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Dual Impact of Impurity on Crystal Growth Interface and Electrical Homogeneity of Metal Oxide Nanowires in Vapor-Liquid-Solid Process

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Abstract

Vapor-liquid-solid (VLS) growth process of single crystalline metal oxide nanowires have shown the promises for various electronic applications. However, accurate control of electrical properties has not been achieved because of unintentional doping effects via vapor-solid (VS) interface growth. In this study, we investigate the impact of impurity ions on interface crystal growths and electrical homogeneity of VLS oxide nanowires. We experimentally demonstrate that the impurity ions significantly enhance the VS interface growth. Furthermore, electrical homogeneity in an entire nanowire is achieved via the spatially-resolved electrical resistivity measurement of Sb-doped SnO_2 nanowires without unintentional doping effects. The presented results are important for realizing practical applications of oxide nanowire based devices.

Introduction

Metal oxide nanowires formed via a vapor-liquid-solid (VLS) growth are attracting much attention due to their unique properties which cannot be obtained in other materials. In metal oxide nanowires, on the other hand, accurate control of electrical property is fundamentally difficult as compared with group IV and III-V semiconductors due to unintentional carrier doping effects. Recently, we have clarified that the unintentional doping originates in vapor-solid (VS) interface crystal growth in VLS process. [1] By controlling material flux, we have found the "flux window principle" [2] for nanowires grown via a true VLS route where the unintentional doping is sufficiently suppressed. However, the impacts of impurity ions on the crystal growth interfaces have not been clarified in spite of their crucial importance for electrical controllability of metal oxide nanowires.

In this work, the impacts of Sb ions on VLS-grown SnO_2 nanowires are investigated as to crystal growth interfaces and spatial electrical homogeneity. By evaluating the flux window for various Sb content, we found that impurity ions significantly affect the crystal growth interfaces. Furthermore, controllable and uniform carrier doping via intentionally-incorporated impurity ions was successfully achieved by suppressing VS growth interface in Sb-included VLS process.

Experiments

Pulsed laser deposition method was utilized to grow metal oxide nanowires. SnO_2 and Sb_2O_3 mixed powders (Kojundo 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. The vapors of material species were supplied by ablating metal oxide tablets. The material flux was controlled by changing the laser energy from 40 to 80 mJ. Oxygen and argon gases were introduced into the vacuum chamber with the total pressure of 10 Pa and the oxygen partial pressure of 10^{-3} Pa. The temperature of substrate was set to 750 °C. Synthesized nanowires were characterized by field emission scanning electron microscope (FESEM, JEOL JEM JSM-7610F). The electrical conduction measurement was performed in the form of four-probe and multi-electrode single nanowire device. [3] The device was constructed onto 100 nm SiO_2 coated Si (100) substrate by the electron beam (EB) lithography. The electrical conduction measurements were performed in the probe station connected with a semiconductor parameter analyzer (Keithley, 4200SCS) at room temperature in vacuum condition (10^{-3} Pa).

Results and Discussion

Fig.1 shows the schematic of two crystal interface growths in a VLS crystal growth process. Widely reported tapered VLS-grown metal oxide nanowires consist of an untapered inner core (liquid-solid (LS) interface crystal growth) and outer tapered shell (VS interface crystal growth on the sidewall of LS interface). Since unintentional doping occurs in the outer VS interface crystal growth, the VS growth should be suppressed for accurate control of electrical property: e.g. uniform and low carrier concentration doping. The VS growth can be suppressed when the material flux is lower than a critical vapor flux for VS growth. [1]

Fig.2 shows the experimental evaluation of Sb impurity effects on crystal growth interfaces. The tapered nanowire structures were observed in a higher vapor flux region (Fig.2a). By measuring nanowire diameters at top and bottom

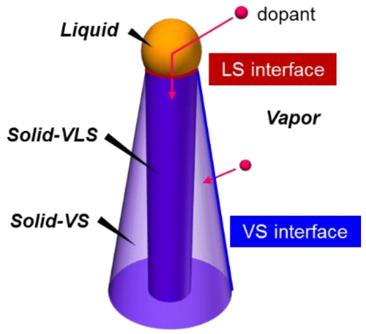

Fig.1. Schematic of impurity incorporation process at two crystal growth interfaces.

