

Mechanism of critical catalyst size effect on MgO nanowire growth by pulsed laser deposition

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(Received 5 December 2007; accepted 7 April 2008; published online 1 July 2008)

The size controllability of oxide nanowires formed via vapor-liquid-solid (VLS) mechanism is desired for the oxide nanowire-based device applications. However, the complex nature of oxide nanowire VLS growth has held back such size controllability. Here we demonstrate the critical size effect of a Au catalyst on MgO nanowire VLS growth by pulsed laser deposition. The presence of a critical catalyst size was found. Above such critical size, an oxide nanowire VLS growth is no longer feasible. Interestingly, such critical size increased with increasing growth temperature. The mechanism of the critical phenomenon is interpreted in terms of the catalyst size dependence on the amount of adatoms diffused from surroundings into the catalyst. © 2008 American Institute of Physics. [DOI: 10.1063/1.2937194]

One-dimensional nanowires formed via the vapor-liquid-solid (VLS) mechanism show great promise as multifunctional components in a number of emerging device technologies.^{1–5} One of the advantages of nanowires is the size controllability in nanoscale, where a top-down technique is not applicable. Within the framework of classical VLS mechanism, the catalyst droplet size essentially determines the nanowire size.^{6–8} Thus, controlling the catalyst droplet size is one of the important issues for the desired functionalities of nanowire devices. Oxide nanowires and the heterostructures are potential candidates through which the rich functionalities may be incorporated into nanowire devices.^{9–11} Pulsed laser deposition (PLD) technique allows us to fabricate such various functional transition metal oxide nanowires via the heterostructures.^{9–11} In these oxide nanowires fabricated by PLD, the controllability of nanowire size is also strongly desired to explore not only the physical properties at nanoscale but also the ultimate small oxide nanodevices. Principally controlling the catalyst droplet size is necessary for this purpose. When varying the catalyst droplet size, the concentration inside catalyst droplets must be altered. Such concentration variations should affect the oxide VLS growth by changing the degree of supersaturation within the catalyst droplets. However, the catalyst size effect on an oxide nanowire VLS grown by PLD is not well understood.^{12–16} MgO has been used as a versatile single crystal substrate for oxide heterostructures,^{17–19} and therefore, the feasibility of such MgO nanowires by PLD offers a nanoscale substrate for oxide nanowire heterostructures. These backgrounds motivated us to investigate the catalyst size effect on MgO nanowire grown by PLD.

MgO nanowires were grown on MgO (100) single crystal substrate by Au catalyst-assisted PLD technique.^{12–15} Prior to the nanowire growth, Au catalysts were deposited on a MgO single crystal substrate. The thickness of Au catalysts ranged from 0.3 to 8 nm via controlling the deposition time.

The background pressure of the PLD chamber was 10^{-4} Pa. ArF excimer laser (Lambda-Physik COMPex 102, $\lambda = 193$ nm) operating at a pulse repetition rate of 10 Hz and a laser energy of 40 mJ was used for laser ablation. A MgO single crystal was used for the source of Mg species vapor during the nanowire growth. Oxygen gas was introduced into the chamber while controlling the ambient pressure. It was confirmed that the presence of ambient oxygen gas rather than the oxygen of MgO single crystal was crucial in supplying the oxygen into MgO nanowires by performing experiments under 10^{-5} Pa background pressure. The ambient pressure was 10^{-2} Pa and was kept constant during deposition. Prior to laser ablation, the Au-coated MgO (100) substrate was preheated at the desired growth temperature for 10 min. The growth temperature was varied from 400 to 850 °C. After the deposition, the samples were cooled down to 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 300 samples in HRTEM images for statistical reliability. HRTEM measurement was performed at an accelerating voltage of 300 kV.

