Low-Temperature Catalytic Growth of β-Ga_2O_3 Nanowires Using Single Organometallic Precursor

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β-Ga_2O_3 nanowires have been synthesized at a low temperature of 550 °C using a single precursor of gallium acetylacetonate through the vapor−liquid−solid (VLS) mechanism. Synthesis of very thin β-Ga_2O_3 nanowires with an average diameter of 8 nm was achieved using this method. The influences of substrate temperature, pressure, and Ga vapor concentration on the growth and the diameter distribution of β-Ga_2O_3 nanowires were investigated in this work. It was found that the diameters of the Ga_2O_3 nanowires are also affected by the growth conditions, in addition to being correlated to the diameters of the initial Au catalysts on the substrates.

Introduction

One-dimensional nanostructures have great potential for learning the fundamental concepts of the roles of both dimensionality and size in physical properties as well as for application in nanodevices and functional materials.[1] Due to its wide-band gap (E_g = 4.9 eV) with the potential application in optoelectronic device and high-temperature stable sensor, monoclinic Ga_2O_3 (β-Ga_2O_3) nanowires have been synthesized by various high-temperature methods (800−1240 °C) through a vapor−liquid−solid (VLS) mechanism, such as thermal evaporation[2] or electric arc discharge[3,4] of GaN powders with the presence of oxygen, high-temperature treatment of GaAs in a dry oxygen atmosphere[5] and direct reaction of Ga and H_2O vapor.[6] Catalyst-free growth of the Ga_2O_3 nanowires by laser ablation of Ga_2O_3 target[7] and thermal annealing of milled GaN powders[8] have also been developed. The β-Ga_2O_3 nanowires produced by these high-temperature methods exhibited broad diameter distributions.

In the present work, β-Ga_2O_3 nanowires were synthesized on Au precoated Si substrates at a low temperature of 550 °C, which is lower than those that have been previously reported. A single precursor of gallium acetylacetonate with a low-decomposition temperature (∼196 °C) was employed as both gallium and oxygen sources for the Ga_2O_3 nanowires growth via the VLS mechanism. The influences of growth temperature, pressure, and Ga vapor concentration on the synthesis and the diameter distribution of β-Ga_2O_3 nanowires were investigated in this work. In addition to be correlated to the diameters of the initial Au catalysts on the substrates, the diameters of the Ga_2O_3 nanowires are also affected by the growth conditions.

Experimental Section

The Ga_2O_3 nanowires were synthesized on Au precoated Si substrates placed in the high-temperature-zone of a two-temperature-zone furnace. All silicon substrates were coated with a layer of Au using an e-beam evaporator under the constant conditions after being cleaned in an ultrasonic bath of acetone for 20 min, HF solution for 1 min, and deionized water for 10 min. Gallium acetylacetonate (($CH_3COCHCOCH_3)_3$Ga, Aldrich, 99.99%), which was employed as the Ga and O sources, placed on a cleaned Pyrex glass container was loaded into the low-temperature zone of the furnace. A N_2 line (so-called N_2(Ga)) separated from the main N_2 stream was connected to the Pyrex glass to carry sufficient Ga and O sources to the high-temperature zone. It should be noted here that there is no O_2 flow supplied in the whole process. The distance between the source and the substrate is 35−55 cm. The system was preevacuated to ∼9 mTorr, and then the high-temperature zone was increased to the growth temperature at a rate of 14−17 °C/min in the N_2 ambient of 200 Torr. The low-temperature zone was increased to 185 °C to vaporize the source after the high-temperature zone reaching the growth temperature.

The morphologies of the nanorods were examined using scanning electron microscopy (SEM, Hitachi, S-4200 and Philip Field-Emission SEM, XL-40 FE-SEM). The crystal structures of the nanowires were investigated using X-ray diffraction (XRD, Rigaku D/MAX-2000) and transmission electron microscopy (TEM, JEOL 2010 and JEOL 3010). The diameters and lengths of the Ga_2O_3 nanowires were analyzed from over 50 nanowires in TEM images.