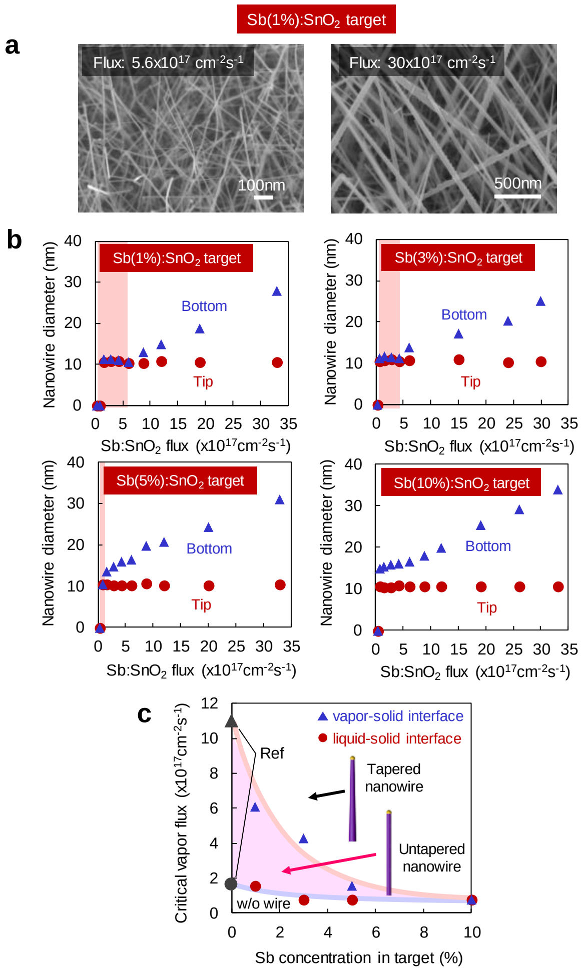

Fig.2. (a) SEM image of untapered nanowires and tapered nanowires. (b) Sb:SnO_2 flux dependence of nanowire diameter. (c) Relationship between flux window width for untapered (LS) nanowires and Sb concentration in target. Flux window width of non-doped SnO_2 nanowires is also shown. [1]

of nanowires, the degree of tapering, namely the amount of VS interface growth, can be quantitatively evaluated as shown in Fig.2b. The agreement of top and bottom diameters indicates no VS interface growth (or untapered nanowire) at the vapor flux. Interestingly, the critical vapor flux for VS interface growth is significantly decreased with Sb:SnO_2 flux increases, indicating that true VLS nanowires with impurity ions are fundamentally difficult to grow compared with undoped SnO_2 nanowires (Fig.2a,b). Further investigation such as molecular-dynamics calculation of VLS growth process is needed to clarify the physical mechanism of the Sb effects.

Although the clear impacts of impurity ions on crystal growth interfaces are demonstrated, that on electrical homogeneity are still unclear. Therefore, spatially-resolved electrical resistivity was measured for the tapered and untapered nanowires as shown in Fig.3. For the tapered nanowires, the apparent resistivity largely decreases as measured position shifts from top to bottom, indicating radial carrier distribution due to highly-doped VS interface growth. Therefore, general assumption of uniform carrier density cannot be applied to tapered metal oxide VLS nanowires, which are commonly

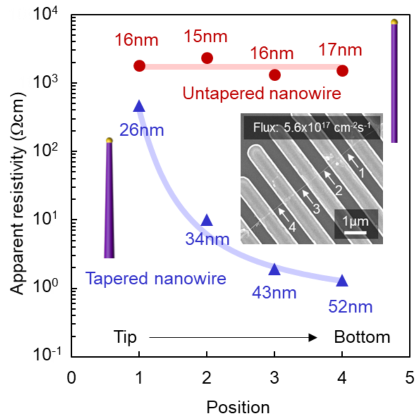

Fig.3. Spatial distribution of 4-probe electrical resistance for untapered and tapered Sb doped SnO_2 nanowires. Inset SEM image shows the multi-electrode single nanowire device.

obtained. For the untapered nanowires, on the other hand, nanowire resistivity is identical independent of the measured position due to Sb incorporation via LS interface growth without unintentional doping. Thus, the accurate control of uniform and low carrier density of VLS metal oxide nanowires is successfully achieved. The presented approach will be an important platform for realizing the functional nanodevices using metal oxide nanowires.

Conclusions

In this study, we investigate the impacts of impurity ions on 1) crystal growth interface in a VLS process and 2) electrical homogeneity of metal oxide nanowires. By evaluating a critical vapor flux for the two growth interfaces, it is clarified that the Sb incorporation enhances VS interface crystal growth of SnO_2 nanowires. Furthermore, the radial electrical homogeneity in an entire nanowire was clearly demonstrated via the spatially-resolved electrical resistivity measurement of Sb-doped nanowires without any unintentional doping effects. Since the radial electrical homogeneity is necessary for accurate evaluation of electrical properties of oxide nanowires, the presented results are important for realizing practical applications of oxide nanowire based devices.

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