopted.

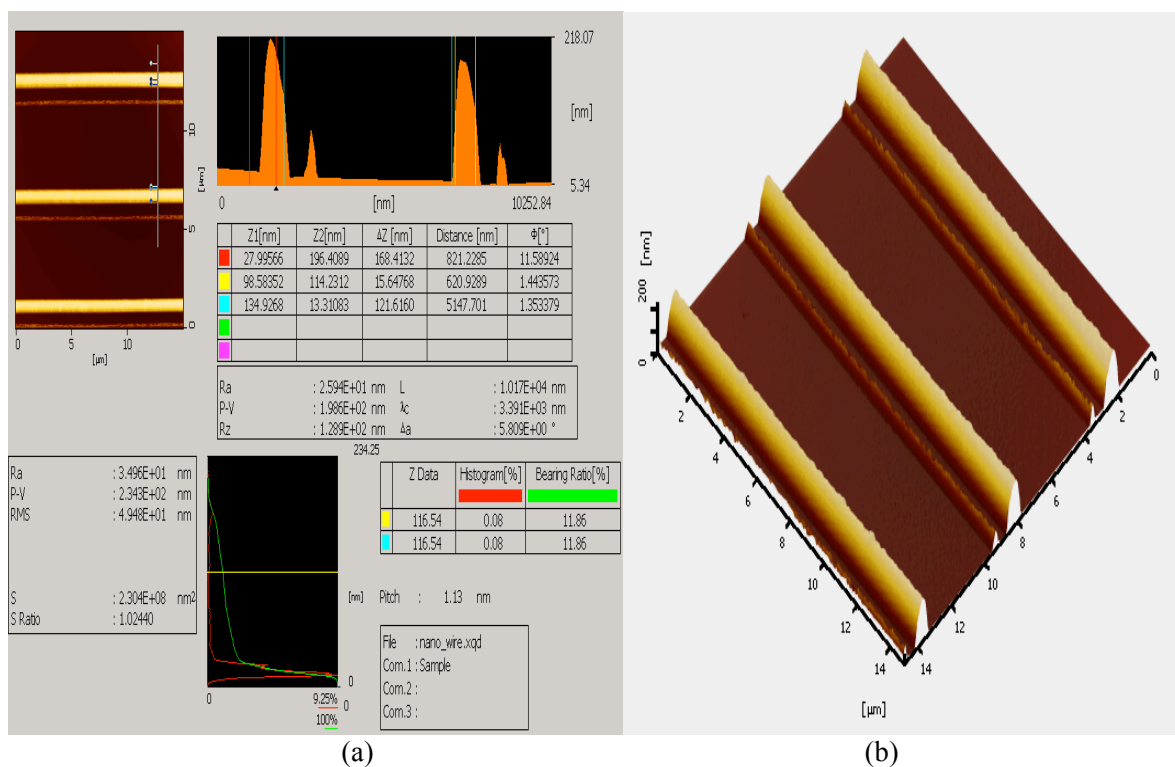


Figure1. (a) 2D view of the surface morphology (b) top view of the 3D structure of the nanowires arrays

