

Conductive Films of Ordered High-Density Nanowire Arrays

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ABSTRACT

Encapsulation of nanowires within an ordered template offers the possibility of manipulating nanowires into useful configurations and allows their aspect ratios and, hence, their physical properties to be tailored. In our laboratories, we have prepared high-density, ordered arrays of semiconductor nanowires within the pores of mesoporous thin films (MTFs) and anodized aluminum oxide (AAO) matrices using a supercritical fluid solution-phase inclusion technique. Conductive atomic force microscopy (C-AFM) was utilized to study the electrical properties of the nanowires within these arrays. Nearly all of the semiconductor nanowires contained within the AAO substrates were found to possess similar electrical properties demonstrating that the nanowires are continuous and reproducible within each pore. The ability to synthesize ordered arrays of semiconducting nanowires is a key step in future 'bottom-up' fabrication of multi-layered device architectures for potential nanoelectronic and optoelectronic devices.

Keywords: germanium nanowires, supercritical fluids, conductive AFM, anodic aluminium oxide

1. Introduction

The ability to pack high densities of memory storage and processing circuitry into specific nanoscale arrays, and utilize the unique transport properties associated with these architectures, is expected to lead to future generations of computer processors with device sizes many times smaller and faster than current silicon based processors [1,2]. However, both physical and economic constraints are expected to limit continued miniaturization of electronic and optical devices using current lithography based methods. Consequently, alternative nonlithographic methodologies for constructing the smallest features of an integrated circuit will soon be required.

Nanowires are expected to play a role in future integrated circuits as both devices and interconnects [3]. One of the most successful approaches for producing nanowires is based on the vapour-liquid-solid (VLS) growth process

[4,5]. One inherent problem with these approaches however, is the formation of entangled meshes of nanowires. While significant progress has been made in manipulating these nanowire meshes into useful configurations for potential electronic devices [6] some researchers have focused on forming nanowires in predefined architectures to allow easier processing and integration of the nanostructures into functioning devices [7-11].

Encapsulation of nanowires within an ordered template offers the possibility of manipulating nanowires into useful configurations and allows their aspect ratios and, hence, their physical properties to be tailored. Nanomaterials have been synthesized within the pores of mesoporous solids [7,8] having uni-directional arrays of pores using chemical vapour deposition (CVD) [9], electrodeposition [10] and incipient wetness techniques [11]. But these approaches often lead to incomplete pore inclusion due to pore plugging where the surface tension of the liquid solvent prevents precursor penetration into the pores. CVD approaches are less prone to pore plugging but can undergo capillary condensation resulting in liquid phases within the pores.

In our laboratories, we have developed a supercritical fluid (SCF) solution-phase method for forming metal, metal oxide, and semiconductor nanowires within mesoporous and anodized aluminium oxide (AAO) membranes [12]. The high-diffusivity, high precursor solubility, and reduced surface tension of the SCF results in rapid nucleation and growth of the nanowires within the pores reducing the reaction time for pore inclusion by at least an order of magnitude compared to CVD. Additionally, SCFs cannot be condensed to a liquid phase reducing the problems of pore plugging and incomplete inclusion seen with CVD, electrodeposition, and incipient wetness techniques.

Here we describe the preparation of germanium nanowire arrays within AAO membranes (GeNW-AAO). Conductive atomic force microscopy (C-AFM) was utilized to investigate the electrical properties of GeNW-AAO. Additionally, the nanowires formed within each pore of the AAO membranes were observed to have similar electrical

characteristics. These results suggest that each nanowire is continuous throughout the length of the substrate demonstrating the reproducibility of nanowire synthesis within the pores. Furthermore, nearly all of the nanowires formed within the AAO membranes are conducting suggesting nearly complete inclusion of nanowires within the matrix.

