Crucial role of doping dynamics on transport properties of Sb-doped SnO₂ nanowires

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Impurity doping on semiconductor nanowires grown by vapor-liquid-solid (VLS) mechanism remains an important challenge. Here we demonstrate the importance of doping dynamics to control the transport properties of Sb-doped SnO₂ nanowires. Sb doping decreased the resistivity of SnO₂ nanowires down to 10⁻³ Ω·cm range, while there was the lower bound of resistivity even increasing further the dopant concentration from supplied source. We found that the doping limitation is related to the re-evaporation events of dopant through vapor-solid growth process rather than VLS process. Thus understanding the dopant incorporation dynamics is essential to control the transport properties of SnO₂ nanowires by impurity doping. © 2009 American Institute of Physics.

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Semiconductor nanowires grown via the vapor-liquid-solid (VLS) mechanism are attracting much attention due to not only the nanoscale scientific interests but also the potential device applications.1 Impurity doping is an important process to control the transport properties of semiconductors. Feasibility of the impurity doping for VLS grown nanowires has been intensively investigated due to the complex nature of dopant incorporation dynamics.2 The essential difference between VLS grown nanowires and thin films on the impurity doping is the presence of a metal catalyst, which is a liquid state during VLS, and the mass transport events through liquid-solid, vapor-liquid, and vapor-solid (VS) interfaces. Thus the complex dynamics of the impurity doping on VLS growth has held back the arbitrary controllability of the electric properties. Although the dopant incorporation processes on growths of nanowires comprised of single element including Si and Ge are complex enough,2–4 the doping process for nanowires comprised of multielements would be more complex. Although metal oxides exhibit many interesting physical properties,5 current knowledge as to the impurity doping on VLS grown oxide nanowires is still scarce and far from the comprehensive understanding. For example, impurity-doped SnO₂ nanowires by VLS have been investigated due to the transparent conductivity of SnO₂.6–8 The wide variation of the measured conductivity was found, however, the mechanism of such wide variation has not been identified due to the lack of understanding of the dopant incorporation process. In addition, the uniform dopant distribution within nanowires has been assumed in previous investigations.6 The lack of understanding and the variation of transport properties would be detrimental for the reliable device applications. These backgrounds motivated us to investigate the transport properties of Sb-doped SnO₂ nanowires grown by VLS and the dopant incorporation mechanisms. Our results highlight the crucial role of dopant incorporation dynamics on the transport properties of Sb-doped SnO₂ nanowires.

SnO₂ nanowires were grown on Al₂O₃ (110) single crystal substrate by Au catalyst-assisted pulsed laser deposition technique (ArF excimer laser, λ = 193 nm).7 The background pressure of the chamber was 10⁻⁵ Pa. Sn and Sb₂O₃ mixed powders (Koujundo Chemical) were used as the target with varying the Sb dopant concentration. The Sb dopant concentration (at. %) is hereafter defined as the atomic ratio of Sb to Sn. Oxygen and argon mixed gas was introduced into the chamber with controlling the ambient total pressure 10 Pa with the flux ratio of oxygen and argon (1:1000). Prior to the laser ablation, the Au-coated Al₂O₃ substrate was preheated at 750 °C for 20 min. The typical growth temperature was

![Image of FESEM](image_url)

FIG. 1. (a) FESEM image of Sb (5 at. %)-doped SnO₂ nanowires. (b) HR-TEM image and SAED pattern. (c) X-ray diffraction (XRD) data. (d) EDS data. The inset shows the data around Sn K and Sb K shell peaks.
750 °C. The nanowire morphology was characterized by field emission scanning electron microscopy (FESEM) (S-4300) at an accelerating voltage of 30 kV. High-resolution transmission electron microscopy (HRTEM) (JEM-3000F) coupled with energy dispersive spectroscopy (EDS) at an accelerating voltage of 300 kV was used to evaluate the diameter, the crystallinity, and the composition of the fabricated nanowires. We employed two different methods to measure the transport properties of nanowires, including a microwave conductivity measurement (MCM) and a four-probe conductivity measurement (FPCM). Detail apparatus of MCM can be seen elsewhere. All the above experiments were carried out at room temperature in Ar or SF6 atmosphere. For FPCM, we utilized devices composed of individual nanowires, which were fabricated by combining photolithography and electron-beam (e-beam) lithography processes. Then the metal deposition of Pt/Au 20/100 nm was carried out at room temperature in Ar or SF6 atmosphere.

Sb composition in the target was 5 at. %. It can be seen that the MCM data is an averaged value of 10 11 nanowires. Thus the reliable transport data of MCM affords us to focus our studies on the MCM data of MCM in the following discussions.

Two-probe and four-probe method is almost identical to that obtained from the four-probe method. Table I shows the comparison between MCM and FPCM in the resistivity data for both non-dope and Sb (7 at. %)-doped SnO2 nanowires. The reasonable agreement between MCM and FPCM data can be seen. The agreement between ac and dc measurements is theoretically understandable when considering the mobility range of impurity-doped SnO2, which is typically ranged from 20–50 cm2 V−1 s−1.

