Rational Concept for Reducing Growth Temperature in Vapor–Liquid–Solid Process of Metal Oxide Nanowires

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ABSTRACT: Vapor–liquid–solid (VLS) growth process of single crystalline metal oxide nanowires has proven the excellent ability to tailor the nanostructures. However, the VLS process of metal oxides in general requires relatively high growth temperatures, which essentially limits the application range. Here we propose a rational concept to reduce the growth temperature in VLS growth process of various metal oxide nanowires. Molecular dynamics (MD) simulation theoretically predicts that it is possible to reduce the growth temperature in VLS process of metal oxide nanowires by precisely controlling the vapor flux. This concept is based on the temperature dependent "material flux window" that the appropriate vapor flux for VLS process of nanowire growth decreases with decreasing the growth temperature. Experimentally, we found the applicability of this concept for reducing the growth temperature of VLS processes for various metal oxides including MgO, SnO₂, and ZnO. In addition, we show the successful applications of this concept to VLS nanowire growths of metal oxides onto tin-doped indium oxide (ITO) glass and polyimide (PI) substrates, which require relatively low growth temperatures.

KEYWORDS: Metal oxide nanowires, vapor–liquid–solid growth, low temperature growth, material flux window, temperature dependence

The vapor–liquid–solid (VLS) method has shown the promises to fabricate well-defined single crystalline nanowires composed of various functional inorganic materials.¹⁻⁶ By using the VLS growth method, the diameter and the spatial position of nanowires can be tailored by adjusting the size and the spatial position of metal catalyst.⁷⁻⁸ Furthermore, the heterostructures within nanowires can be designed by choosing the growth interface (liquid–solid (LS) or vapor–solid (VS) interfaces) during the VLS process.⁹ These interesting features are hardly attainable by other nanowire growth methods. However, when compared with conventional liquid methods including hydrothermal nanowire synthesis,¹⁰¹¹ the growth temperature range of VLS process is relatively high.¹²⁻¹³ Typically, the growth temperatures of VLS growth of metal oxides were ranged from 600 to 1000 °C.¹⁴⁻¹⁹ This high temperature operation frequently limits the application range of VLS method. Within the framework of VLS nanowire growth, the metal catalysts are required to be a liquid state, which essentially determines the range of growth temperature.²⁰⁻²¹ Although choosing the metal catalysts with lower melting points is a straightforward approach to reduce the growth temperature, it is frequently unfeasible due to the affinity between metal catalysts and desired materials of nanowires.²² This issue is rather critical especially for the VLS nanowire growth of metal oxides, since metal species, which can be oxidized in the presence of surrounding oxygen, are not preferred.²³ Thus, a strategy to reduce the growth temperature without altering metal catalysts is desired for the VLS nanowire growth of metal oxides. We recently proposed a "material flux window" concept for designing metal oxide nanowires via a VLS route.²⁴ Within the framework of this concept, the size of critical nucleus at LS interface is smaller than that at VS interface due to the surface energy gain by the surrounding metal oxides and liquid catalyst atoms. Therefore, the critical material flux for VLS nanowire growth is always lower than that for VS film growth. Since VLS nanowire growth competes with VS film growth, the occurrence of nucleation only at the LS interface is crucial for enhancing the VLS nanowire growth. The preferential crystal growth only at the LS interface can be obtained by controlling the material flux within the material flux window between the two critical material fluxes of VLS nanowire growth and VS film growth. Since the growth temperature inherently affects the nucleation dynamics, the temperature dependence of the "material flux window" might give a solution to reduce the growth temperature of VLS process. However, such temperature dependent "material flux window" concept has never been examined theoretically and experimentally. This work proposes a strategy to reduce the growth temperature of VLS nanowires composed of metal oxides including MgO, SnO₂, and ZnO. In addition, we show the successful applications of this concept to VLS nanowire growths of metal oxides onto tin-doped indium oxide (ITO) glass and polyimide (PI) substrates, which require relatively low growth temperatures.
Figure 1. Schematic of the temperature dependent “material flux window” concept to reduce the growth temperature of VLS nanowire growth for metal oxides. Upper schematic figure shows the temperature dependence of materials flux window, where the nucleation preferentially occurs at LS interface. