

Zinc Oxide Nanowire Sensor Packaging

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Abstract

This paper describes nano device packaging topology using array of ZnO nanowire-based devices. The single nanowire device has been fabricated through focused ion beam and e-beam lithography techniques while the SEM and EDAX analysis have been used to characterize the device. The IV characteristics of the ZnO nanowire-based array devices have been measured through a semiconductor parameter analyzer.

Key words

Zinc oxide nanowires, chemical vapor deposition, nanosensors.

I. Introduction

Nanostructured materials have been extensively researched for a broad spectrum of applications. Especially, development and application of nanomaterials for chemical and biological sensing have been widely reported [1-4]. The unique surface-related properties, with tunable size and shape-dependent physical and chemical properties, offer great potential for manipulating and improving sensing behavior. These characteristics have been demonstrated to aid in improving sensitivity and response rate of sensors [5, 6]. Maturity of synthesis techniques and availability of variety in terms of morphology and structure of these nanomaterials have provided immense flexibility to researchers for application-specific sensor development. These nanosensors have, therefore, proven to be quite useful in areas, such as environmental sensing, homeland security, vehicular emission control, industrial gas detectors, and biosensing. In this work we compare two distinct device fabrication techniques and present a comparative case study for ZnO nanowire sensors for sensitive determination of trace amounts of *p*-nitrophenol vapor under ambient conditions. First, a single ZnO nanowire device was fabricated by using focused ion beam and E-beam lithography techniques. After appropriate characterization and analysis the drawbacks and limitations of this approach are highlighted. Second, a multi-nanowire array-based device topology is investigated. Subsequently, its successful operation is demonstrated by using saturated *p*-nitrophenol

as a model analyte under a concurrent opto-electronic excitation. Both devices utilize receptor-functionalized ZnO nanowires. We would use the sensor chemistry we developed earlier and focus exclusively on device topology and configuration effects on sensor reliability, sensitivity, and selectivity. A refresh strategy for the sensor is also posited.

II. Experimental Procedure

The ZnO nanowires for device fabrication were synthesized through a chemical vapor deposition (CVD) process as explicated in our previous works. Briefly, ZnO nanowire growth resulted from the templated substrate (sapphire) due to vapor-liquid-solid (VLS) mechanism of nanowire growth at a temperature of 950°C. A single nanowire device was fabricated through extraction and manipulation of a nanowire from the ensemble of nanowires. This was accomplished by using micro-fabrication techniques of E-beam lithography and focused ion beam (FIB). First, inter-digitated electrodes on insulating sapphire substrates were made using E-beam lithography. The substrates were coated with 100 nm of positive resist (PMMA A2) at 4500 rpm for 45 seconds and were baked at 180°C for 90 seconds to make them adequate for the E-beam process. An inter-digitated pattern designed using CAD package with NPGS (Nanometer Pattern Generation System) was written on the resist-coated substrates. The exposed substrates were developed using 1:1 (v/v) solution of MIBK and acetone for 90 seconds. Subsequently, a 70 nm coating of gold was deposited followed by lift-off to complete

fabrication of inter-digitated electrode. Thereafter, these substrates were introduced in a focused ion beam (FIB) system (FEI Quanta 3D Dual-beam) along with receptor-functionalized ZnO nanowires on sapphire substrates. A single ZnO nanowire was extracted from the ensemble of nanowires using an in-situ micromanipulator and laid across the inter-digitated electrode. Subsequently, the nanowire was welded at its extremities, where it overlaps the electrode, with platinum using the in-situ GIS (gas injection system) to complete fabrication of the device. Before extracting the single ZnO nanowire device from the FIB chamber, EDAX analysis of the exposed nanowire area was performed. This was done to identify any prospective contamination that might have happened as a result of subjecting the single nanowire to an intense device fabrication procedure. The multi-nanowire device fabrication utilized receptor-functionalized ZnO nanowire arrays on sapphire substrates. To fabricate these devices colloidal silver solution (Ted Pella, Inc.) in a volatile solvent was coated at the extremities of the receptor-functionalized nanowire substrates to function as electrodes. Silver was used to make an ohmic contact between functionalized ZnO nanowires and the electrode.