Results and Discussion

Ga_2O_3 nanowires were synthesized on Au-pretreated Si (100) substrate at temperatures of 850, 650, and 550 °C under the following constant conditions: source vaporizing temperature, N_2(Ga)/N_2 flow rate ratio, and total pressure of 185 °C, 96/46 sccm and 200 Torr, respectively. Figure 1 shows the FESEM images of the nanowires grown for 6 h at these three temperatures as well as the distributions of the nanowire diameters estimated from low-magnification TEM images. Figure 1a−d reveals that the nanowires grown at both 850 and 650 °C possess rough surfaces and rather wide range distributions of the diameters. With further decreasing, the substrate temperature to 550 °C, as shown in Figure 1, parts e and f, the surfaces of the nanowires are smoother and the diameters of the nanowires are not only more uniform but also smaller in comparison with those synthesized at higher temperatures.

The structures of the nanowires grown at these three temperatures are examined using XRD and TEM. As shown in Figure 2, all of the diffraction peaks in the XRD spectra can be

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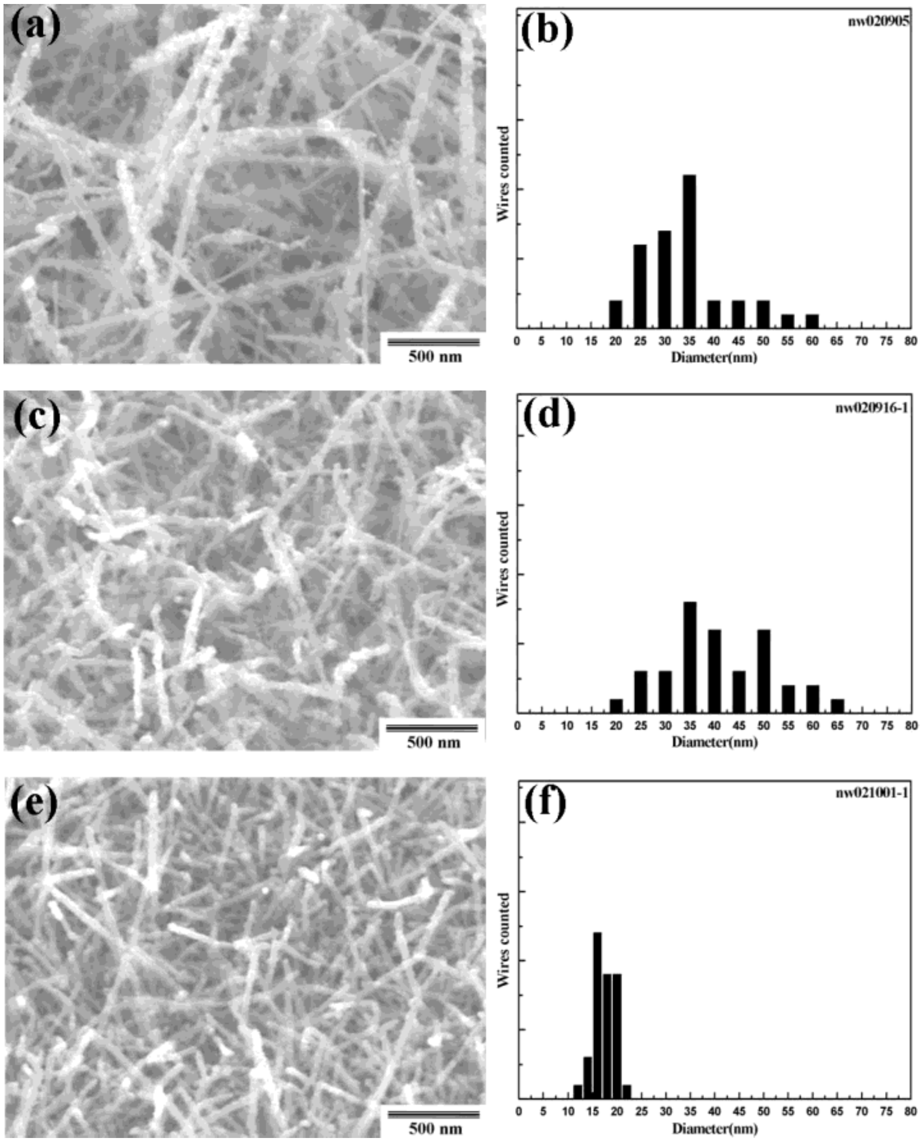