2. Experimental

AAO membranes of appropriate sizes were fabricated using methods reported in literature. Germanium nanowires were synthesized within the pores AAO membranes (GeNW-AAO) by the degradation of diphenylgermane in supercritical CO₂. Briefly, the AAO membranes were placed inside a 25 mL high-pressure reaction cell with diphenylgermane placed inside an open top quartz glass boat adjacent to the membranes under an inert atmosphere. The reaction cell was attached via a three-way valve to a stainless steel reservoir (48 mL). A high-pressure ISCO pump was used to pump CO₂ through the reservoir into the reaction cell. The reaction cell was placed in a tube furnace and heated to 873 K using a platinum resistance thermometer and temperature controller. The pressure was simultaneously ramped to 37.5 MPa and the reaction proceeded at these conditions for 30 min.

To remove contaminants and possible oxides present at the end of the nanowires within the AAO membranes, the surface was cleaned by RF Ar plasma. This plasma cleaning removed approximately 30 nm of the surface layer. The AAO membranes were also mechanically polished to remove any bundles of nanowires. GeNW-AAOs were placed inside the chamber of a sputter coater and a gold film was then deposited onto the film surface 200 nm thick. A custom-built conductive atomic force microscope was utilized for simultaneous measurement of the surface topography and conductance mapping as shown in Fig. 1.

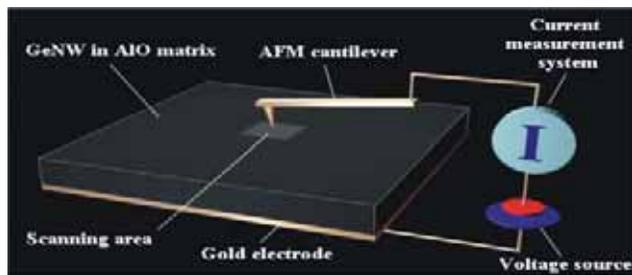


Figure 1. Schematic of C-AFM setup.

3. Results and Discussion

The inclusion of nanowires in AAO membranes combined with C-AFM yields the electrical properties of thousands of

individual nanowires that are aligned in ordered architectures.

AAO membranes have pores running perpendicular through the substrate hence all the pores should be accessible to the C-AFM tip. This would rule out the problems associated with the MTF preparation. The C-AFM results in Fig. 3 show that a large portion of the substrate is conductive. Furthermore, the areas of conductivity correlate strongly with the pore diameter seen in the SEM and the nanowire diameter seen in the topography map. The uniformity of the conductance suggests that there is little difference between the nanowires within each pore. This is an important result and suggests that the substrate consists of highly reproducible continuous nanowires within each pore that are uniform and running throughout the substrate.

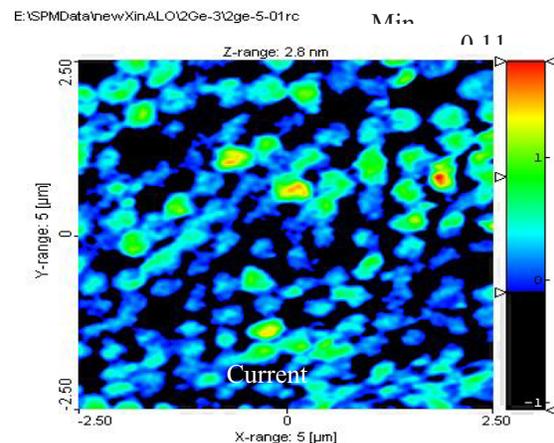
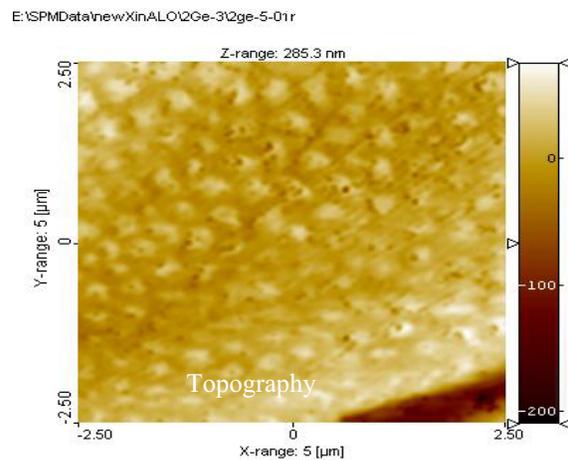


Figure 3 a-Topography and b-Current Map of GeNW-AAO

However, the uniformity of the conductance through each pore contained within the substrate clearly suggests complete pore inclusion of continuous nanowires from end-to-end. Comparison of the average density of pores within the AAO substrate to the average density of conducting

GeNWs within the AAO substrate shows that approximately 90% of the pores contain conducting nanowires.

