

Control of magnesium oxide nanowire morphologies by ambient temperature

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Although controlling morphologies of oxide nanowires formed using vapor-liquid-solid (VLS) mechanism is desired in developing functional oxide-nanowire applications, a comprehensive understanding of the key factors affecting oxide-nanowire VLS growth is still lacking. Here, the authors demonstrate the controllability of magnesium oxide nanowire morphologies by varying the ambient temperature and discuss the underlying mechanism. Decreasing the ambient temperature resulted in shorter, tapered, and square-rod shaped nanowires, whereas increasing the ambient temperature allowed fabricating longer and untapered nanowires. The variation of oxide-nanowire morphologies is interpreted in terms of the competition between the VLS growth and the sidewall growth due to the variation of adatom transport. © 2007 American Institute of Physics.

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One-dimensional inorganic nanostructures formed using vapor-liquid-solid (VLS) growth mechanism are potential candidates for a range of device applications in nanoelectronics, optoelectronics, and biosensors.¹⁻³ Although, the investigations in this field have been concerned with silicon and compound semiconductors,⁴⁻⁸ integrating functionalities of various materials into the nanowires might expand the application range of nanowire-based devices. For example, oxide materials are known to exhibit a rich variety of physical properties including ferromagnetism, ferroelectric, and superconducting,⁹⁻¹¹ and it would be an interesting and challenging issue to incorporate such diverse functionalities of oxide materials into nanowires. In developing such functional oxide nanowires for applications, controlling arbitrarily morphologies of oxide nanowires formed using VLS is strongly desired. However, a comprehensive understanding of the key factors affecting complex oxide nanowire VLS growth is still lacking, since an understanding of the VLS nanowire growth in Si nanowires, which has been most intensively investigated last decade, is even not comprehensive.⁵⁻⁸ This has held back the arbitrary controllability of oxide nanowire morphologies. Magnesium oxide (MgO) has been used as a versatile single crystal substrate for oxide thin film growth due to the small lattice mismatch with various functional transition metal oxides.⁹⁻¹¹ As such the feasibility and controllability of MgO nanowires enable us to integrate arbitrarily desired transition metal oxides into the oxide nanowires via heteronanowires.^{12,13} There are several experimental parameters to control the nanowire morphologies in VLS growth, including catalyst droplet size, pressure, temperature, and so on.^{6,14,15} The variation of the ambient temperature strongly affects the VLS growth and consequently the nanowire morphologies.¹⁵ However, the role of such temperature variation on the oxide VLS growth is not fully understood.^{16,17} Here, we demonstrate the crucial role of the ambient temperature to control the morphologies of MgO nanowires formed using VLS growth. In addition,

we discuss the underlying mechanism of the morphology variation in terms of the transport of adatoms during VLS growth when varying the ambient temperature.

MgO nanowires were grown on MgO (100) single crystal substrate by Au catalyst-assisted pulsed laser deposition technique. Prior to the nanowire growth, Au catalysts were sputtered with the thickness of 1 nm. ArF excimer laser ($\lambda = 193$ 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 as a target. The ambient oxygen pressure was kept to be 10 Pa during depositions. The substrate temperature for growth was varied from 500 to 850 °C. The nanowire morphology was characterized by field emission scanning electron microscopy (FESEM) (JEOL JSM-6330FT). The length and the size of MgO nanowires were analyzed by averaging data for 500 samples in FESEM images for statistical reliability. High-resolution transmission electron microscopy (HRTEM) (JEM-3000F) coupled with energy dispersive spectroscopy (EDS) was used to evaluate the diameter, the crystallinity, and the composition of the fabricated nanowires. The tip size of MgO nanowires was analyzed by averaging data for 300 samples in HRTEM images. Atomic force microscopy (AFM) (Veeco DI3100 tapping mode) was used to measure the morphology of Au catalyst droplet before nanowire growth.

Figure 1 shows the FESEM images of the MgO nanowires grown on MgO (100) single crystal substrate when varying the ambient temperature. The nanowires were grown perpendicular to the substrate, indicating the epitaxial growth of the MgO nanowires. Figures 1(a) and 1(b) show the top-view images of the MgO nanowires grown at and 500 800 °C, respectively. The variation of nanowire morphologies in the side-view images when varying the ambient temperature was shown in the middle between Figs. 1(a) and 1(b). The morphologies of nanowires tend to be shorter, tapered, and square-rod shape as decreasing the ambient temperature. In addition, in the top-view image the diameter size tends to increase as decreasing the ambient temperature. On the other hand, increasing the ambient temperature results in longer and relatively untapered nanowires.

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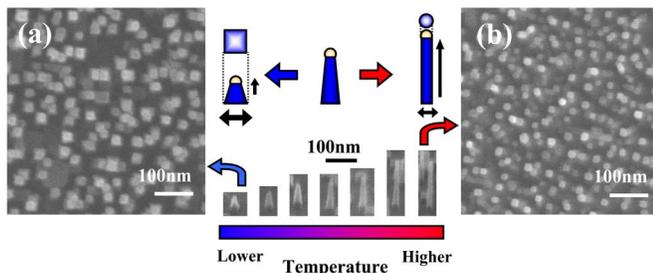


FIG. 1. (Color online) FESEM images of MgO nanowires grown on MgO (100) single crystal substrate when varying the growth temperature. (a) The top-view image of nanowires grown at 500 °C and (b) 800 °C. The FESEM images in the middle between (a) and (b) show the side-view structures. The schematic illustration of observed trend is shown above the side-view images.

Figure 2 shows the ambient temperature dependence on the nanowire growth rate in the length. The growth rate systematically increased with increasing the ambient temperature below 750 °C, and through the maximum then decreased. There are two possible factors affecting the MgO nanowire growth when varying the ambient temperature, such as (i) the diffusion of adatoms and (ii) the desorption and evaporation of adatoms.¹⁸ It is well known that the diffusion of adatoms is enhanced with increasing the ambient temperature.¹⁸ Thus the increase of ambient temperature induces faster diffusion on the surface and also increases the equilibrium concentration of adatoms. These result in the increase of the diffusion flux to the catalyst at the nanowire tip, and consequently the enhancement of nanowire growth below 750 °C observed in Fig. 2. On the other hand, increasing the ambient temperature gradually enhances the desorption and evaporation of adatoms from the substrate surface and the sidewall.¹⁸ This effect essentially limits the adatom flux to the nanowire tip. Therefore, the competition between the diffusion and the desorption of adatoms when varying the ambient temperature plays an important role on the nanowire

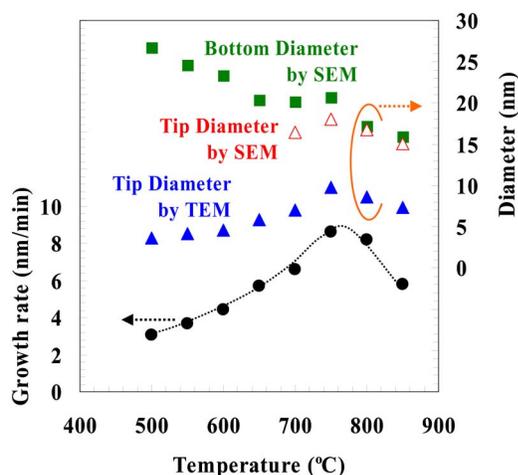


FIG. 2. (Color online) Ambient temperature dependences on the MgO nanowire growth rate in the length and the diameter sizes of MgO nanowires at both the bottom and the tip near the catalyst. The tip sizes (red: by FESEM, blue: by HRTEM) and the bottom sizes (green: by FESEM). Although there was a quantitative difference between FESEM and HRTEM values due to the resolution and the metal coating for FESEM measurements, the variation in tip sizes was consistent in both measurements. All the nanowires were deposited for 60 min.

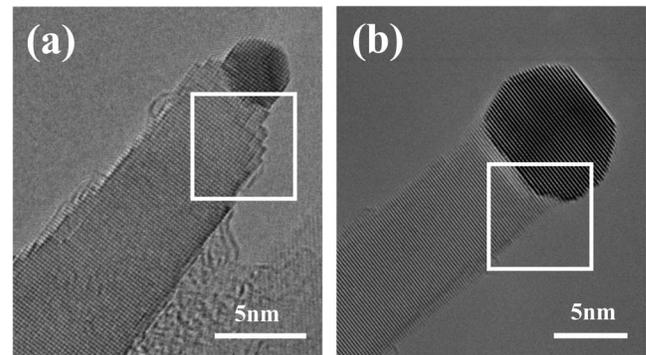


FIG. 3. (Color online) HRTEM images of MgO nanowires when varying the ambient temperature: (a) 500 and (b) 800 °C. Framed area highlights the difference between high temperature and low temperature grown MgO nanowires in the morphology near the tip.

growth via changing the adatoms flux to the catalyst at the tip.¹⁸

Figure 2 also shows the ambient temperature dependence on the diameter sizes of nanowires at both the bottom and the tip near the catalyst. The tip diameters were measured by both TEM and SEM images, and the bottom diameters were identified from SEM images. In relatively low temperature range below 700 °C, the size difference between the bottom and the tip diameters was found, highlighting the occurrence of tapering. Such tapering tends to be more significant as the ambient temperature decreases. In higher ambient temperature above 800 °C, the decrease of both the bottom and the tip was observed. In fact, similar trend when increasing the growth temperature was recently reported on ZnO nanowire growth.¹⁹ There are two possible scenarios to interpret the occurrence of tapering. One is based on the catalyst diffusion from the tip during growth.^{5,8} Since the nanowire diameter size is determined by the catalyst size within the framework of the VLS mechanism, such catalyst diffusion causes the tapering via changing the catalyst size during growth.¹⁴ Generally, increasing the ambient temperature enhances the diffusion of catalyst, and consequently the tapering in the VLS growth. This clearly contradicts with the experimental trend, in which the tapering tends to occur with decreasing the ambient temperature. The other scenario is based on the effect of sidewall growth. This scenario assumes that (i) the sidewall growth is not negligible compared with the VLS growth and (ii) the adatom diffusion flux tends to concentrate at the bottom position due to the limited diffusion length.