Figure 1. FESEM images of the nanowires grown for 6 h at different temperatures and the distributions of the nanowire diameters estimated from low-magnification TEM images. (a and b) 850 °C; (c and d) 650 °C, and (e and f) 550 °C. Other conditions are: source vaporizing temperature, $N_2(Ga)/N_2$ flow rate ratio, and total pressure of 185 °C, 96/46 sccm and 200 Torr.

indexed to those of the monoclinic structure of β-Ga_2O_3 (a = 12.23 Å, b = 3.04 Å, c = 5.80 Å, $\alpha = 90°$, $\beta = 103.7°$, and $\gamma = 90°$) according to JCPDS, powder diffraction file No. 41-1103. The microstructure of β-Ga_2O_3 nanowires were further examined using TEM. A TEM image of the thicker nanowire formed at 850 °C is shown in Figure 3a. A gold particle appears at the top of the nanowire, demonstrating the formation of the Ga_2O_3 nanowires via the VLS mechanism. EDS analyses further confirm that the nanowires are composed of Ga and O. Both sides of the nanowire reveal obvious step edges, which cause the rough surface and nonuniform diameter along the nanowire. The high-resolution image of the broken-box region of Figure 3a is illustrated in Figure 3b. It reveals that microtwins extend along the whole length of the nanowire. The twin boundaries indicated by the arrows represent (200) planes, and the two parts separated by twins boundaries represent (001) planes. The diameter of the Ga_2O_3 nanowire is larger than that of metal particles at the top as shown in Figure 3a. The corresponding SAED pattern, as illustrated in the Figure 3c, can be indexed to the [010] zone axis of the Ga_2O_3 nanowire. The spots denoted by the cross contribute from the twin structures. It is well-known that the twins are often associated with a distortion of the lateral sides of the Ga_2O_3 nanowire.[9] Also the step edges on the surface of the nanowires have been recognized as sites preferring the occurrence of the VS mechanism for enhancing diameters after the formation of the nanowires by VLS mechanism.[10,11] A low-magnification TEM image of the nanowires grown at 550 °C is shown in Figure 4a. Because most of the diameters of the Ga_2O_3 nanowires are slightly larger than those of nanoparticles at their tops, as shown in Figure 4b, we cannot rule out the possibility of the VS mechanism occurring after the formation of the nanowire by the VLS mechanism. The corresponding selection area electron diffraction (SAED) pattern of the Ga_2O_3 nanowire illustrated in Figure 4c indicates that the nanowire possesses a single crystalline structure. Figure 4d show a high-resolution TEM image taken from the region indexed in Figure 4b. Lattice fringes of the $(20\bar{1})$ planes of the β-Ga_2O_3 structure with the d spacing of 0.47 nm are observed, indicating that the Ga_2O_3 nanowire was grown along the $[20\bar{1}]$ direction.

Ga_2O_3 nanowires were successfully synthesized at a rather low temperature of 550 °C via the VLS mechanism employing the single organometallic precursor $(CH_3COCHCOCH_3)_3Ga$ that could provide not only sufficient Ga vapor but also O vapor during the nanowire growth. The thinner nanowires were

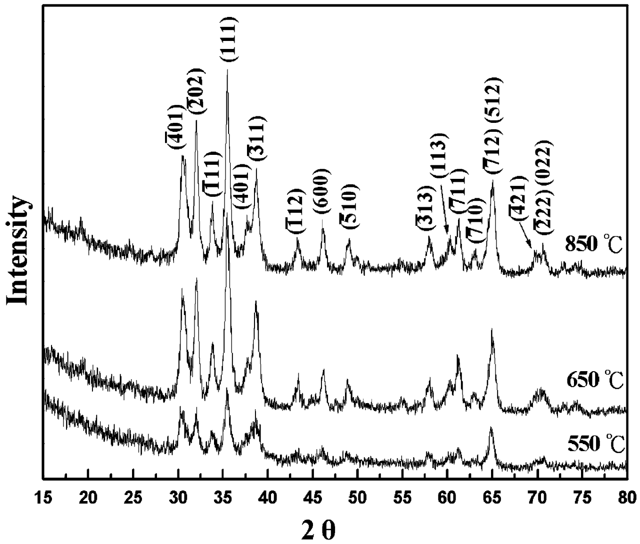

Figure 2. XRD spectra of the Ga_2O_3 nanowires grown at different temperatures.