To obtain a measure of the quality of the contact between the gold coating and the AAO membrane, a gold electrode 2 mm in diameter was deposited onto the top surface of the GeNW-AAO membranes in a similar approach to the bottom contact and is shown in Figure 4. The resistance of an individual GeNW measured above through C-AFM was approximately $R_i = 450 \text{ G}\Omega$. The number of GeNWs contained within the gold contact area was determined to be approx. 1.9×10^7 nanowires (N). The expected resistance between the electrodes would be $R_{calc} = R_i/N = 0.02 \text{ M}\Omega$; however, the measured resistance between the two contacts is often close to $5 \text{ M}\Omega$. The high measured resistance suggests that better contacts are required to further study the electrical properties of individual nanowires.

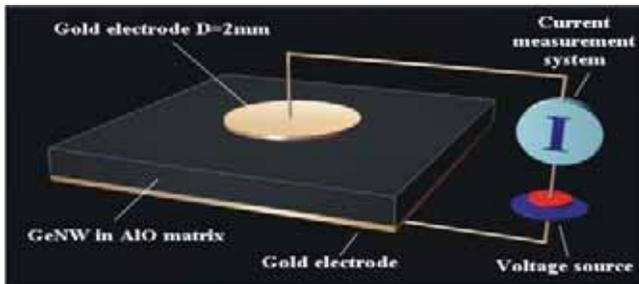


Figure 4: Schematic of a macrocontact measurement setup.

4. Conclusions

The preparation of GeNW-AAO substrates shows that a significant portion of the pores are filled with nanowires and that nearly all of the nanowires formed are conducting. Furthermore, the consistency of the conductivity of the nanowires within these GeNW-AAO substrates suggests that the nanowires are continuous throughout the length of the substrate and do not vary from pore to pore. The preparation of better contacts will also be required before the electrical properties of individual nanowires within the arrays can be studied.

5. References

1. Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H., *Adv. Mater.* **2003**, *15*, 353.
2. Trindade, T.; O'Brien, P.; Pickett, N. L., *Chem. Mater.* **2001**, *13*, 3843.
3. Zhang, X.; Zhang, L.; Meng, G.; Li, G.; Jin, N., *Adv. Mater.* **2001**, *13*, 1238.
4. Wagner, R. S.; Ellis, W. C., *Appl. Phys. Lett.* **1964**, *4*, 89

5. Wagner, R. S.; Ellis, W. C.; Jackson, K. A.; Arnold, S. M., *J. Appl. Phys.* **1964**, *35*, 2993.
6. J. Wang, M. S. Gudiksen, X. Duan, Y. Cui and C. M. Lieber, *Science*, 2001, **293**, 1455
7. Schult, F.; *Chem. Mater.* **2001**, *13*, 3184.
8. Attard, G.S.; Glyce, J. C.; Goltner, C. G.; *Nature*, **1995**, *378*, 366.
9. Dag, O.; Ozin, G. A.; Yang, H.; Reber, C.; Bussiere, G.; *Adv. Mater.*; **1999**, *11*, 474.
10. Banerjee, S.; Dan, A.; Chakrovorty, D.; *J. Mater. Sci.*, **2002**, *37*, 4261
11. Zhang, Z.; Dia, S.; Blom, D. A.; Shen, J.; *Chem. Mater.*, **2002**, *14*, 965
12. Holmes, J. D.; Lyons, D. M.; Ziegler, K. J., *Chem. Eur. J.* **2003**, *9*, 2144.