Figure 3 shows the dependence of supplied dopant concentration on the resistivity. Interestingly there was the lower bound of resistivity even increasing further the dopant concentration from supplied source above 3 at. %. The inset shows the Sb concentration data within nanowires, demonstrating that the incorporated dopant concentration approached the limited value around 2 at. % above 3 at. % of supplied dopant concentration. Clearly there is a reasonable correspondence between the resistivity and the incorporated dopant concentration. As such the lower bound of resistivity is closely related to the dopant incorporation dynamics. The dopant incorporation dynamics is related to three major processes, including (1) the supplied process of dopant from the source, (2) the re-evaporation process of supplied dopant from the surface, and (3) the dopant incorporation process into nanowires. We examined the effects of each process in the following discussions. First in (1), the supplied process, the dopant concentration supplied onto the surface was investigated by measuring the dopant concentration of thin films formed under RT, where the re-evaporation process is negligible. The electron probe microanalysis on the Sb (20 at. %)-doped SnO2 films demonstrated that the dopant concentration within the film was 20.07 at. %, which is almost identical to the nominal value. Thus there is no significant difference between the dopant concentration supplied onto the surface and the nominal dopant concentration in the present experiments. Second, the re-evaporation process of dopant on the surface was studied by measuring the dopant concentration during the re-evaporation process. The agreement between ac and dc measurements is theoretically understandable when considering the mobility range of impurity-doped SnO2, which is typically ranged from 20–50 cm2 V−1 s−1.

<table>
<thead>
<tr>
<th>Sb % in target</th>
<th>MCM</th>
<th>FPCM</th>
</tr>
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<tbody>
<tr>
<td>Non-dope</td>
<td>6.67 × 10⁻¹</td>
<td>3.86 × 10⁻¹</td>
</tr>
<tr>
<td>Sb: 7 at % in target</td>
<td>4.35 × 10⁻³</td>
<td>7.12 × 10⁻³</td>
</tr>
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</table>

Table I. Comparison between MCM and FPCM on the resistivity data of non-dope SnO2 nanowires and Sb (7 at. %)-doped SnO2 nanowires.
concentration of thin films grown at 400 °C. The remaining dopant concentration within the film was 1.73 at. %, which is much lower than the nominal value 20 at. %. Although above experiments were performed in the absence of Au catalysts, the re-evaporation process must be substantial when performing a nanowire growth above 400 °C. Based on above experimental implications, an enhancement of the dopant incorporation above 400 °C might be achieved by decreasing the growth temperature, i.e., the reduction of re-evaporation events. Figure 4(a) shows the dopant concentration data within nanowires when varying the growth temperature from 550 to 750 °C. Note that there was no SnO2 nanowire growth below 550 °C. The nominal dopant concentration in supplied source was 5 at. %. The significant enhancement of dopant incorporation was observed when reducing the growth temperature from 750 to 650 °C. The dopant concentration within nanowires grown under 650 °C was nearly 4%, which is in fact twice when compared with the value for 750 °C. As such the reduction of re-evaporation process can be achieved by controlling the nanowire growth temperature. Further decreasing the growth temperature from 650 to 550 °C resulted in the decrease of the dopant concentration within nanowires. This is presumably due to (i) the suppression of diffusion length of dopant adatoms on the surface and (ii) the presence of an activation energy barrier for incorporating dopant adatoms into nanowires. Although Sb re-evaporation from the SnO2 nanowire surface must occur, our results indicate the dominance of Sb re-evaporation events before the dopant incorporation process rather than the re-evaporation from the solid surface. Figure 4(a) also shows the resistivity data of nanowires when varying the growth temperature. Clearly there is a remarkable correspondence between the incorporated dopant concentration and the conductivity of nanowires when varying the growth temperature. Figure 4(b) summarizes the relationship between the incorporated dopant concentration and the resistivity of nanowires for various conditions. The reasonable correspondence can be seen. Thus it is very important to control the dopant incorporation process rather than varying the supplied dopant concentration. Further remained issue is the dopant incorporation pathway. There are two distinct incorporation pathways of dopant adatoms, including a VLS process via metal catalysts and a VS process through the nanowire surface. The VS mechanism assumes the inhomogeneous dopant distribution within nanowires, whereas the VLS mechanism assumes the homogeneous dopant distribution. Assuming the homogeneous dopant distribution within nanowires, the experimental data of resistivity should agree with theoretical value estimated by the following formula: \[ \rho = \frac{1}{\mu e n} \], where \( e \) is an elementary electric charge, \( \mu \) is a mobility, and \( n \) is a carrier density. Adapting the data of the \( \mu \) (40–50 cm² V⁻¹ s⁻¹) and \( n \) \((3.0–8.0) \times 10^{20} \text{ cm}^{-3}\) for our experimental configurations, the theoretical value is \( \rho_{\text{theory}}: (1.7–5.2) \times 10^{-4} \) Ω cm, which is an order of magnitude lower than our experimental value \( \rho_{\text{exp}}: 4.3 \times 10^{-3} \) Ω cm. The discrepancy cannot be solely explained in terms of the variation of \( \mu \) and \( n \) data for the estimation. This thus indicates the inhomogeneous dopant distribution within nanowires, in other words, the dominance of VS incorporation mechanism rather than the VLS. Recently Lauhon and co-workers reported such inhomogeneous dopant distribution of P-doped Ge nanowires with the relation to the differences in precursor decomposition rates, and the similar mechanisms might govern our experimental system. These results highlight that understanding the dopant incorporation dynamics is rather essential to control appropriately the transport properties of SnO2 nanowires by impurity doping.

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