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Zinc Oxide Nanowires Grown by Vapor-Phase Transport Using Selected Metal Catalysts: A Comparative Study

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The search for new methods of synthesizing nanomaterials is a key goal of the national nanoscience initiative. Our research involves a comparative study of metal-surface-catalyzed growth of ZnO nanowires using four different metal catalysts and using substrates of differing materials and differing crystal orientations. We have employed multiple materials diagnostic techniques to compare the material, structural, and optical properties of nanowires grown using these different surface systems. In particular, we have found that the growth modes of nanowires are dependent on the choice of surface catalysts, e.g. for the Fe thin-film catalysts, the growth of ZnO nanowires may occur via a vapor-solid process, while, for the case of Au, Ag, and Ni catalysts, the vapor-liquid-solid process usually dominates the wire growth.

Nanowire growth has been investigated as a route to low-dimensional crystal structures. These nanostructures have potential applications in a variety of optical- and electronic-devices, such as lasers or light-emitting diodes. While the growth of these wires has been achieved under a wide variety of conditions, including liquid and vapor growth, one of the most reliable and well-studied approaches uses vapor-phase transport of the constituents coupled with surface catalysis of the nucleation and growth steps. Prof. Peidong Yang and his collaborators at Lawrence Berkeley National Laboratory have described an excellent example of this approach for the growth of ZnO nanowires. In this method, small surface-bound droplets of Au are formed on a solid substrate surface, such as Si(100), by heating a thin Au film and depositing it on the Si surface. These droplets served as alloying sites for the condensation of Zn vapor from a nearby solid-ZnO source. Single-crystal ZnO nanowires then grew from the supersaturated AuZn alloy, in the presence of constant trace amounts of oxygen (**Figure 1**). The orientation of the wires was thought to be governed by registration on the substrate crystalline lattice.

The success of this method in growing nanoobjects caused us to ask a series of questions: Can other catalysts be used? How general is the technique? What exactly controls the properties of the nanowires? Answering such questions is difficult because both the catalyst and substrate play important roles in determining the properties and the structure of the nanowires. In addition, the attainment of good nanowire material properties, such as good crystallinity and low impurity concentration, plays an important role in the practicality of various nanowire applications in electronics and optics.

Thus, we have employed multiple materials diagnostics, including x-ray diffraction, to compare the material, structural, and optical properties of the nanowires grown using these different surface systems. In particular, our research shows that the growth modes of nanowires depends on the exact metal surface catalysts used. Thus, for Fe or Ni thin-film catalysts, the growth of ZnO nanowires apparently proceeds via a vapor-solid process, while, for the case of Au, Ag, and sometimes Ni catalysts, the vapor-liquid-solid process appears

to dominate the wire growth. These differences are apparent in the high-resolution SEMs taken at the BNL Center for Functional Nanomaterials (CFN); see **Figure 2**. Further, as shown in **Figure 3**, our study shows that the degree of nanowire alignment on the substrates is a function of both the substrate lattice matching with the lattice of the nanowires, as well as the growth mode and its role in affecting the substrate-interfacial properties.

From a more general point of view, our investigation shows that the use of different catalysts provides versatility in the growth of one-dimensional ZnO nanostructures with different ranges of parameters such as diameters, areal densities, and aspect ratios. In particular, our studies suggest that, compared to noble-metal catalysts, the rate of growth using transition-metal catalysts is relatively faster and therefore typically yields thicker wires with a higher aspect ratio. However, this high growth rate is achieved at the expense of inducing more oxygen vacancies. These differences in growth properties would be expected to affect other properties of the wires, such as their electrical transport and surface chemistry. Exploring these aspects is of interest for practical applications of ZnO and other metal-oxide nanowires in nanodevices and chemical sensors.

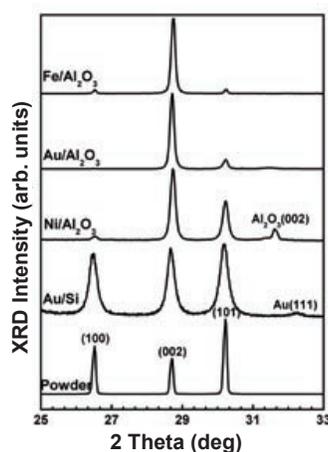


Figure 3. A series of XRD spectra for ZnO nanowires synthesized using several different metal catalysts. The spectra were recorded at angles covering three major characteristic XRD diffraction peaks of the wurtzite ZnO.

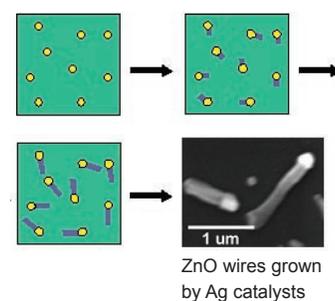


Figure 1. Illustration of the vapor-phase-transport process for ZnO nanowire growth.

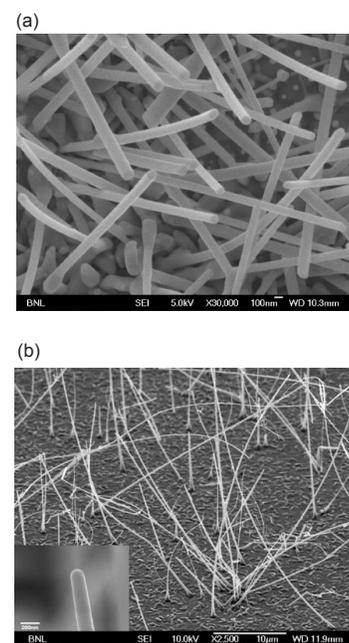


Figure 2. A FE-SEM image of ZnO nanowires grown on (a) a Si(111) substrate with Au as the catalyst; the predominant growth direction is 30° to the surface; (b) an a-plane (110) sapphire substrate with Fe as the catalyst; the predominant growth direction is at the surface normal. (Pictures taken at the BNL/CFN).