

Metal-oxide Nanowires for Toxic Gas Detection

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ABSTRACT

The feasibility of using Electric field enhanced oxidation (EFEO) to fabricate metal-oxide nanowires for sensing toxic gases was investigated. The effects of fabrication parameters such as film thickness, ambient relative humidity, atomic force microscope (AFM) tip bias voltage, force, scan speed and number of scans on the growth of nanowires were determined. The chemical composition of indium-oxide (In_2O_3) nanowires was verified using Auger electron spectroscopy. It was found that oxygen to indium ratio was 1.69, 1.72, 1.71 and 1.84 at depths of 0, 1.3, 2.5, and 3.8 nm, which was near the 1.5:1 expected for stoichiometric In_2O_3 film. Future work will include characterizing the electrical and gas sensing properties of the metal-oxide nanowires.

Keywords— Electric field enhanced oxidation, nanosensors.

1. INTRODUCTION

Toxic gas emissions from automobiles and industry are a major source of hazardous gases such as nitric oxides (NO_x), ozone (O_3) and carbon monoxide (CO). Studies have shown that human health could benefit from even a slight reduction (in range of ppb) in the concentration of these pollutants. The ability to detect toxic gases may allow automobile manufacturers and industry to re-design air-fuel mixture systems to control toxic gas emissions and smog levels [1]. Automobile manufacturers and other industries use sensors interfaced with computer controlled fuel systems to increase fuel economy and to control toxic emissions to meet regulations set by federal agencies [2].

A wide variety of metal oxide materials have been investigated for toxic gas sensing in the past five decades. The first commercially available sensors for the detection of combustible gases were developed by Taguchi in 1962. The advantages of these sensors are low cost and sensitivity to hydrogen (H_2) and hydrocarbons but their drawbacks includes poor selectivity, stability and high power consumption (0.8W) since they must be heated [3, 4]. Since the late 1980's there has been a considerable effort to make use of microelectronic device fabrication techniques to manufacture low cost and low power microsensors such as those based on micro hotplates [5, 6]. Demarne and Grisel [5], and later, Corcoran et al [6] reported low cost, low power silicon-based tin oxide gas microsensors. In the mid-1990's Motorola Inc developed a low cost and low power commercial sensor based on the microhotplate technology for the detection of CO for the automobile industry [6]. In 2001, Mitzner et al [7] studied a

microhotplate-based gas sensor array for detecting toxic gases such as hydrogen sulphide (H_2S), ammonia (NH_3) and methane (CH_4) in agricultural animal confinement facilities. It was reported that tin oxide/platinum (SnO_2/Pt), tungsten oxide/gold (WO_3/Au), and zinc oxide (ZnO) sensing films were sensitive to the target gases NH_3 , H_2S and CH_4 respectively, but had some cross sensitivity. The limitations of this sensor array were baseline drift, high resistance, and long recovery time. In 2002, Sternhagen et al [8] studied a microhotplate-based gas sensor array for detecting automotive emissions and reported that SnO_2 /aluminum (Al), SnO_2/Pt and undoped SnO_2 sensing films were sensitive to NO_2 , CO and H_2O respectively. A limitation of this array was sensitivity to interferent gases such as NH_3 , H_2S and CH_4 .

Coles et al [9] investigated the advantages of using nanosize powders to produce metal oxide gas sensors. It was found that the sensitivity of nanosize alumina (Al_2O_3), zirconia (ZrO_2) and SnO_2 powders for detecting gases like CO, H_2 and CH_4 respectively was greater than corresponding microcrystalline powders. In particular, the sensitivity increased by a factor of five for SnO_2 powders. Gurlo et al [10] investigated the operation of nanocrystalline indium oxide (In_2O_3) and molybdenum oxide (MoO_3) - In_2O_3 thin films as toxic gas sensing materials. In their work, thin film layers were prepared using a sol-gel method. It was found that In_2O_3 and MoO_3 - In_2O_3 thin films were very sensitive to low concentrations (100-200 ppb) of O_3 and NO_2 , and the response of In_2O_3 films to NO_2 increased significantly when the grain size of the film was less than 50 nm. The operating temperature of these In_2O_3 based sensors was between 25° C and 250° C. The major disadvantage of the In_2O_3 films was that its performance characteristics were highly influenced by fabrication process temperatures.

