Manufacturable, Highly Responsive Gold Nanowire Mercury Sensors

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ABSTRACT

We have developed a manufacturable and highly responsive gold nanowire sensor capable of detecting ppb concentrations of mercury in air and water. The nanowire sensor exhibits a superior response compared to thin film sensors and we have observed that this response is closely related to the morphology of the nanowire. By carefully controlling the sensor fabrication steps, we are able to obtain reproducible smooth, continuous nanowire morphologies and consequently obtain highly responsive and reproducible sensors. Additionally, these nanowire sensors are very robust and capable of withstanding regeneration temperatures without significant changes in the nanowire morphology or baseline electrical properties.

Keywords: gold, nanowire, sensor, detector, mercury

1 INTRODUCTION

Mercury is a severe neurotoxin [1,2,3] whose contamination in the U.S. has increased three-fold since the industrial revolution. It is estimated that nearly 40% of this pollution is due to emissions released by coal-burning power plants [4]. With the increasing use of coal as an energy source it is imperative to have inexpensive, precise, real-time monitoring of mercury levels. To address this need, we have developed a manufacturable and highly responsive gold nanowire sensor capable of detecting ppb concentrations in both air and water.

Previously we gave a development report on our nanowire mercury sensor and compared its performance to an equivalent thin film device [5]. The nanowire sensor exhibited a superior response (Fig. 1), but, at that time, had shortcomings in reproducibility and manufacturability. Since then, several improvements have been made to the nanowire sensor processing allowing for better control of the sensor response and manufacturability.

2 DEVICE FABRICATION

The nanowire sensors (Fig. 2) reported here were fabricated using the electron-beam lithography/ evaporation/lift-off process flow described in a previous report [5]. In actual manufacturing, other, more manufacturable lithography techniques, such as nano-imprinting would be utilized. Field-emission scanning electron microscopy was used to determine the width and length of the nanowires (40nm and 20µm respectively), and atomic force microscopy was used to determine the average thickness of the wires (~20nm). Both multiple and single nanowire devices were investigated in this study.

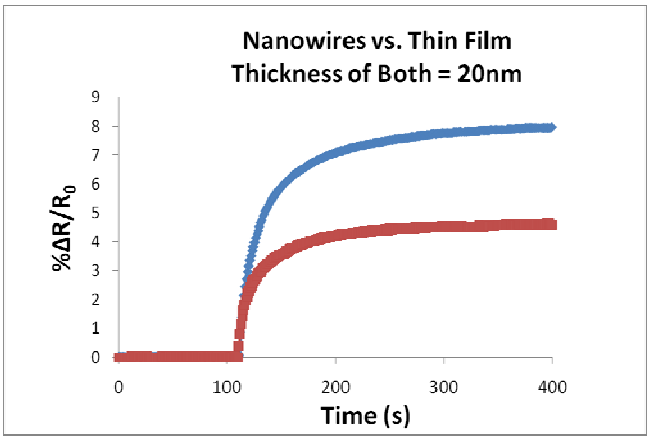

Figure 1. Comparison of the response of a gold nanowire (40nm width) and a thin film (1µm width) to 1µM of $HgCl_2$ dissolved in an aqueous solution.

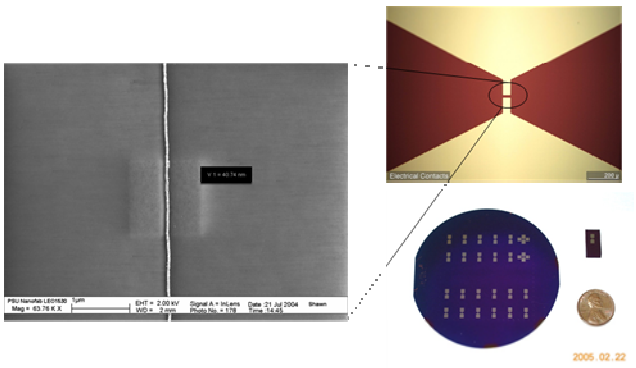

Figure 2. Picture showing the fabricated nanowire sensors on a 3 inch wafer, an optical microscope image of the platinum contacts, and an FESEM image of a 40nm wide, 20µm long nanowire in between the contacts.