The electrical properties of the multi-nanowire devices were measured using a semiconductor parameter analyzer (Agilent Technologies). I-V curves of both pristine and receptor-functionalized ZnO nanowire array devices were measured. It is to be noted that device testing of single ZnO nanowires was not pursued due to alteration of chemical composition of the device due to unavoidable contamination resulting from the device fabrication procedure. This will be discussed in the forthcoming section. Subsequent to preliminary testing of the functionalized multi-nanowire device, an additional optical stimulus from a 342 nm UV lamp was provided to test for opto-electronic sensing behaviour of the device. Current was then measured from the device under a bias of 0.1V. Subsequently, the device chamber was allowed to saturate from *p*-nitrophenol vapors by introducing a few milligrams of the solid powder. Current was then measured from this device after 5 minutes to validate the sensing behavior of the device. The test assembly to establish sensor operation is illustrated in Fig. 1. The benefit of this assembly is that it permits transduction of optical response from the sensor to an amperometric signal, which makes it easier to measure with conventional electronics without the use of sophisticated optical detectors. However, utilizing sophisticated optical detection and transduction electronics will only serve to improve the sensitivity and selectivity of the device in addition to minimal false positive rate.

To determine the appropriate refreshing methodology for the fabricated sensor, thermogravimetric analysis (TGA) was used [12]. Nitrogen was used as a purge gas. First, pure receptor powder was tested for weight loss from the range of 25-600°C with the temperature rate of 5°C/min in a

TGA/DSC 1-Thermogravimetric Analyzer (Mettler Toledo, Inc.) Values from the blank run were automatically subtracted from the data. Second, receptor-functionalized ZnO nanowire samples were subjected to the TGA analysis under similar experimental conditions. Results from both sets of experiments were used to suggest a possible strategy to refresh the multi-nanowire sensor.

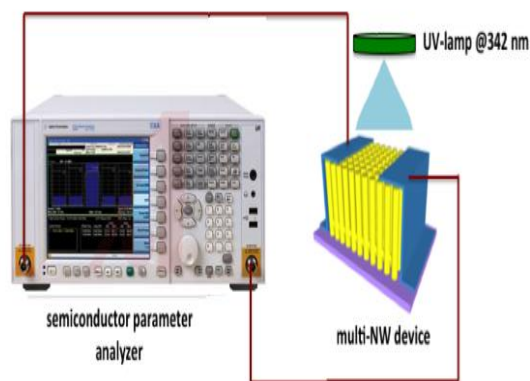


Figure 1. I-V test assembly to validate ZnO nanowire array-based sensor device operation.

III. RESULTS

For fabricating a single nanowire device a receptor-functionalized ZnO nanowire was extracted from the ensemble of nanowires grown on the substrate using the micromanipulator in-situ the FIB system and was placed across the inter-digitated electrode. Fig. 2(a) and 2(b) show the E-beam mask design and the optical micrograph of the completed electrode, respectively. After successfully positioning the nanowire across the electrodes, platinum was deposited at its extremities to complete the fabrication of the device. Figure 2(c) exhibits the schematic of the single nanowire device while Figure 2(d) shows the completed device. Before retrieving the finished nanowire device from the FIB system, EDAX analysis of the exposed nanowire area was performed. This was done to ensure the compositional integrity of the sensor device fabrication procedures. It was observed that the platinum deposited was not confined to the electrode area but also contaminated the sensing area resulting in unintentional doping. Fig. 3 shows the EDAX spectrum of the selected area on the exposed functionalized nanowire surface. We observed platinum peaks, which indicate its incorporation in the sensing area. Pertaining to such findings, the single functionalized ZnO nanowire device was evaluated to be unsuitable for *p*-nitrophenol sensor fabrication. Furthermore, electrical tests on these single ZnO nanowire devices yielded inconsistent, erratic results confirming unreliability and minimal signal-to-noise.