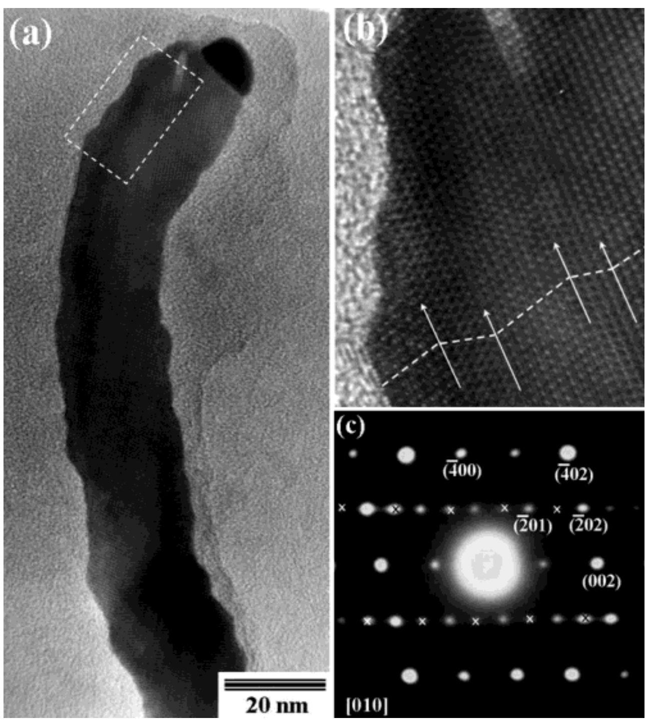

Figure 3. (a) Low-magnification TEM image of the Ga_2O_3 nanowires grown at 850 °C. (b and c) A HR-TEM image marked in (a) and the corresponding diffraction pattern of an individual Ga_2O_3 nanowire grown at 850 °C.

synthesized at 550 °C in comparison with those grown at higher temperatures. It is well-known that the diameters of the nanowires grown by the VLS mechanism are correlated to the diameters of the initial catalysts on the substrates.[12] In this study, the initial Au thin films on the silicon substrates were all deposited under the same conditions; however, the sizes of the Au nanoparticles after elevating the substrate temperatures to the growth ones would be distinct. To systematically study the correlation between the diameters of the nanowires and the grain sizes of the Au nanoparticles on the substrates at the beginning of the nanowires growth, the size distributions of the Au nanoparticles formed after annealing under N_2 ambient for 40−50 min at the three temperatures of 850, 650, and 550 °C were analyzed further. As shown in Figure 5a−c, the SEM images

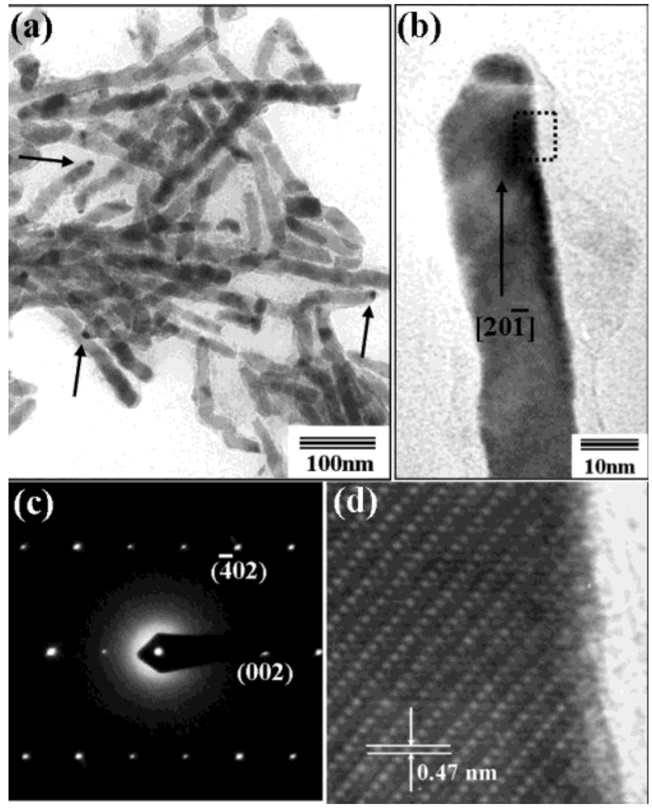

Figure 4. (a) Low-magnification TEM image of the Ga_2O_3 nanowires grown at 550 °C. (b and c) A TEM image and the corresponding diffraction pattern of an individual Ga_2O_3 nanowire grown at 550 °C. (d) The HR-TEM image of the Ga_2O_3 nanowires marked in (b).