Nanostructure-based metal oxide sensors appear to be promising candidates for toxic gas sensing since they offer a large surface area to bulk ratio and may have unique properties that could increase the sensitivity, selectivity and response time. Control of nanostructure growth is expected to increase the sensor stability and reproducibility while small size should reduce power consumption since there is less thermal mass and surface area.

Several investigators have used electrical field enhanced oxidation (EFEO) to grow nano-oxide wires from silicon, GaAs and Ti [11-14]. In the EFEO process, an atomic force microscope (AFM) tip is brought in contact with a metal or semiconductor film surface. This results in the formation of a water meniscus between the AFM tip and film due to humidity in the ambient air, as shown in Figure 1. When a

negative bias voltage is applied to the AFM tip, the electric field dissociates the water meniscus into hydrogen and hydroxyl ions. The negatively charged hydroxyl ions react with the film surface to form the metal-oxide nanowires as the AFM tip is moved across the surface [11-14]. The feasibility of using EFEO to create indium, tin and tungsten (In, Sn and W) oxide nanowires however has not been demonstrated.

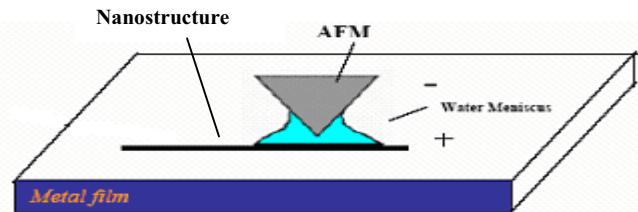


Figure 1. Electric field enhanced oxidation process.

The objectives of this work were to determine the feasibility of using EFEO to fabricate In_2O_3 , SnO_2 and WO_3 nanowires that could potentially be used for sensing NO_2 , O_3 and CO ; and examine the effects of fabrication parameters such as film thickness, ambient relative humidity and AFM tip voltage, force and scan rate on the growth of nanowires.

2. EXPERIMENTAL PROCEDURES

Two photo masks were used in fabricating the metal oxide nanowires. Film patterning mask (mask 1) shown in Figure 2.1a was used in a liftoff process to pattern the metal films. The mask consisted of sixteen 100 μm X 100 μm squares for growing the nanowires. Each square was connected to the vertically adjacent square(s) with a 20 μm line for the electrical connection required to grow the metal oxide structures. Alignment marks were used on mask 1 to locate the nanowires after release and for bonding pad placement on the released nanowires to characterize their electrical properties. An alignment-mark cover mask (mask 2) shown in Figure 2.1b was used to protect the alignment marks on the glass substrate from being etched away during the release of the metal oxide nanowires.

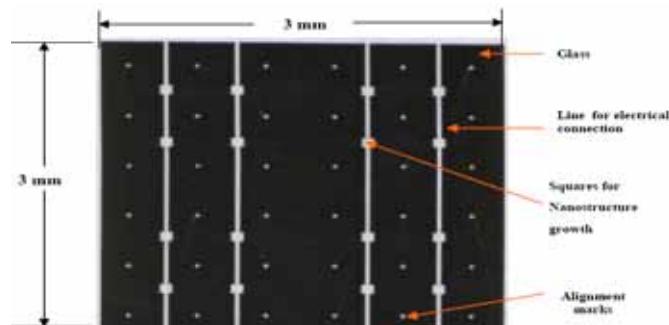


Figure 2.1a. Film patterning mask (mask 1) showing 100 μm X 100 μm squares for nanostructure growth and 20 μm wide lines for electrical connection.

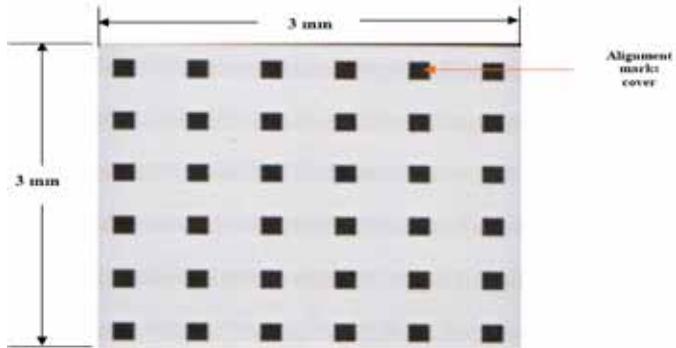


Figure 2.1b. Mask 2 for protecting alignment marks.

Micro glass slides (Corning) diced to 0.75 x 0.75 inch were used as substrates. Five to 20 nm thick metal films (In, Sn, W) were sputter deposited and patterned using the lift-off process. Uncoated silicon ultralever AFM tips were used to grow the SnO_2 and WO_3 nanowires. The number of scans per nanowire was from 1 to 1000. The silicon ultralever AFM tips used to grow the In_2O_3 nanowires were sputter coated with 10 nm thick titanium (Ti) and 20 nm thick Au layers to increase the tip conductivity and lifetime.

The experimental set up used for the EFEO process is shown in Figure 2.3. Silver paint was applied between magnetic mount and the metal film on the glass substrates to provide an electrical connection. The magnetic mount was placed on the sample holder of a Park Scientific AFM operated in the constant force mode. A negative bias voltage between -8 V and -17 V was applied to the AFM tip using an HP6216B power supply. Relative humidity was maintained at 50%. The parameters used for the growth of In_2O_3 , SnO_2 and WO_3 nanowires are given in Table 1.

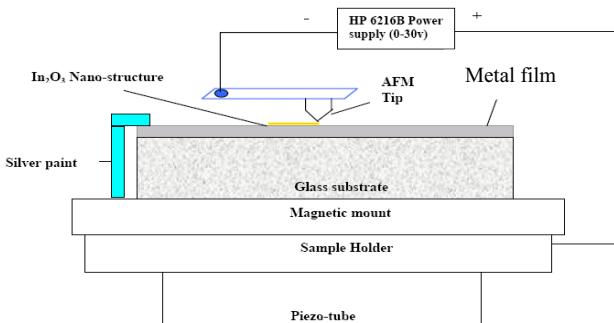


Figure 2.3. Set up for EFEO growth of metal-oxide nanowires.

After growing the nanowires, the alignment marks on the glass substrate were covered with photoresist using mask 2 to avoid chemical etch of the marks. The un-oxidized metal (100 μm x 100 μm squares), and 20 μm lines used for electrical connection on the surface of the glass substrates were etched using the parameters give in Table 2.

Table 1. Parameters for nanowire growth

Metal (Thickness)	Voltage (V)	Force (nN)	Frequency (Hz)	Scans
In (10 nm)	-12 to -17	28 - 32	0.01	3 - 10
Sn (10 nm)	-10 to -12	2 - 6	0.5 - 1.5	850
W (20 nm)	-8 to -15	2 - 6	0.04 - 2.1	1-1050

Table 2. Etch parameters for nanowire release

Metal	Etchant	Ratio	Time (sec)
In	HNO ₃ /H ₂ O	1: 99	90
Sn	HCl/ H ₂ O	1: 100	120
W	H ₂ O ₂ / H ₂ O	1: 39	120

The chemical composition of the In₂O₃ nanowires was analyzed with Auger electron spectroscopy (AES). The Auger measurements were conducted on a Physical Electronics 680 Nanoprobe spectrometer equipped with a field-emitter electron beam source, cylindrical mirror analyzer, and multichannel plate detector. The measurements were taken using a 10 nA, 10 kV beam with a measured diameter of 26 nm. Due to potential charging of the glass substrate, a molybdenum mask was mounted on the sample to dissipate any charge build-up that might have occurred otherwise. Sample cleaning and depth profiling were performed by argon ion sputtering using sputtering rates of 2 nm/min (calibrated against SiO₂). Quantization of the data was performed using pure element sensitivity factors (Handbook of Auger Electron Spectroscopy, Physical Electronics, 3rd edition) after the data had undergone a Savitsky-Golay 9-point smoothing and 5-point derivatization.