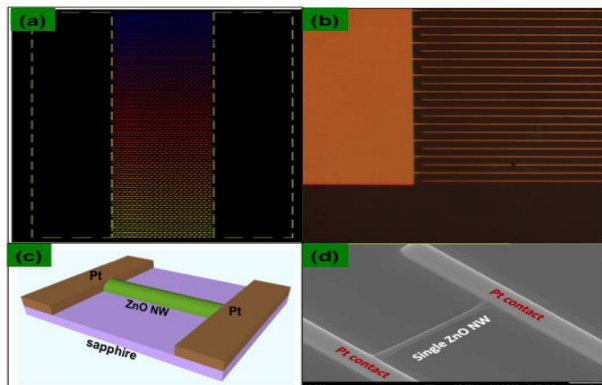


Figure 2. (a) CAD of inter-digitated electrode, (b) Optical micrograph of finished inter-digitated electrode, (c) single ZnO nanowire device, (d) A single ZnO nanowire device fabricated with FIB and e-beam lithography.

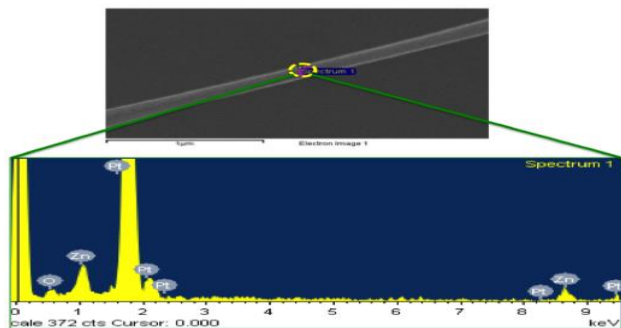


Figure 3. EDAX analysis of the sensing area of the single ZnO nanowire device. Pt peaks indicated contamination of sensing area during fabrication procedure.

Hence, in order to mitigate issues associated with the single ZnO nanowire device for sensor development, an alternate approach was tested. In this approach, ZnO nanowires were grown on sapphire substrates and were functionalized with PBA receptor. Since sapphire is implicitly insulating and has good lattice matching with ZnO, it provided an ideal platform for developing a multi-nanowire array sensor device for *p*-nitrophenol detection. A schematic of the device based on the aforementioned idea is shown in Fig. 4(a), where interlinked and functionalized ZnO nanowire ensembles are contacted with silver electrodes at substrates extremities to complete device fabrication. In addition, Fig. 4(b) also shows the actual completed device. Silver was chosen as the metal for electrodes due to its electron affinity of 4.3 eV, which is approximately equivalent to the fermi energy of ZnO.

The device was optically excited with 341 nm UV stimulus while a bias of 0.1 V was being applied. Under concurrent opto-electronic excitation condition, the conductance of the device was decreased quickly in 45 seconds upon its exposure to saturated *p*-nitrophenol vapors under ambient conditions. This decrease in conductance can be attributed to the transfer of electrons from PBA/ZnO

nanowire DUT (device under test) to the electron-deficient *p*-nitrophenol. This effect is also responsible for the quenching of optical signal from the heterostructure, as discussed in our previous works. It is to be noted that the amperometric response obtained from the sensor is due to dual, optical and electrical, sensing modes that operate in synergy.

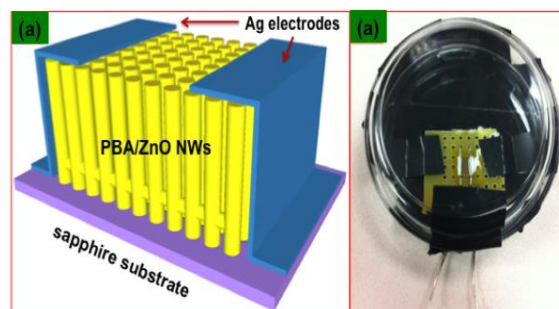


Figure 4. (a) Schematic of a ZnO nanowire-array device, (b) Fabricated ZnO nanowire-array sensor device.