and the size distributions of the Au nanoparticles formed after N_2 annealing reveal that the densities of the Au nanoparticles are enhanced and their average sizes are reduced when the substrate temperature decreases. The average size of the Au nanoparticles formed at 850 °C is 16 nm with a distribution from 10 to 24 nm, resulting in the subsequent nanowires ranging from 20 to 60 nm with an average diameter of 34 nm, as shown in Figure 5, parts a and b. On the other hand, as shown in Figure 5, parts c and f, the Au nanoparticles formed at 550 °C possess an average size of 11 nm with a distribution from 8 to 20 nm and the resultant nanowires exhibit an average diameter of 17 nm with a narrower distribution from 12 to 22 nm, respectively. There is no significant distinction between the average sizes of the Au particles formed at 850 and 550 °C, whereas the diameters of the nanowires increase by a factor of 2 over this temperature range. The formation of the thicker nanowires at a higher temperature of 850 °C is thus suggested to result from not only the little larger Au nanoparticles formed before nanowires growth but also the VS mechanism playing a dominant role on the growth of nanowires at the higher temperature.

To enhance the growth rate of the Ga_2O_3 naowires, the growth of the nanowires was performed under a higher N_2(Ga)/N_2 flow rate ratio of 177/46 sccm at 550 °C. The SEM and low-magnification TEM images shown in Figure 6, parts a and b, reveal that rather straight nanowires are obtained in comparison with those synthesized at a N_2(Ga)/N_2 flow rate ratio of 96/46 sccm. The distribution of the Ga_2O_3 nanowires grown using the higher N_2(Ga) flow rate of 177 sccm is little narrower than that of grown using a N_2(Ga) flow rate of 96 sccm, as shown in Figures 1f and 6c. Moreover, the diameters of the Ga_2O_3 nanowires under a higher N_2(Ga) flow rate are almost the same with those of Au particles at their tops, as shown in Figure 6b,

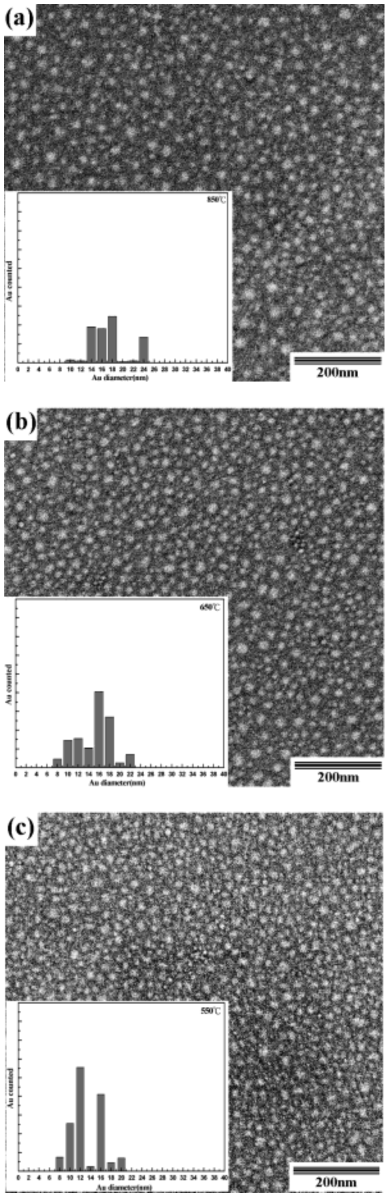

Figure 5. SEM images and size distributions of the Au nanoparticles formed after N_2 annealing at (a) 850, (b) 650, and (c) 550 °C.

in contrast to those synthesized at a lower flow rate. We suggest that the VLS mechanism would be the dominant process for the formation of Ga_2O_3 nanowires when the source is supplied sufficiently. Once the contribution of the VS mechanism is insignificant for nanowire growth, straight Ga_2O_3 nanowires are thus formed such as in the case of using a higher N_2(Ga) flow rate.