3. RESULTS AND ANALYSIS

The liftoff process used to pattern the metal films was successful for 10 nm and 20 nm thick films but not successful below 10 nm, since the metal films lifted off when soaked in acetone.

Approximately 120 metal-oxide nanowires were fabricated with an average height of 10 nm, an average width of 600 nm and lengths ranging from 20 to 75 μm. Ambient relative humidity played a critical role in the growth of nanowires. When the relative humidity dropped below 45% there was either no growth or discontinuous growth. This was attributed to an insufficient water meniscus between the tip and the metal film surface. Fewer scans were required to grow In₂O₃ versus SnO₂ and WO₃ nanowires. This was attributed to higher AFM tip force and coated tips, which enhanced the electric field strength.

Figure 3.1 shows a 3D AFM image of an In₂O₃ nanowire that is representative of what was grown using the EFEO technique. This nanostructure had a height of 13 nm, width of 700 nm and length of 20 μm respectively. Most nanowires fabricated at the optimal parameters listed in Table 3 appeared continuous and free of defects.

Figure 3.2 shows similar oxide structure grown to illustrate x and y axis control using the EFEO technique on a 10 nm In film. This nano-oxide structure had an average height and

width of 10 nm and 400 nm respectively while the length of nanowires varied from 2.5 to 8 μm.

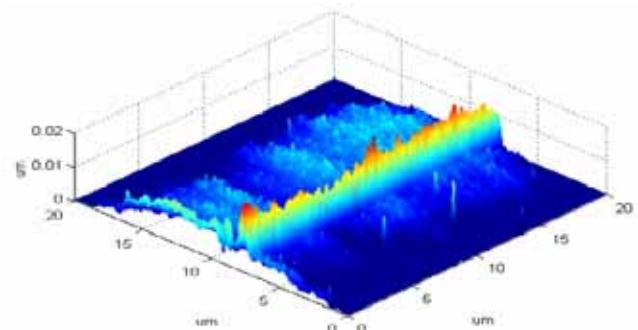


Figure 3.1. Three-dimensional AFM image of representative In₂O₃ nanostructure fabricated by EFEO.

Table 3. Optimal parameters for nanowire growth

Parameter	In	Sn	W
Film thickness (nm)	10	10	20
Relative humidity (%)	50	50	50
Applied voltage (V)	-15	-12	-15
AFM tip force (nN)	28	4	6
Scan speed (Hz)	0.01	0.5	0.04
Scans	10	850	1000

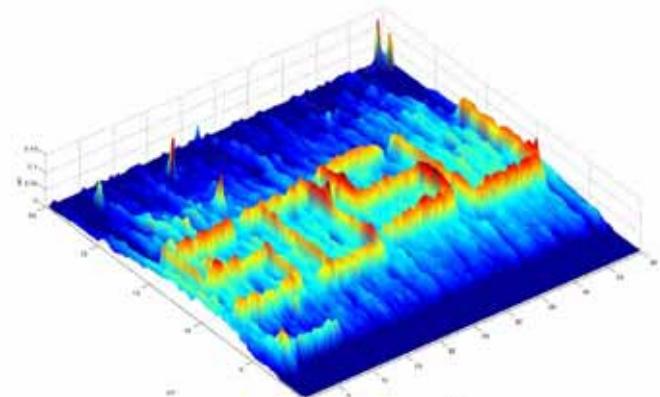


Figure 3.2. Three-dimensional AFM image of In₂O₃ "SDSU" nanostructure fabricated by EFEO.