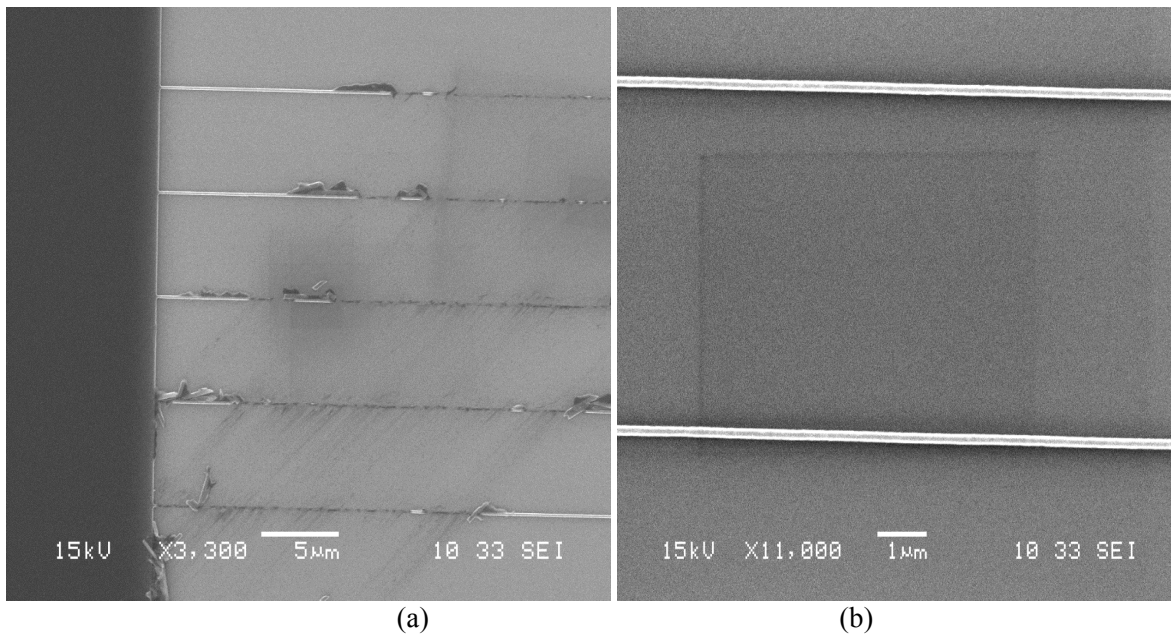


Figure 2. Structural imaging produced under semiconductor electron imaging (SEM) (a) complete wires arrays (b) two wires view

The Electrical characterization was conducted in other to have been done by testing the same device fabricated with several water samples which includes river, tap, treated and deionized water. This is done to prove that different water samples have different heavy metal content. As the graphical representation below it can be concluded that silicon nanowire could detect the deference and the metal content in deionized water has the almost no heavy metal content and followed by treated water, tap water and followed by river water with the inclining content of heavy metals. From Figure 3. The sensor electrochemical response of the Pb heavy metal ions are different in different sensor configuration, the device voltage drop high for the non-surface modified device, immediately the surface is modified the voltage is significantly low. This illustrates the important of the surface modification in increasing chemical activities of the sensor. Moreover, obtaining the consideration of sensitivity for the detection of heavy metal ions, the surface modification is necessary.