Figure 7, parts a and b, shows a higher magnification TEM image and the corresponding SAED of an individual Ga_2O_3 nanowire, demonstrating again that the diameter of the nanowire is consistent with that of the catalyst on its top and the nanowire possess a single crystalline structure, respectively. Figure 7c illustrates a HR-TEM image taken from the region indexed in Figure 7a. Lattice fringes of the $(20\bar{1})$ planes of the β-Ga_2O_3 structure with the *d* spacing of 0.47 nm are observed, indicating the Ga_2O_3 nanowire was grown along the $[20\bar{1}]$ direction.

The effects of the pressure on the Ga_2O_3 nanowire growth were further studied at a growth temperature of 550 °C and a N_2(Ga)/N_2 flow rate ratio of 177/46 sccm under the pressures of 100 and 300 Torr for comparing with those grown under 200 Torr shown in Figure 6. Figure 8a shows that rather straight

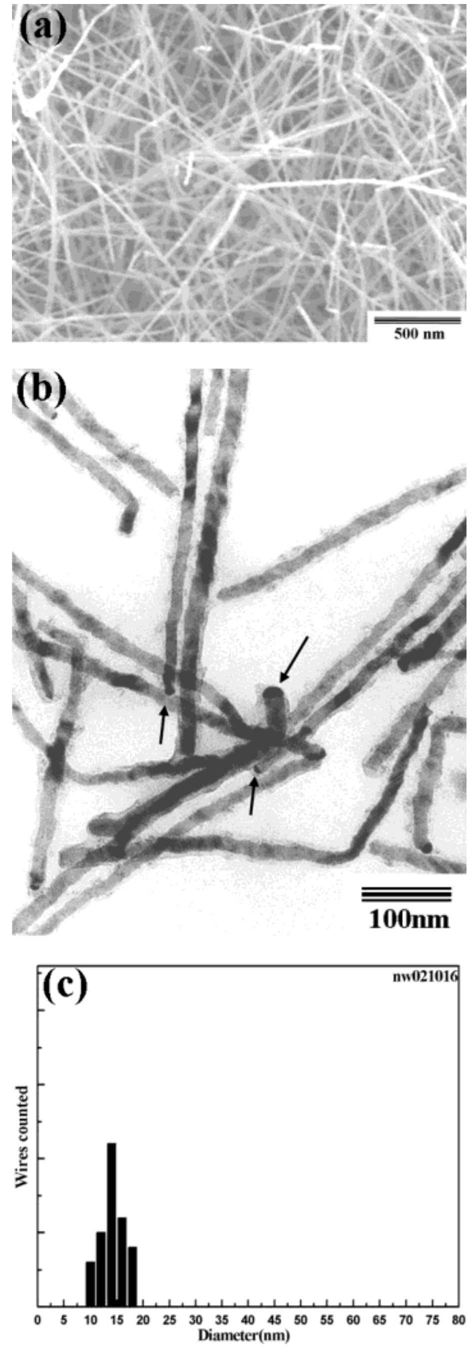

Figure 6. (a) SEM image, (b) TEM image, and (c) the distributions of the nanowire diameters of the Ga_2O_3 nanowires grown at 550 °C, 200 Torr and a N_2(Ga)/N_2 flow rate ratio of 177/46 sccm.

nanowires with similar morphology to those grown at 200 Torr were obtained at a lower pressure of 100 Torr. However, Ga_2O_3 nanowires with much thinner diameters were synthesized at a higher pressure of 300 Torr, as shown in Figure 8, parts b and c. A size distribution of the Ga_2O_3 nanowires grown at 300 Torr is illustrated in Figure 8d. It is obvious that the distribution is quite narrow from 5 to 10 nm and the average diameter of these nanowires is around 8 nm that is much lower than those of nanowires grown at lower pressures. A TEM image shown in the inset of Figure 8c indicates that the nanowire was grown via the VLS mechanism at a temperature of 550 °C and a pressure of 300 Torr due to the presence of a catalyst on the top. Moreover, the rather thin nanowire possesses a single crystalline structure. Figures 8e and 8f illustrate a HR-TEM image and the corresponding SAED pattern of the nanowire