Figures 3(a) and 3(b) show the typical HRTEM images of the near-tip MgO nanowires fabricated at (a) 500 °C and (b) 800 °C, respectively. Clear lattice fringes with the preferential orientation of MgO nanowire along [100] direction were observed in both images, indicating the high crystallinity. The eutectic formation of Au and Mg within catalyst droplets seems to be responsible for VLS growth of MgO nanowires, which is similar to GaAs nanowire formation,²⁰ since HRTEM-EDS analysis for catalyst droplets demonstrated that the catalyst droplets were mainly composed of Au with a small amount of Mg. The catalyst droplet size was found to be smaller for lower ambient temperature. If a shrinking of catalyst droplet via the diffusion during growth tends to occur as decreasing the ambient temperature, this may cause the tapering, as assumed by the first scenario. However, as mentioned above, the enhancement of catalyst

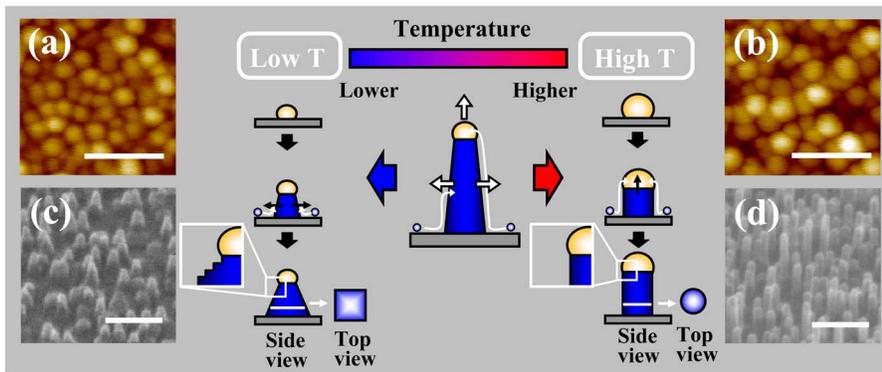


FIG. 4. (Color online) Schematic illustration of the ambient temperature dependent MgO nanowire growth. The inset figures of (a) and (b) show the AFM images of the initial catalyst droplet state before growth at 500 and 800 °C of the ambient temperature, respectively. (c) and (d) show the FESEM images of the MgO nanowire morphologies after growth at 500 and 800 °C of the ambient temperature, respectively. The scale bar is 50 nm for AFM images and 100 nm for FESEM images.

diffusion with decreasing the ambient temperature is quite unlikely. In addition, the size difference of catalyst droplets was observed even in the initial catalyst droplets before growth, as shown in the AFM images in Figs. 4(a) and 4(b). The size ratio of catalyst droplets (at the high temperature of 800 °C: at the low temperature of 500 °C) was found to be almost 2 in both before and after the nanowire growth. In fact, such temperature dependence on catalyst droplet size was reported elsewhere.^{21–23} These results highlight that the size change of the catalyst droplet during growth is not significant in present experiments and at least not responsible for the occurrence of tapering observed. Based on the second scenario, the sidewall growth should tend to occur as decreasing the ambient temperature. In the nanowires grown at high ambient temperature 800 °C, the smooth sidewall and the catalyst-size dependent nanowire growth were clearly seen in Fig. 3(b). On the contrary, the facetlike structure near the tip was found for nanowires grown at low ambient temperature of 500 °C in Fig. 3(a). In addition, the diameter size of the nanowire is much larger than the droplet size even just below the droplet. These indicate the occurrence of sidewall growth for low ambient temperature range. Thus, these experimental results consistently support the second scenario based on the sidewall growth to interpret the tapering.

Figure 4 shows the schematic illustration of the effect of ambient temperature on MgO nanowire growth. In the low ambient temperature range, the adatoms diffused from the surface contribute not only to the VLS growth but also to the sidewall growth, resulting in the tapering since near the bottom the sidewall growth tends to be enhanced due to the distribution of diffused adatoms. On the other hand, in the high ambient temperature range, the diffusion flux of adatoms is large enough to reach the tip, resulting in the dominance of VLS growth. This physical picture also explains why the high temperature grown nanowires showed the catalyst diameter dependent longer and untapered morphologies. The square-rod-like structures of nanowires grown at lower ambient temperature can be also understood in terms of the occurrence of the sidewall growth at the bottom, since MgO is a rocksalt crystal structure. These experimental results demonstrate the crucial role of the ambient temperature to

control arbitrarily the morphologies of oxide nanowires via VLS mechanism. The present understanding of the underlying mechanism would also contribute to further controllability of complex oxide nanowire VLS growth and the potential applications.

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