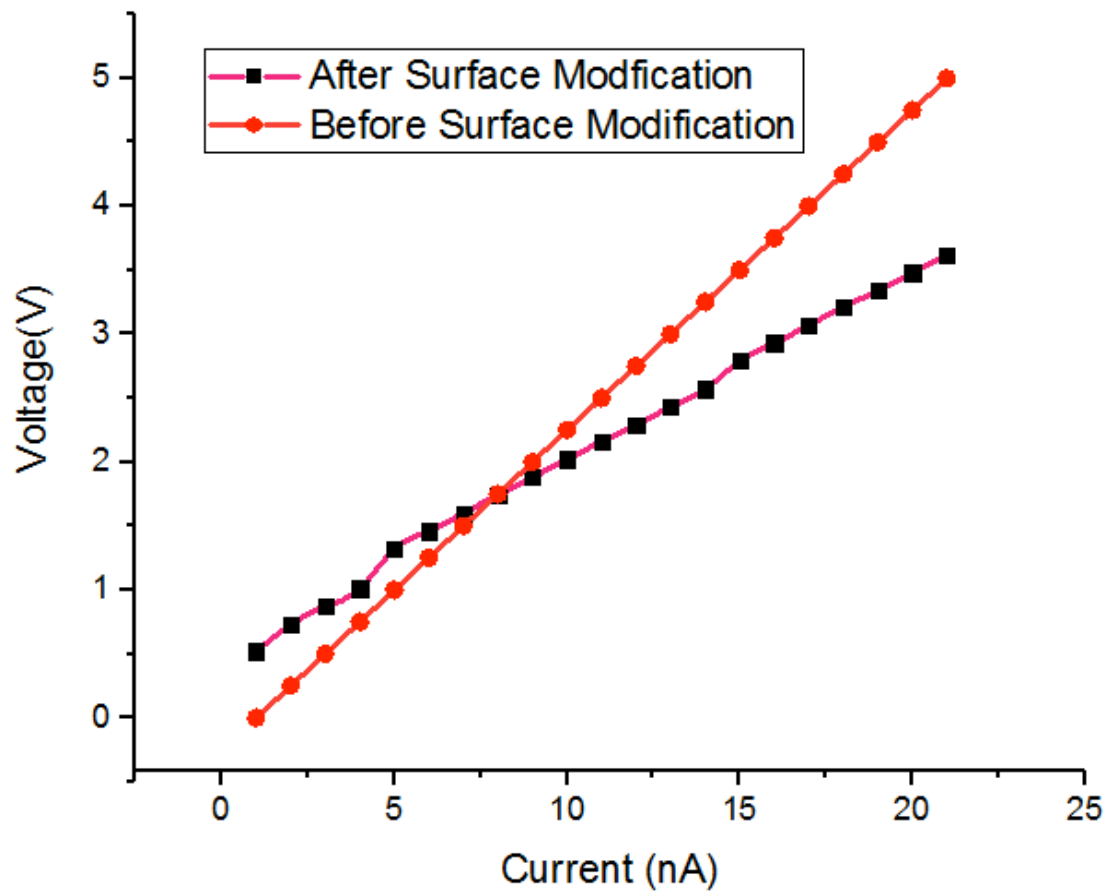


Figure 3. Comparison of the I-V response before and after surface modification

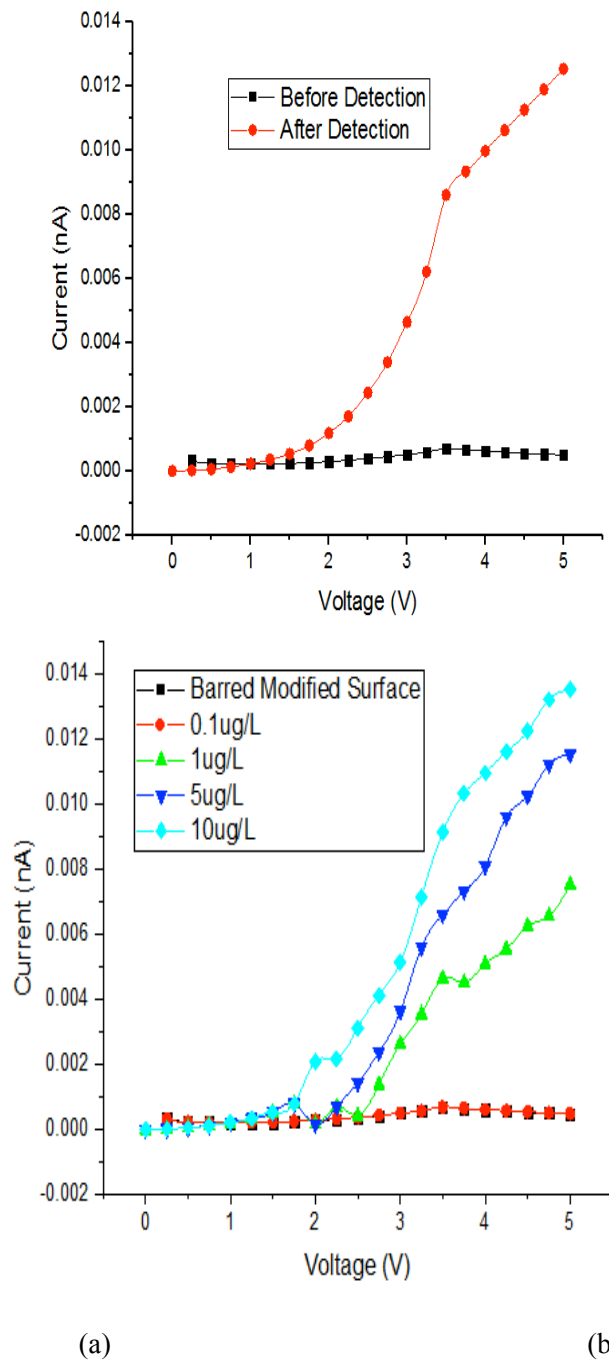


Figure 4. (a) Comparison of the I-V response before and after heavy metal detection (b) Comparison of the I-V response of nanowire arrays with different heavy metal concentrations

To determine the feasibility and capability of the device for responding to various concentration, the device was first measured without target sample and subsequently monitored against the various concentration (10 μg/l, 5 μg/l, 1 μg/l and 0.1 μg/l) as shown in fig.4a and 4b. The characterization was conducted in routine analysis, this sensor was subjected to detect Pb ions in the water sample. The response was very precise and accurate. The response was linear indicating the abilities of the proposed sensor in real target samples analysis. The sensing capabilities for the Pb ions are 0.02 ± 0.1 nA in various concentration. The reliabilities and reproducibility's of the chemical sensor was assessed based on repetitive measurement conducted in every sample for 7 times. This shows the device reliable and can easily be fabricated, the

detection limit of 0.1 μ g/l is quite significant to classified this device as having low detection limit and high sensitivity.

4. Conclusion

The student proposed a highly sensitive or selective heavy metal sensor that could be used to detect heavy metal species. In this paper the manipulation of silicon nanowire to detect heavy metal content in liquid sample is shown as a fabricated which has been surface modified with APTES. The modified fabricated nanowire structures are subjected to certain concentration of lead ions. Electrical characterization done by semiconductor parametric analyzer (SPA) proves that the surface modified nano-sensor show a linear behavior with current response between 2-140pA, the detection limit for the lead ions was 0.1 μ m/l. The water samples which were collected in Taman Tasik Damam in Malaysia show similar characterization for area of around 20 square meters.

5. Acknowledgement

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