To investigate the reliability of this device further, the sensing chip was subjected to thermogravimetric analysis (TGA) to determine the breakdown temperature of the PBA/ZnO heterostructure. The opto-electronic sensor operation of the multi-nanowire array device is contingent upon chemical integrity of the heterostructure. Therefore, the advantages of using TGA are two-fold. First, it aids in determination of the temperature range, where the PBA receptor coating would be stable on ZnO nanowire surface. This would serve as a measure to qualitatively determine the robustness of the device under field conditions, since the sensor could be subjected to a varied temperature regime while being deployed on the field. Second, it would allow for identification of a prospective strategy to reset the device. Figure 5 shows the TGA spectrum of pure PBA receptor. It can be observed that in the temperature range of 250-450°C the sample exhibited maximum weight loss, which indicated the decomposition of PBA receptor. This means that the sensor operation limit is less than 250°C. Figure 5(b) shows a TGA spectrum of PBA-functionalized ZnO nanowire sensors. The maximum weight loss in the sensing chip happened in the range of 250-450°C indicating breakdown of the chemisorbed organic layer of PBA on ZnO nanowire surface. The data was normalized to minimize the effect of instrument drift. It was especially useful for the analysis of PBA/ZnO heterostructure, where subtle weight changes in the sub-milligram range could be observed. However, drift at large temperatures became large and could not be removed even with normalization.

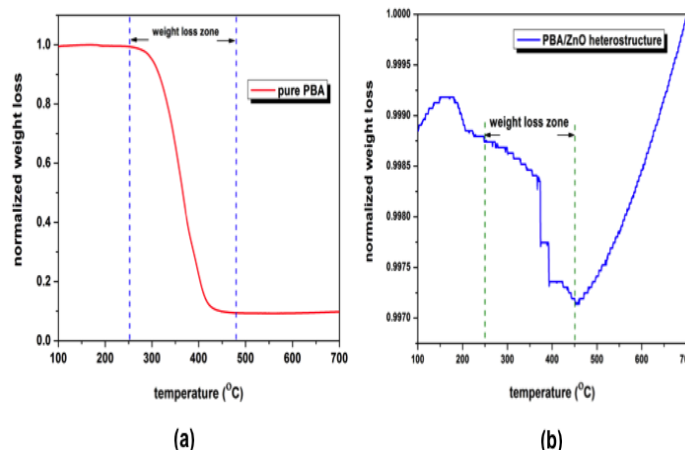


Figure 5. Thermogravimetric Analysis (TGA) of (a) pure PBA receptor, (b) PBA/ZnO heterostructure.

Based on aforementioned results it was concurred that for developing a reliable ZnO nanosensor device for detecting hazardous compounds, a multi-nanowire array device is a much better alternative than a single nanowire sensor device. While a multi-nanowire device would be easy to interface with back-end electronics, it also exhibits far more reliability in terms of field deployment as compared to a single nanowire device.

Fig. 6(a) and 6(b) exhibit the morphology of ZnO nanowires on sapphire substrate. These single crystalline nanowires predominantly possess vertical orientation while being interlinked near their extremity to facilitate carrier transport. This interlinked, open structure is conducive to analyte permeation leading to enhanced sensitivity of the device. The interlinking can be confirmed by Fig. 6(d), where ohmic characteristics of the nanowire ensemble on insulating sapphire signify interlinked current pathways. This is a critical design parameter as it leads to efficient utilization of high surface-to-volume ratio of functionalized ZnO nanowires. It provides enhanced interaction between analyte molecules and nanowire surface that aids in improving sensitivity of the device. Dominant near band-edge emission (3.7 eV), as observed in Fig. 6(c), can be attributed to a high quality, low defect crystalline structure of pristine nanowires. This is a desirable characteristic as it minimizes electron decay into defect-induced trap states. This is crucial for consistent sensor operation in opto-electronic mode.

