Mechanism and control of sidewall growth and catalyst diffusion on oxide nanowire vapor-liquid-solid growth

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Oxide nanowires formed via the vapor-liquid-solid (VLS) mechanism are attractive building blocks toward nanowire-based electronic devices due to their fascinating physical properties. Although well-defined oxide nanowires are strongly required for the applications, tapering during oxide nanowire VLS growth has been detrimental and uncontrollable. Here we demonstrate the mechanism to control the tapering during oxide VLS growth. Suppressing simultaneously both the oxidization of adatoms at the sidewall and the catalyst diffusion from the tip was found to be essential to avoid the tapering. This mechanism would be universal in various oxide nanowire VLS growths. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2978347]

Oxide nanowires formed by the vapor-liquid-solid (VLS) growth mechanism and the heterostructures are natural candidates to incorporate various functionalities of transition metal oxides into nanowire-based devices.[1–5] In developing these applications, it is important to fabricate long, straight nanowires with constant diameters.[6–8] In many VLS growths, tapering[9–14] has been detrimental for the purpose and sometimes uncontrollable. However, a comprehensive understanding of the key factors affecting the tapering is still lacking due to the complex nature of oxide VLS growth.[15,16] We have therefore investigated the mechanisms and control of the tapering in oxide VLS growth by carrying out MgO nanowire VLS growth using pulsed laser deposition (PLD) technique.[17–23] MgO is a rocksalt crystal structure and has been utilized as a versatile single crystal substrate for oxide heterostructures due to the small lattice mismatch with various transition metal oxides.[24,25] Since the MgO nanowires can be a promising "nanosubstrate" for the nanowire heterostructures,[3–5,21,22] the well-defined nanowire morphologies are strongly desirable. Previously we have investigated the MgO VLS growth mechanisms and the kinetics.[17–23] However, the control of the tapering has been unfeasible due to the unknown physical mechanism. In this letter, we show the mechanisms and controllability of the tapering in MgO VLS growth. We found the significant role of the oxidation at the sidewall in controlling the tapering phenomena. This mechanism would be universal in various oxide VLS growths.

MgO nanowires were grown on MgO (100) single crystal substrate by Au catalyst-assisted PLD technique.[17–23] Prior to the nanowire growth, Au catalysts were deposited on MgO single crystal substrate. The background pressure of the PLD chamber was 10^{-5} Pa. ArF excimer laser (Lamda-Physik COMPex 102, $\lambda = 193$ nm) operating at the pulse repetition rate of 10 Hz and the laser energy of 40 mJ was used for the laser ablation. MgO single crystal was used for the source of Mg species vapor during the nanowire growth. Oxygen and argon mixed gas was introduced into the cham-

ber with controlling the ambient pressure. The ambient pressure was 10 Pa with varying the ratio of oxygen and argon. Prior to the laser ablation, the Au-coated MgO (100) substrate was preheated at 800 °C for 20 min. The growth temperature was 800 °C. After the deposition, the samples were annealed in oxygen atmosphere for 30 min and cooled down at room temperature for 30 min. The nanowire morphology was characterized by field emission scanning electron microscopy (FESEM) (JEOL JSM-6330FT) at an accelerating voltage of 30 kV. High-resolution transmission electron microscopy (HRTEM) (JEM-3000F) coupled with energy dispersive spectroscopy was used to evaluate the diameter, the crystallinity, and the composition of the fabricated nanowires. The size of MgO nanowires was analyzed by averaging data for 500 samples in FESEM and for 300 samples in HRTEM images for statistical reliability. HRTEM measurement was performed at an accelerating voltage of 300 kV.

Figure 1 shows the HRTEM and FESEM images of the MgO nanowires grown under pure oxygen pressure. It can be seen that the nanowires were grown over 3 μm for 300 min. Note that such relatively long MgO nanowires are not feasible when reducing the ambient pressure due to the catalyst diffusion from the tip, as reported elsewhere.[20] The Au catalyst droplet remaining on the tip can be also seen in the
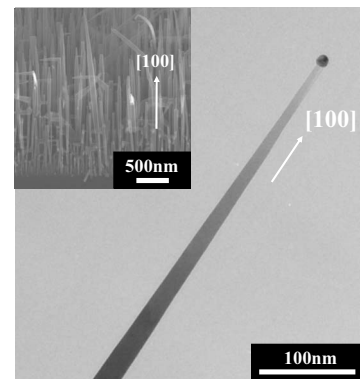

FIG. 1. HRTEM image of MgO nanowire. The nanowire was grown under 10 Pa pure oxygen ambient pressure and 800 °C growth temperature for 300 min. The inset shows the FESEM image.

