Impact of Preferential Indium Nucleation on Electrical Conductivity of Indium-Tin-Oxide (ITO) Single Crystalline Nanowires

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Abstract

Here we demonstrate a crucial role of preferential indium nucleation on the electrical conductivity of VLS grown ITO nanowires. The VLS growth of ITO through gold catalysts significantly differs from ITO film formations due to the emergence of preferential indium nucleation only at a liquid-solid interface. We demonstrate that the averaged resistivity of ITO nanowires can be decreased down to $2.1 \times 10^{-4} \ \Omega \cdot \text{cm}$, which is the lowest compared with values previously reported, via increasing tin concentration within nanowires.

1. Introduction

A vapor-liquid-solid (VLS) method is one of most powerful techniques to synthesize well-defined single crystalline nanowires for various inorganic materials. Among various inorganic nanowires, metal oxide nanowires exhibit fascinating physical properties, which are hardly attainable to other conventional semiconductor nanowires. For example, indium-tin-oxide (ITO) single crystalline nanowires offer an excellent metallic conductivity with the transparency. Since a high conductance of single crystalline ITO nanowires is desirable for most applications of ITO, increasing further the conductivity of ITO nanowires will open up novel device applications. Unfortunately, controlling the transport properties of VLS grown ITO nanowires is still a challenging issue due to the intrinsic difficulty in understanding the material transport phenomena during VLS growth across three phases. According to the scenario based on two metal elements whose vapor pressures are similar, ITO is an ideal material since the vapor pressures of indium and tin are relatively similar compared with other dopants such as Sb and Ta. However, the incorporation dynamics of tin into In$_2$O$_3$ nanowires during VLS process is still not well understood. Here we report that the nanowire growth of ITO through gold catalysts significantly differs from ITO film formations due to the emergence of preferential indium nucleation only at a liquid-solid interface. In addition, we show that the electrical conductivity of ITO nanowires can be enhanced by increasing intentionally tin concentration within nanowires.

2. Results and Discussion

Figure 1 (a)-(d) shows the SEM, XRD and TEM-EDS data of fabricated ITO nanowires. These ITO nanowires were fabricated by using the target of Sn:10 at.%. As seen in XRD and TEM data, the nanowires only show the bixbyite structure of In$_2$O$_3$ not the rutile structure of SnO$_2$. The growth direction can be assigned to be [100]. STEM mapping images of ITO nanowires with the incorporated tin concentration of 20 at.% were shown in Figure 1 (e). The spatial distribution of tin within nanowires is homogeneous, which is in fact sharp contrast to the trend for Ta-doped SnO$_2$ nanowires, where Ta-rich shell layer was preferentially formed on the nanowire sidewall via VS growth mode for Ta species. Thus the relatively similar vapor pressures of tin and, indium seem to allow us to create homogeneous VLS nanowires composed of multicomponent, which is important for nanowire-based device applications.

We measured the tin concentration data within ITO nanowires, measured by TEM-EDS, when varying the nominal tin concentration of target. Data ranged from 0-50 at.% are shown in the figure. Note that it is crucial to identify the presence and the concentration of tin within nanowires via utilizing Sn K shell peaks rather than Sn L shell peaks due to the significant overlapping of tin and indium peaks. It can be clearly seen that tin concentration within nanowires is always lower than the nominal tin concentration. In the case of 10 at.%-nominal composition, the tin concentration incorporated into nanowires was about 5 at.% Even for the highest tin nominal concentration-50 at.%, the tin concentration within nanowires was about 18-20 at.%. These lower tin concentrations within nanowires cannot be readily understood in terms of a conventional model based on the vapor pressure trends of metal elements during depositions. Because the vapor pressure of tin is lower than that of indium for the temperature range employed here, for example, at 750 $^\circ$C, 2.4$\times 10^{-2}$ Pa for indium and 1.9$\times 10^{-5}$ Pa for tin. In other words, indium concentration should be lower than tin if a re-evaporation causes the discrepancy of composition during depositions due to the vapor pressure difference. Our experimental trend is also completely opposite to that of Sb-doped SnO$_2$ nanowires, where the higher vapor pressure of Sb resulted in the lower Sb concentration within nanowires due to the evaporation of Sb during VLS growth.

Next, we examine the effect of tin concentration on the transport properties of ITO nanowires. Figure 2(a) show the distribution data of measured resistivity values to ensure the statistical difference between different tin concentrations. Figure 2(c) shows the correlation between the tin concentration incorporated into nanowires and the resistivity. Clearly there is a straightforward relationship between the incorporated tin concentration and the resistivity. The
higher the tin concentration the lower the resistivity due to increased carrier concentration. Thus understanding the preferential nucleation of indium during ITO nanowire formation is essential to enhance the conductivity of ITO nanowires via increasing tin concentration of ITO nanowires. The averaged resistivity of ITO nanowires can be decreased down to \(2.1 \times 10^{-7} \ \Omega \cdot \text{cm}\), which is lower than the resistivity values of ITO nanowires previously reported. Although the typical averaged resistivity of VLS grown ITO nanowires has been reported to be around \(10^{-5} \ \Omega \cdot \text{cm}\) up to \(10^{-3} \ \Omega \cdot \text{cm}\), the discrepancy between previous works and the present study might be the different tin concentrations within ITO nanowires. Our highly conductive ITO nanowires also exhibit the metallic behaviors, as shown in the temperature dependence data. Since the lowest value of ITO resistivity at RT is \(7.7 \times 10^{-3} \ \Omega \cdot \text{cm}\) in an epitaxial ITO single crystal film grown on YSZ substrate, our averaged resistivity value of \(2.1 \times 10^{-4} \ \Omega \cdot \text{cm}\) with almost 20% of \(10^{-3} \ \Omega \cdot \text{cm}\) range conductivity seems to be already quite low but can be further enhanced by optimizing and enhancing tin incorporation into ITO nanowires. To improve further the electrical conductivity of ITO nanowires, it would be a key issue to enhance not only carrier concentration via increasing tin concentrations but also the mobility by an appropriate passivation of nanowire surface.

![Figure 1](image1.png)

**Figure 1** Morphology and microstructures of indium-tin-oxide (ITO) nanowires. (Sn:10 at.%) (a) FESEM image of nanowires grown on MgO(100) substrate, (b) TEM, HRTEM and electron diffraction data, (c) XRD data of ITO nanowires, (d) TEM-EDS data of nanowires, (e) STEM elemental mapping images.

Figure 2 Transport properties of ITO nanowires with varying tin concentrations. (a) Resistivity distribution data, (b) Relationship between tin concentration incorporated into ITO nanowires and the resistivity of ITO nanowires.

3. Conclusions

In summary, we demonstrate a crucial role of preferential indium nucleation on the electrical conductivity of VLS grown ITO nanowires using gold catalysts. In spite of the fact that the vapor pressure of tin is lower than that of indium, we found that the indium concentration within nanowires is always higher than the nominal composition. Thus a VLS growth of ITO through gold catalysts significantly differs from ITO film formations due to the difference between the two metal elements on the nucleation probability at LS interface. Furthermore we demonstrate that the conductivity of ITO nanowires can be increased by considering the tin incorporation dynamics during ITO nanowire formation. We believe that the present findings will be a foundation to design and tailor novel multicomponent VLS nanowires.

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References