Figure 1 shows the FESEM images of the MgO nanowires grown at 800 °C the substrate temperature when varying the thickness of Au catalyst. Images (a)–(d) show the top-view surface morphologies with thicknesses of 0.7, 1.9, 4.2, and 8 nm, respectively. The insets show the tilted images. There are two major trends when varying the catalyst thickness. First, below 5 nm thickness, the presence of MgO nanowires is clearly seen in images (a)–(c). In addition, the average diameter of nanowires systematically increases with increasing catalyst thickness via enlarging the catalyst droplet size. Figure 2 shows the variation of the nanowire diam-

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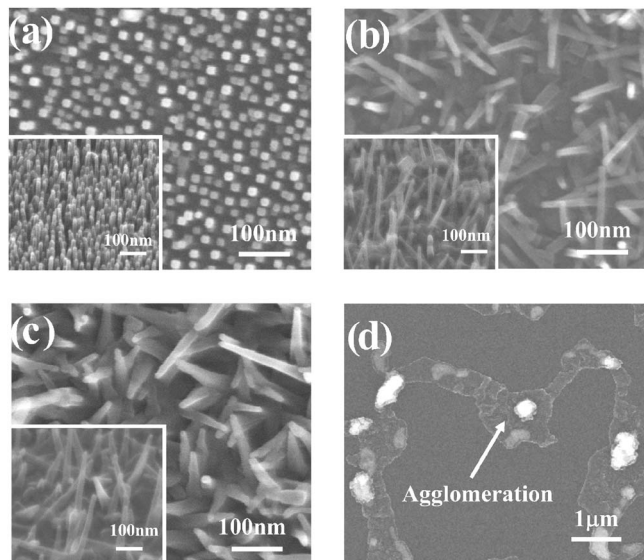


FIG. 1. MgO nanowires grown on MgO (100) single crystal substrate when varying the catalyst thickness. (a)–(d) shows FESEM top-view images of the nanowire morphologies grown under (a) 0.7 nm, (b) 1.9 nm, (c) 4.2 nm, and (d) 8 nm of the catalyst thickness. Side-view images are tilted 60° to the substrate surface plane. The nanowires were grown at 800 °C for 60 min.

eters determined from the HRTEM images when varying the catalyst thickness. Such an increase in the catalyst droplet size when increasing the thickness can be easily interpreted in terms of the agglomeration of Au catalyst.^{20–22} Second, above 5 nm thickness, nanowires are no longer observable and only Au agglomerates exist as seen in Fig. 1(d). This indicates the upper critical limit of the Au catalyst thickness for the MgO nanowire VLS growth. The presence of such a threshold is certainly related to the growth mechanism of oxide nanowires in catalyst-assisted PLD. Since a supersaturation within the catalyst droplet is an important process within the framework of the VLS mechanism,^{6–8} the observed critical behavior might also be related to such a supersaturation process. Note that the implication of the super-

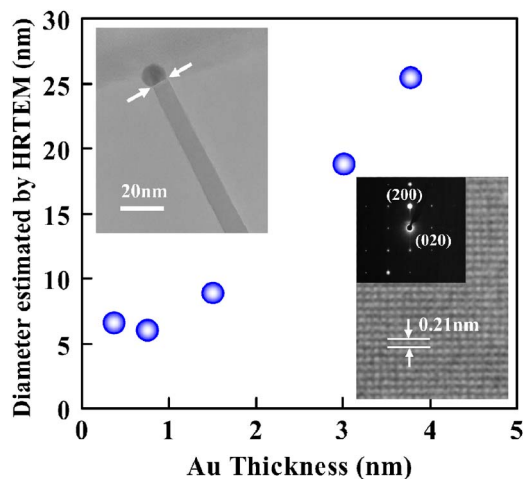


FIG. 2. (Color online) Variation of nanowire diameters determined by HRTEM when changing the catalyst thickness. The nanowires were grown at 800 °C for 60 min. The insets show the typical HRTEM images and the selected area electron diffraction pattern of MgO nanowires grown under 10 Pa oxygen pressure.

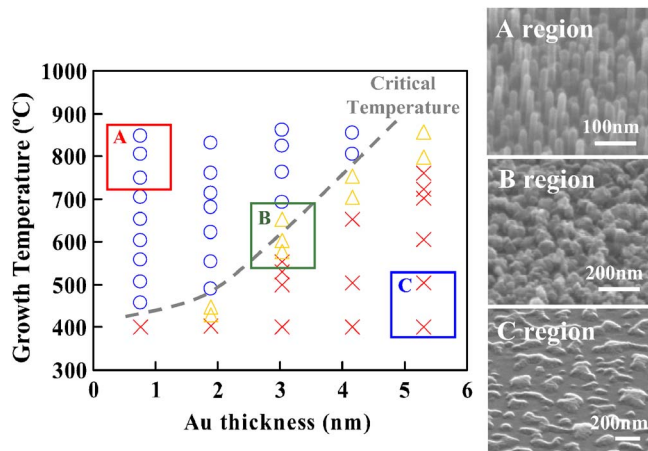


FIG. 3. (Color online) Effects of the catalyst thickness and the growth temperature on MgO nanowire VLS growth. Open circle (\circ), triangle (Δ), and cross (\times) symbols represent the presence of nanowire growth, the partial formation of nanowires, and the absence of nanowire growth, respectively. The FESEM images of nanowire morphologies at the upper-left region A, region B, and the lower-right region C in the figure are shown in the right. The nanowires were grown for 60 min.