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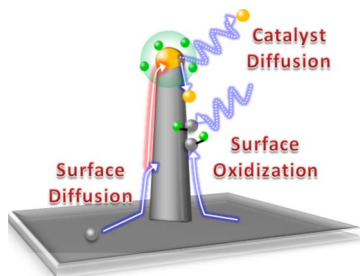[b]Electronic mail: kawai32@sanken.osaka-u.ac.jp.

FIG. 2. (Color online) Schematic of oxide VLS growth with possible mechanisms affecting the tapering phenomenon.

HRTEM image. More importantly it can be clearly seen that the nanowire diameter size tends to gradually increase below the droplet. This indicates the occurrence of tapering during the oxide nanowire growth even under relatively high ambient pressure, which cannot be interpreted in terms of previous implications.[20] Since such tapering is highly detrimental in controlling arbitrarily the nanowire morphologies, a way to overcome this critical issue is strongly desired.

Considering the mechanisms of oxide VLS growth in Fig. 2, there are several scenarios to explain the occurrence of the tapering. The first most well known mechanism for the tapering phenomenon is based on the catalyst diffusion from the tip.[9–12,20] Since the interface area between the liquid droplet and the solid determines the nanowire diameter size in principle, the change in the droplet size due to the catalyst diffusion during growth results in the tapering. However, in our experiments the maximum of the nanowire diameter appeared at the middle position of nanowires, as seen in the FESEM image. In fact this experimental trend is contradictive to the catalyst diffusion scenario since it is quite unlikely to assume that the catalyst droplet size shows the maximum during growth even in the presence of the catalyst diffusion. In addition, our previous investigation[20] clarified that the catalyst diffusion from the tip at 10 Pa ambient pressure is not significant compared with the VLS growth rate. Thus the mechanism based on the catalyst diffusion from the tip alone cannot explain the observed tapering phenomenon.

The other scenario is based on the sidewall growth due to the crystallization at the sidewall. In this scenario, the crystallization at the sidewall is not negligible compared with VLS growth rate. If this scenario was appropriate to explain the observed tapering phenomenon, reducing the crystallization at the sidewall would be crucial in preventing the detrimental tapering. Considering the mechanisms of the crystallization at the sidewall, there are two possible factors to suppress the sidewall growth, such as (i) enhancing the diffusion length of adatoms with the incorporation of adatoms into the catalyst droplet and (ii) reducing the oxidation at the sidewall. Thermodynamically reducing the ambient atmosphere, i.e., increasing the temperature and reducing the oxygen pressure, satisfies both requirements. However, increasing further the ambient temperature from the current temperature of 800 °C might cause the evaporation of Au catalyst droplet,[18] and in our experimental setup the ambient temperature range above 900 °C is not feasible. On the other hand, it is quite controllable to reduce the oxygen pressure. However, reducing the ambient oxygen pressure enhances the catalyst diffusion from the tip, resulting in the tapering, as reported elsewhere.[20] Thus here we have a dilemma to reduce the sidewall growth via controlling the ambient oxy-
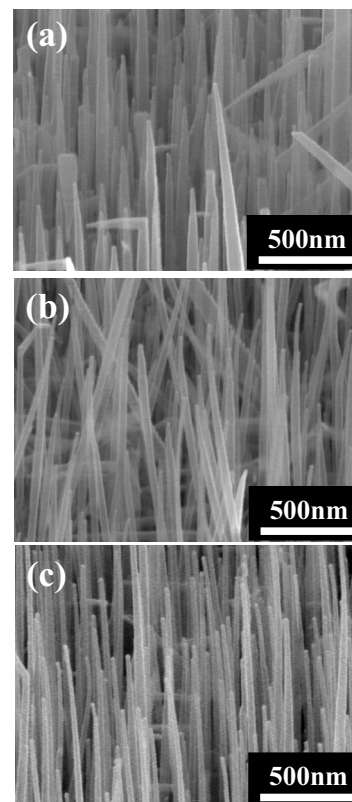