About 90 nanowires grown on 10 nm thick In films were successfully released. Figure 3.3 shows optical microscope images of a representative 10 nm thick In film on a glass substrate before (left) and after (right) release. The nanowires are too small to be seen, however, the alignment marks protected with photoresist during the release process can be seen in both images. Figure 3.4 shows a 3D view of the In₂O₃ nanostructure after release. The released structure's average height and width were 12 nm and 700 nm respectively.

A Scanning electron microscopy (SEM) image of the nanostructure analyzed with AES is shown in Figure 3.5. The oxygen to indium ratio was found to be 1.69, 1.72, 1.71 and

1.84 at depths of 0, 1.3, 2.5, and 3.8 nm, which was near the 1.5:1 expected for stoichiometric In_2O_3 film.

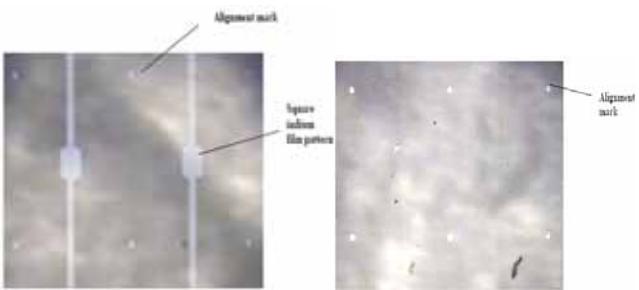


Figure 3.3. Optical image (250X) of a sample before (left) and after (right) In_2O_3 nanostructure release.

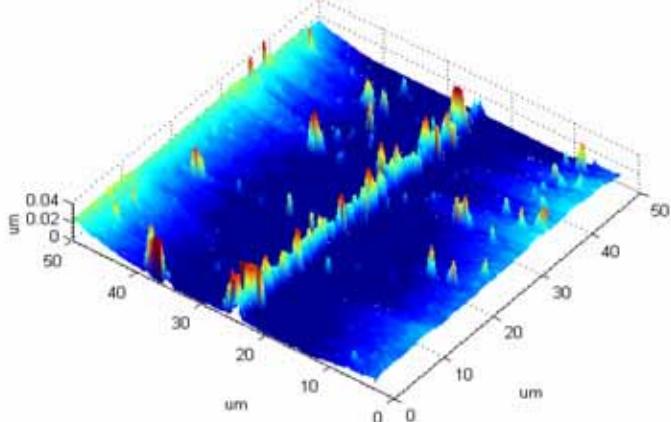


Figure 3.4. AFM image: 3D view of a representative In_2O_3 nanostructure after release.

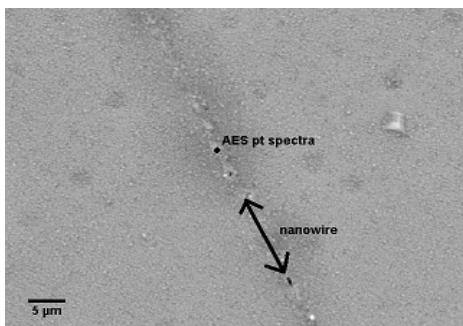


Figure 3.5. SEM image of In_2O_3 nanostructure on which AES analysis was performed.

4. CONCLUSIONS

Nanowires were successfully fabricated on indium, tin and tungsten films using the electric field enhanced oxidation technique (EFEO) and released by chemical etching. The field enhanced oxidation process was strongly dependant on film thickness, relative humidity, AFM tip bias (electric field strength), force, scan speed and number of scans. The optimal values for these parameters to obtain consistent growth and release of the indium-oxide (In_2O_3), tin-oxide (SnO_2) and tungsten-oxide (WO_3) nanowires were determined.

5. FUTURE WORK

Future work should include fabrication of additional nanowires to measure their electrical and gas sensing properties. Methods to enhance the selectivity of indium-oxide, tin-oxide and tungsten-oxide nanowires to nitrogen dioxide, ozone and carbon monoxide should also be examined.

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