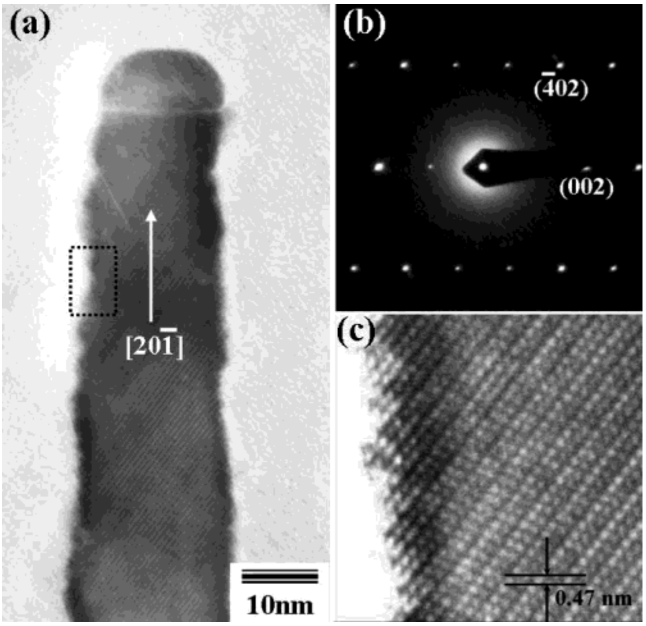

Figure 7. (a and b) TEM image and the corresponding diffraction pattern of an individual Ga_2O_3 nanowire grown at 550 °C, 200 Torr and a $N_2(Ga)/N_2$ flow rate ratio of 177/46 sccm. (c) The HR-TEM image of the nanowires Ga_2O_3 marked in (a).

taken from the region indexed in the inset of Figure 7c. Lattice fringes of the (002) planes of the β-Ga_2O_3 structure with the d spacing of 0.28 nm are observed.

Because the annealing processes for the formation of the Au nanoparticles are all performed at the same pressure and temperature, i.e., 200 Torr and 550 °C, for the study of the effect of pressure on the β-Ga_2O_3 nanowire growth, we suggest that the diameter distributions of the initial Au particles on the substrates are all the same for the subsequent nanowire growths conducted at various pressures. It is interesting that the average diameter of the nanowires formed at 300 Torr are much smaller than that of the Au nanoparticles, as shown in Figures 8d and 5c. The Ga_2O_3 nanowires seem to be grown via the VLS mechanism through the smaller Au nanoparticles at a pressure of 300 Torr whereas the Au nanoparticles larger than 10 nm could not be the efficient catalysts for the syntheses of the Ga_2O_3 nanowires, resulting in the formation of the rather thin and uniformly distributed Ga_2O_3 nanowires at 300 Torr. It has been demonstrated that the growth rates of carbon nanofibers or carbon nanotubes formed via the VLS mechanism decrease with increasing the size of catalytic particles due to the longer diffusion path for the precursor within the catalyst.[13] We suggest that the distinction of the diffusion fluxes through the catalytic particles with various sizes, resulting in the growth rate difference of the nanowires, would be enhanced by increasing the growth species concentration in gas phase. By assuming the process is in the steady state and the rate-limiting step for the nanowire growth is the diffusion of the precursor through the catalyst, as shown in Figure 9, distinction of the diffusion fluxes through the catalytic particles with various sizes (ΔN) can be qualitatively estimated from Henry's law and Fick's law with the following equations:[14]

$$C_0 = HP_G \tag{1}$$

$$\Delta N = D\frac{(C_0 - C_s)}{X_1} - D\frac{(C_0 - C_s)}{X_2} = (HP_G - C_s)D\left(\frac{1}{X_1} - \frac{1}{X_2}\right) \tag{2}$$