FIG. 3. FESEM images of nanowires when varying the mixed gas ratio.

gen pressure. The way to overcome simultaneously both the sidewall growth and the catalyst diffusion issues would be to use a mixed ambient gas of oxygen and argon with varying the oxygen partial pressure. The use of the mixed gas is based on the following reasons. First, controlling the total ambient pressure enables to suppress the catalyst diffusion from the tip. Second, reducing the oxygen partial pressure under constant total ambient pressure suppresses the oxidation at the sidewall without the catalyst diffusion from the tip.[20] Thus, this method is promising to control simultaneously the sidewall growth and the catalyst diffusion issues in principle.

Figures 3(a)–3(c) show the FESEM images of the MgO nanowires grown when varying the mixed gas ratio of oxygen and argon. The drastic variation in the nanowire morphology can be seen in the images, indicating the significant role of the mixed gas ratio on the oxide VLS growth. Figure 4 shows the dependence of the mixed gas ratio on the degree of the tapering and the nanowire diameter size. Here we define the degree of the tapering T_d as $T_d = (D_b - D_t)/D_b \times 100$, where D_b is the diameter at 500 nm below from the tip and D_t is the diameter at the tip. The diameters were measured from HRTEM images for 300 samples. The nanowire diameter size was measured near the tip. The data clearly demonstrate that the tapering nature is strongly suppressed when reducing the oxygen partial pressure under constant total ambient pressure. In addition the use of relatively high total ambient pressure retained the catalyst droplet on the tip via suppressing the catalyst diffusion, resulting in a nonsignificant dependence on the diameter size near the tip. Figure 5 shows the HRTEM images and selected area electron diffraction (SAED) pattern of nanowires grown under 1:1000 of O_2:Ar ratio. The nanowire morphology clearly
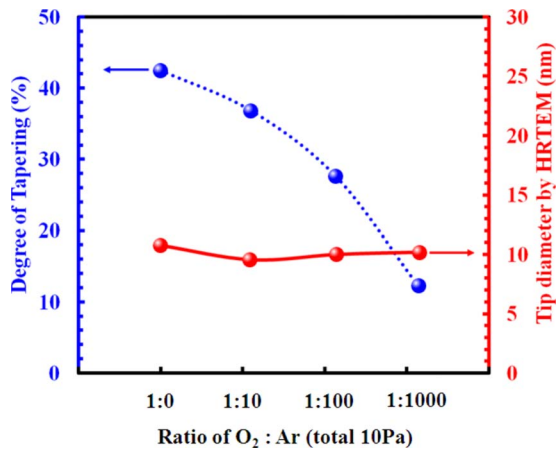
FIG. 4. (Color online) Variation in the degree of tapering (dotted line) and the tip diameter (solid line) when varying the mixed gas ratio.

differs from that in Fig. 1 with pure oxygen ambient atmosphere. The untapered shape for the long scale and the high crystallinity were confirmed. The observed suppression of the tapering when reducing the oxygen partial pressure indicates that the oxidation at the sidewall plays an important role on the sidewall growth. Thus the above experimental results highlight that it is possible to control simultaneously the sidewall growth, the catalyst diffusion, and the resultant tapering, which have been very detrimental and uncontrollable. Since oxide nanowires must be fabricated under oxygen ambient atmosphere, the mechanism proposed herein would be universal in many oxide VLS growths.
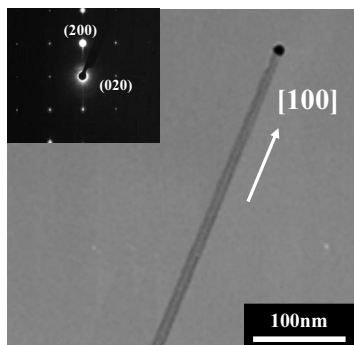

FIG. 5. HRTEM image of MgO nanowire. The nanowire was grown under 10 Pa total ambient pressure with 1:1000 of O_2:Ar and 800 °C growth temperature for 300 min. The inset shows the SAED pattern.

In summary, we have demonstrated the mechanism to control the tapering during oxide VLS growth, which had been uncontrollable. Suppressing both the oxidization of adatoms at the sidewall and the catalyst diffusion from the tip was found to be essential to avoid the tapering. This mechanism would be universal in many oxide nanowire VLS growths.

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