3 NANOWIRE MORPHOLOGY CONTROL

We found that the surface condition prior to the gold deposition determines the roughness of the nanowires

produced by our approach. Several factors can affect this surface condition and lead to variable morphologies. For example, if chemical residues from the e-beam resist development procedure are left on surface of the exposed regions, then the wire is likely to have a rough morphology. By adding an additional rinsing step, we are able to remove this residue from the surface and ensure smooth nanowire morphology. Using such surface treatments, we now have excellent control over the deposited nanowire morphology. In addition, we have found a technique which allows us to avoid the surface treatments, if we so choose, and to reproducibly modify the morphology and electrical properties of deposited gold nanowires with less than ideal morphologies. This post-deposition modification technique involves applying a prescribed electrical stress to the contacted nanowire structure. High current densities (~$9x10^{11}A/m^2$) are needed in this approach for brief periods of time (<10s) and it is likely that this electrical stress induces significant joule heating and electromigration of the gold wire. Once the electrical stress is removed, the resulting nanowire exhibits a smoother morphology (Fig. 3) and a decrease in resistance up to three orders of magnitude (Fig. 4). We have found that these results could not be reproduced using thermal annealing. If the applied current density was too large (above $10^{12}A/m^2$) or applied for too long, the nanowire would inevitably fail and an irreversible increase in resistance would be seen. The FESEM analysis of the failed nanowires was indicative of a thermally assisted electromigration failure [6]. This electrical stressing technique gives us the ability to selectively and reproducibly alter the morphology for post-deposited nanowires. We have found that both types of smooth morphology Au nanowires, those attained by pre-deposition surface treatments and those attained by post-deposition electrical stressing, behave the same as Hg sensors.

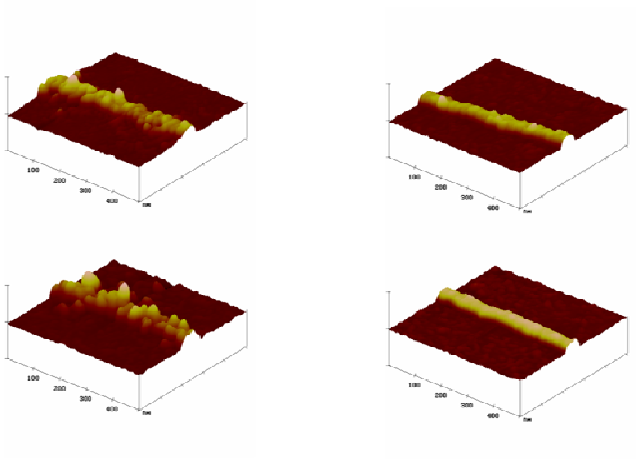

Figure 3. AFM images of gold nanowires. The nanowires on the left are of the as-fabricated, rough type. The nanowires on the right have been electrically stressed to alter their morphology using our post-deposition approach to morphology control.

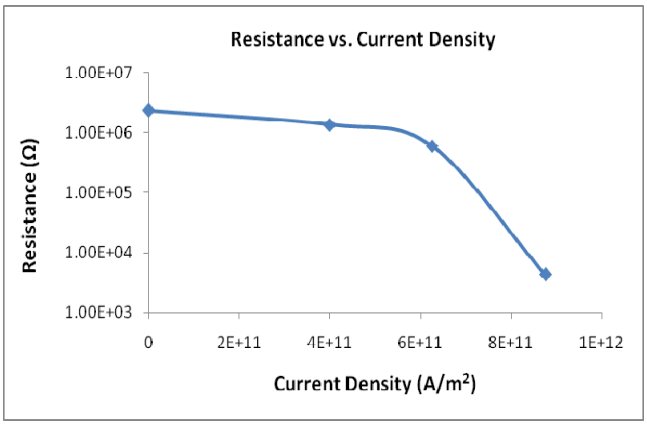

Figure 4. Plot of the resistance of a single gold nanowire (rough morphology) versus an applied current density. Since the surface is very rough, the cross-sectional area used in the current density calculation is an approximate average derived from AFM analysis.

4 ELECTRICAL CONDUCTION IN GOLD NANOWIRES

It is well known that the resistivity of metallic thin films increase as the thickness approaches the dimensions of the mean-free-path (MFP) of the conduction electrons [7]. More recently it has been demonstrated that similar principles apply to metallic nanowires with lateral dimensions approaching the MFP [8,9,10]. The increase in resistivity is due to the additional surface and grain-boundary scattering at this size scale. Matheissen's rule states that the scattering events are additive and independent of each other. Therefore, the total resistivity of a nanowire can be expressed as equation (1) below:

$$\rho_{Total} = \rho_0(T) + \rho_{ss} + \rho_{gb} \quad (1)$$

where ρ_{Total} is the total resitivity, $\rho_0(T)$ is the phonon-scattering controlled bulk, temperature dependant component of resistivity, ρ_{ss} is the component of resistivity due to surface scattering, and ρ_{gb} is the component of resistivity due to grain-boundary scattering.

The temperature dependence of resistance gives some insight into the contributions of each of these components. If the nanowire behaves as a continuous film, it is expected that the temperature coefficient of resistance (TCR), given by equation (2), will be linear at temperatures well above 20K. This is due to the linear relationship between phonon scattering and the temperature dependant portion of the resistivity in equation 1.

$$TCR = \frac{R}{R_0}\frac{1}{\Delta T} \quad (2)$$

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where R_0 and R are the initial and final resistances respectively and $\Delta T=T_1-T_0$ is difference between the initial and final temperatures.