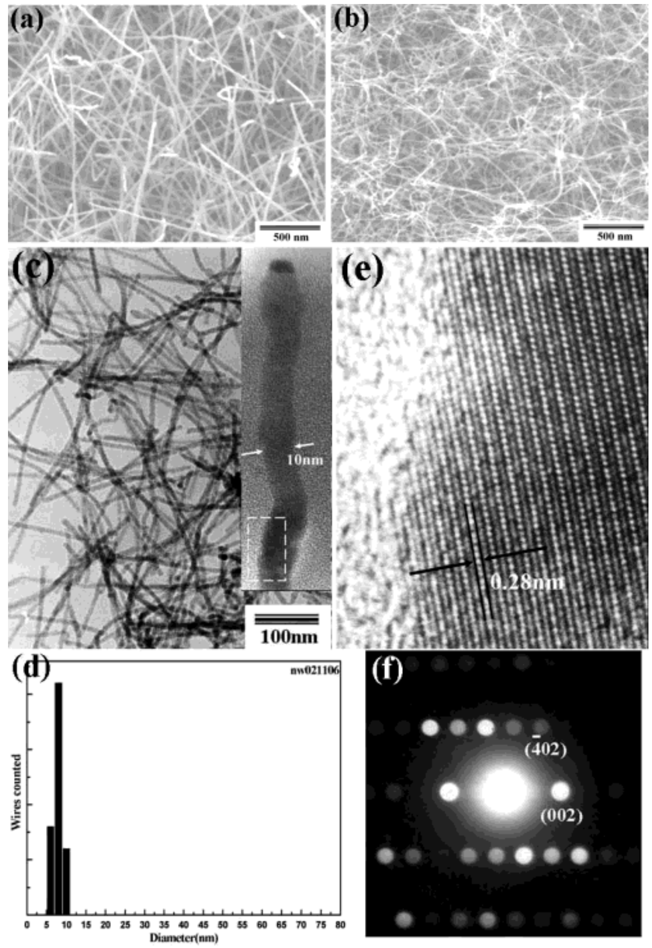

Figure 8. (a and b) SEM images of the Ga_2O_3 nanowire grown at 100 and 300 Torr, respectively, under 550 °C and a $N_2(Ga)/N_2$ flow rate ratio of 177/46 sccm. (c and d) A TEM image and the diameter distribution of the Ga_2O_3 nanowire grown at 300 Torr. (e) The HR-TEM image of the Ga_2O_3 nanowires marked in the inset of (c). (f) Nano-beam diffraction pattern taken from the Ga_2O_3 nanowire shown in the inset of (c).

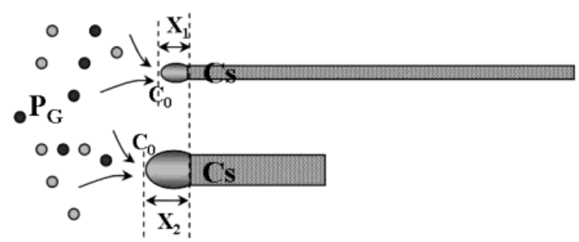

Figure 9. Distinction of the diffusion fluxes through the catalytic particles with various sizes.

where P_G is the partial pressures of the precursors, C_0 and C_s are the concentrations of the Ga or O in the catalyst surface and the nanowire, respectively, H and D are the Henry's law constant and the precursor diffusivity in the catalytic particle, respectively, and X_1 and X_2 are the diameters of the catalysts. The H, C_s, D, X_1, and X_2 are constants for Ga_2O_3 naowires and Au nanoparticles at 550 °C. Once the partial pressure of the precursor, P_G, in the gas phase is increased, the distinction of the diffusion fluxes, ΔN, and thus the growth rate difference of the nanowires from the various sizes of catalytic nanoparticles would be enlarged. We thus speculate that the thinner Ga_2O_3 nanowires formed at 300 Torr results from more sufficient precursors provided at a higher pressure than at lower pressures that enhances the growth rates of the Ga_2O_3 nanowires grown through the smaller Au nanoparticles. The thicker Ga_2O_3 nanowires grown at a higher temperature through the larger Au nanoparticles are seldom observed from TEM analyses due to the relatively slow growth rate.

Conclusions

Low-temperature catalytic growth of Ga_2O_3 nanowires has been demonstrated using a single precursor of gallium acetylactonate through the VLS mechanism. Due to smaller Au nanoparticles formed before nanowires growth, thinner nanowires with a narrower distribution range were grown at 550 °C, in comparison with those formed at 850 and 650 °C under a pressure of 200 Torr. Straighter nanowires are obtained when the N_2(Ga)/N_2 flow rate ratio increases from 96/46 sccm to 177/46 sccm. Moreover, in comparison with 200 Torr, Ga_2O_3 nanowires with much thinner diameters were synthesized at a higher pressure of 300 Torr under the same substrate temperature of 550 °C. Formation of the thinner Ga_2O_3 nanowires at 300 Torr is speculated that more sufficient precursors provided at a higher pressure results in the enhancement of the growth rates of the Ga_2O_3 nanowires through the smaller Au nanoparticles. Thus, in addition to be correlated to the diameters of the initial Au catalysts on the substrates, the diameters of the Ga_2O_3 nanowires are also affected by the growth conditions.

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