saturation herein is a supersaturation of Mg within the catalyst droplet of Au. The growth temperature is one of the important factors affecting supersaturation, and therefore, it is valuable to investigate the dependence of growth temperature on the critical value of the catalyst thickness.

Figure 3 shows the effects of the growth temperature and the catalyst thickness on the MgO nanowire VLS growth. It can be seen that the threshold thickness systematically decreases with decreasing growth temperature. Thus, this critical phenomenon strongly depends on the growth temperature. There are several possible factors, that might affect the presence of such a critical event. The first possible scenario is based on the variation of melting temperature of Au when changing the particle size.²³ Within the framework of the VLS mechanism, the catalyst must be a liquid droplet. However, the variation in the critical temperature range from 450 to 900 °C seems to be much wider compared to the typical variation of Au melting temperature, since the size dependence on Au melting temperature was reported to be significant in the range of the particle size less than 5 nm.²³ In addition, as seen in Fig. 1(d), nanowires were not observable at all even in the presence of Au droplets via melting. Thus, this size effect on the melting temperature alone cannot explain the critical phenomenon of MgO nanowire growth when varying the catalyst thickness and the growth temperature, although such effect might partially contribute to the critical event. The second possible scenario is based on the variation of the supersaturation within the catalyst due to the growth temperature. Since the degree of supersaturation increases with decreasing growth temperature, such temperature effects on the supersaturation alone cannot explain the experimental trend. The other possible scenario is based on the diffusion length of adatoms. Generally, the diffusion length of an adatom increases with increasing temperature,^{13,24} and in nanowire VLS growth, an incorporation of adatoms diffused from the surrounding area into a catalyst droplet is crucial for supersaturation.²⁵ Thus, in-

creasing the growth temperature enhances such incorporation of adatoms into the catalyst droplet, which, in fact, affects the supersaturation within the catalyst. When increasing the catalyst thickness under constant ambient atmosphere, the catalyst droplet size increases as shown in Fig. 2. Since the effective diffusion length of adatoms can be assumed to be almost constant under constant growth temperature, enlarging the catalyst droplet size via increasing the catalyst thickness might decrease the density of incorporated adatoms per unit cross-sectional area of catalyst droplets. Such effect might limit the MgO nanowire growth via suppressing the supersaturation. That is, the dependence of catalyst size on the density of adatoms diffused from the surrounding area into the droplet governs the observed critical phenomenon of MgO nanowire growth when varying the growth temperature and the catalyst thickness. Assuming that the ratio of the catalyst droplet cross-sectional area to the surrounding effective diffused area corresponds to the density of adatoms diffused from the surrounding area into the droplet, when the catalyst droplet size increases from 5 to 27 nm as shown in Fig. 2, the area ratio for 27 nm can be estimated to be less than 4% of that for 5 nm. As such, the variation of the catalyst droplet size greatly changes the density of adatoms diffused from the surroundings. In addition, the decrease in the critical thickness when decreasing the growth temperature can be interpreted in terms of decreasing effective diffusion length of adatoms. Thus, this scenario seems to be able to explain rigorously the observed critical phenomenon of MgO nanowire growth when varying the growth temperature and the catalyst thickness in Fig. 3.

In summary, we have shown the critical size effect of Au catalyst on MgO VLS grown by PLD. The presence of a critical catalyst size was found, and above such critical size, an oxide nanowire VLS growth is no longer feasible. Interestingly, such critical size increased with increasing growth temperature. The mechanism of the critical phenomenon is interpreted in terms of the dependence of catalyst size on the amount of adatoms diffused from the surroundings into the catalyst. Although the actual nature of oxide nanowire VLS growth is rather complex, the implications obtained herein

would contribute to further controllability of functional oxide nanowires.

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