As shown in Fig. 4, the temperature dependence of resistance is linear for the nanowires exhibiting a smooth morphology. However, the TCR is nearly three times larger than the reported value for bulk gold (0.3816/K). This underscores the contributions of surface and grain-boundary scattering to the total resistivity of the nanowires used in this study and also underscores the need for our successful efforts to attain reproducible morphology.

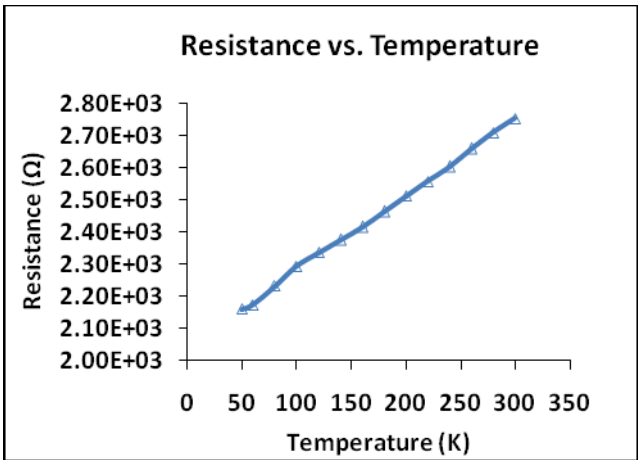

Figure 5. Plot of the resistance of a single smooth gold nanowire as a function of temperature.

5 SENSOR RESPONSE

The response of nanowires exhibiting the rough morphology is not reproducible. Figure 6 is an example of such a sensor. For this sensor, the resistance decreases upon mercury adsorption. One possible explanation for this behavior is that the conduction may be dominated by inter-particle tunneling. In such a case, the adsorption of mercury onto the gold surface may reduce the height and width of the tunneling barrier and hence decrease the resistance. Furthermore, the nanowires with the rough morphology are very sensitive to temperature fluctuations and will change their baseline electrical properties at the temperatures needed for sensor regeneration (~100 C). The response of nanowires exhibiting the smooth morphology, achieved either due to our pre-deposition approach or our post-deposition electrical stress approach, is highly responsive and reproducible (Figure 7). These sensors have a very predictable behavior: the resistance increases after mercury adsorption and generally saturates after an 8-10% change.

6 SUMMARY

We have two methods to achieve the smooth Au nanowire morphology needed for reproducible Hg sensing response: one uses pre-deposition surface treatments and the other uses post-deposition electrical stressing. With this control, we can have manufacturable sensors which possess larger responses than thin film devices and are also robust and capable of withstanding the temperatures required for sensor regeneration.

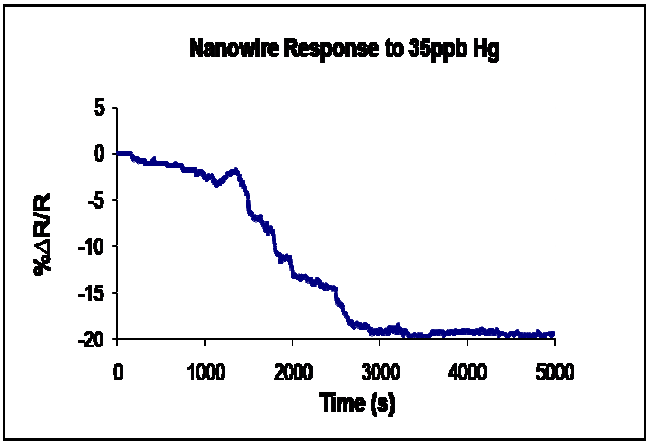

Figure 6. Response of a nanowire sensor (rough morphology) to elemental mercury.

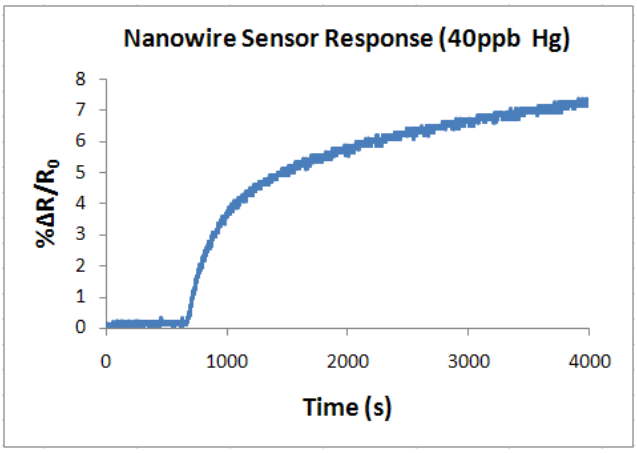

Figure 7. Response of a nanowire sensor (smooth morphology) to elemental mercury.

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