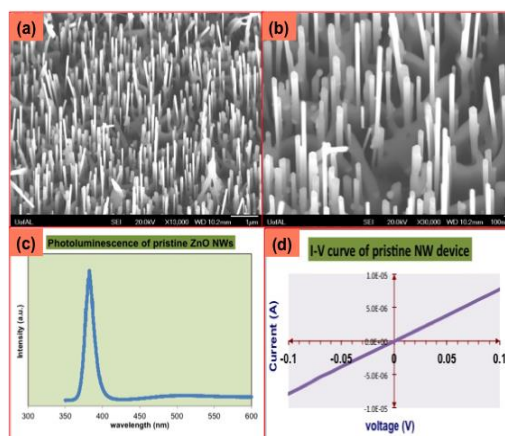


Figure 6: (a), (b) SEM images of ZnO nanowires on sapphire substrates. (c) Photoluminescence behavior of pristine ZnO nanowires. (d) I-V curve of pristine nanowire array device.

As mentioned in preceding sections, we had independently validated sensing chemistry and operation in both electrical and optical modes. Fig. 7(a) elucidates potential of carrier modulation, upon functionalization of pristine ZnO nanowires array device through I-V characteristics. Fig. 7(b), on the contrary, demonstrates the selective fluorescence quenching of ZnO nanowire/PBA heterostructure upon exposure to trace amounts of *p*-nitrophenol vapors [8]. While both these techniques are not alone sufficient to establish true opto-electronic sensor operation, they do present a unique approach for *p*-nitrophenol detection contingent upon their concurrent use. At this juncture, it is beneficial to explicate possible mechanism of sensor operation. It has been determined that differential fluorescence from pyrene excimers can be utilized for rapid screening of explosive molecules. Specifically, strong electron deficient molecules, such as *p*-nitrophenol, exhibit dynamic quenching of excimer complex itself, presenting a sensitive and selective detection technique to detect *p*-nitrophenol from the sampling environment. Functionalization of ZnO nanowires with PBA results in formation of proximity dependent excimers in solid state. Coupled with a ZnO nanowire backbone such an electronic exchange can be transduced as an amperometric response. This highlights a novel paradigm where both optical and electrical responses from the sensor can be utilized to establish a unique fingerprint of *p*-nitrophenol in a sensitive manner.

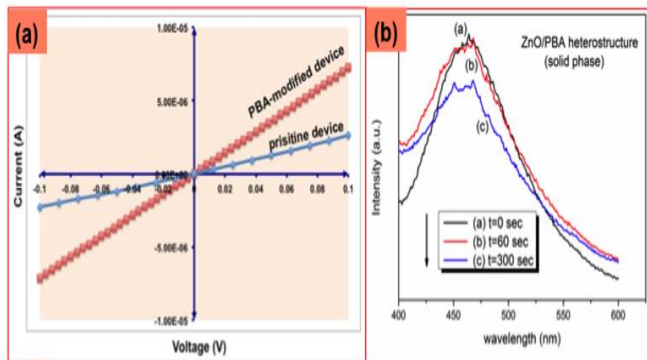


Figure 7: (a) I-V curves of pristine and PBA-modified ZnO nanowire devices establishing carrier modulation in the nanowire backbone upon PBA functionalization. (b) Time-dependent fluorescence response of ZnO nanowire/PBA heterostructure to p-nitrophenol vapors under ambient conditions.

IV. CONCLUSION

Two distinct device fabrication approaches were investigated to determine the most reliable topology of a field deployable ZnO nanosensor device for detecting *p*-nitrophenol vapors. First, a single ZnO nanowire device was fabricated with E-beam lithography and focused ion beam techniques. The EDAX analysis confirmed unintentional doping of Platinum in the sensing area during electrode deposition, which indicated contamination. Second, a multi-nanowire array approach for device fabrication was investigated. The sensor device exhibited good sensitivity and reliable operation. The temperature resilience of the device was tested through thermogravimetric analysis (TGA), where it was determined that the device can be operated up to 250°C.

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