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Fundamental Strategy to Succeed a Vapor-Liquid-Solid Nanowire Growth

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Abstract

Metal oxide nanowires hold great promise for various device applications due to their unique and robust physical properties in air and/or water and also due to their abundance on Earth. Vapor-liquid-solid (VLS) growth of metal oxide nanowires offers the high controllability of their diameters and spatial positions. In addition, VLS growth has applicability to axial and/or radial heterostructures, which are not attainable by other nanowire growth methods. However, material species available for the VLS growth of metal oxide nanowires are substantially limited even though the variety of material species, which has fascinating physical properties, is the most interesting feature of metal oxides. Here we demonstrate a rational design for the VLS growth of various metal oxide nanowires, based on the "material flux window". This material flux window describes the concept of VLS nanowire growth within a limited material flux range, where nucleation preferentially occurs only at a liquid-solid interface. Although the material flux was previously thought to affect primarily the growth rate, we experimentally and theoretically demonstrate that the material flux is the important experimental variable for the VLS growth of metal oxide nanowires. Based on the material flux window concept, we discover novel metal oxide nanowires, which were previously impossible to form via the VLS route.

1. Introduction

The vapor-liquid-solid (VLS) method has proven to have great potential for the synthesis of well-defined single crystalline nanowires from functional inorganic materials. In VLS method, the diameter and spatial nanowire position can be controlled by adjusting the size and spatial position of the metal catalyst. In addition, the heterostructures along the axial or radial directions can be sequentially designed using the VLS process. These unique and fascinating features of the VLS method are not attainable by other nanowire growth methodologies. However, the VLS route for synthesizing nanowires composed of the desired functional materials has been only an approximate and unreliable method. For example, VLS nanowire growth of functional metal oxides, which exhibit unique and robust physical properties, such as photo-catalyst activity, high-Tc superconductivity, ferromagnetism, ferroelectricity and memristive behaviors, has been difficult. In this study, we propose the "material flux window" experimental concept for designing metal oxide nanowires via the VLS route. This concept suggests that experimentalists find an appropriate material flux range (window), in which the nucleation preferentially occurs at the LS interface, to grow the desired metal oxide nanowires via the VLS method.

2. Results and Discussion

First, we examine the material flux effects on the metal oxides, whose nanowires are easily formed by VLS. The growth temperature, oxygen partial pressure, and total pressure are 750 °C, 10^{-2} Pa and 10 Pa, respectively. Au catalysts were utilized for the VLS growth. As shown in Figure1, firstly VLS nanowire growth emerges at a certain metal flux range that is always lower than that required for VS film growth, resulting in a material flux window for VLS regime. These experimental results are consistent with our concept of an appropriate material flux range for the VLS process. Second, a significant material dependence on the material flux window width occurs. We define the material flux window as the flux range between the critical fluxes for VLS nanowire growth and VS film growth. The material dependence on the material flux window width is MgO > ZnO > In_2O_3 > SnO_2. The fundamental issue is to understand the material dependence on the material flux window width in terms of the material properties. One important issue is clarifying the mechanism of the correlation between the compound bonding strength and material flux window width. Understanding this correlation will be a foundation for tailoring the VLS growth of various metal oxide nanowires.

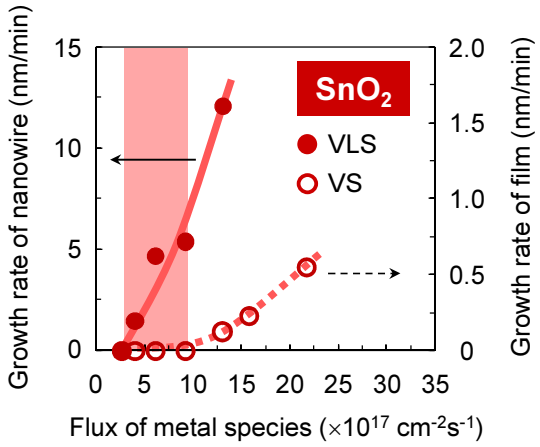

Fig. 1 Flux dependence on SnO_2 nanowires.

We explore these mechanisms by comparing the MD simulation data with classical nucleation theory. In principle, the material flux window width correlates with the difference between the LS and VS interfaces for the critical material flux required for nucleation. Based on classical nucleation theory, the critical material flux is determined by the activation energy barrier height for nucleatione. Therefore, the material flux window width is determined by the difference between the two interfaces (LS and VS) for the interfacial energy. To correlate the bonding strength and the material flux window width in the simulations, we define a dimensionless parameter, Γ, that corresponds to the material flux window width. The MD simulation data suggest that the compounds with the stronger bonding strength exhibit a wider material flux window by modifying the values. Thus, this difference causes the material dependence on the material flux window width. At the LS interface, the presence of surrounding liquid atoms strongly affects the value of LS via the interaction between compound atoms and liquid atoms. Such an interaction lowers the value of LS compared to that of VS.

Our experimental concept based on the material flux window highlights the critical importance of precisely controlling the material flux, which was underestimated in previous studies, when fabricating a metal oxide nanowire via the VLS route. Using this concept, we explored novel VLS growths of metal oxide nanowires. As shown in Figure 2, we have fabricated new metal oxide nanowires including MnO, CaO, Sm_2O_3, NiO, and Eu_2O_3, which have not been fabricated via the VLS route to date. To create these nanowires by VLS, we performed a strict metal flux control at 850°C without any intentional oxygen supply. We did not observe the VLS nanowire growth for MnO, CaO, Sm_2O_3, or Eu_2O_3 when the oxygen gas was intentionally supplied into the chamber. Thus, in terms of the material flux window width, there is a significant difference between the VLS nanowire growth of these metal oxides and the conventional VLS nanowire growth of typical metal oxides (MgO, ZnO, In_2O_3, and SnO_2). It was difficult to completely suppress VS film growth under the conditions employed in our growth experiments for MnO, CaO, Sm_2O_3, and Eu_2O_3. Thus, the present material flux conditions are slightly above the appropriate material flux window and/or critical material flux for the VS film growth. Therefore, the difference between the material flux dependences is caused by the unintentional oxygen supply from the oxide targets rather than the material flux window variations caused by their material dependences. Thus, the unintentional oxygen supply can critically affect the VLS growth of metal oxides. In conventional experiments of VLS oxide nanowire growths, it is often difficult to precisely control the oxygen flux in furnaces due to the high residual oxygen partial pressures. In the presence of an unintentional oxygen supply, the VLS nanowire growth of metal oxides is difficult for some oxides when their material flux windows exist at a relatively low oxygen partial pressure range (below 10^{-1}Pa). The residual oxygen promotes VS film growth rather than VLS nanowire growth by exceeding the critical material flux for VS film growth. The strict oxygen flux control by using material supply that does not contain oxygen species is the possible solution to suppress the detrimental VS film growth for realizing VLS nanowire growth of metal oxides. Thus, our present results highlight that it is now possible to design novel functional metal oxide nanowires via the VLS route by finding the appropriate material flux range based on the concept of the material flux window.

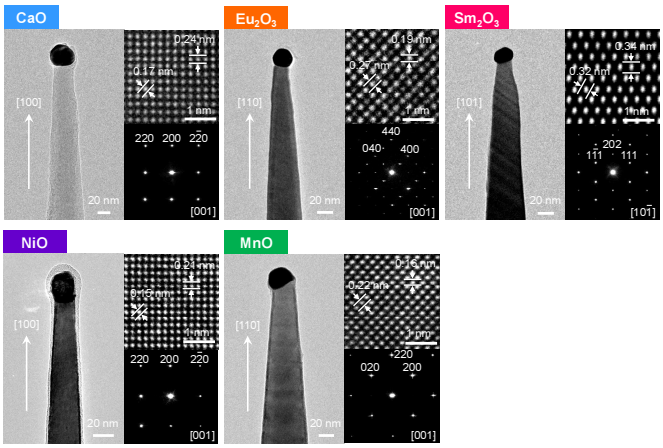

Fig. 2 TEM images of newly fabricated metal oxide nanowires based on our present experimental concept.

3. Conclusions

Here we demonstrate a rational design for the VLS growth of various metal oxide nanowires, based on the "material flux window". This material flux win-dow describes the concept of VLS nanowire growth within a limited material flux range, where nucleation preferentially occurs only at a liquid-solid interface. Although the material flux was previously thought to affect primarily the growth rate, we experimentally and theoretically demonstrate that the material flux is the important experimental variable for the VLS growth of metal oxide nanowires. Based on the mate-rial flux window concept, we discover novel metal ox-ide nanowires, which were previously impossible to form via the VLS route.

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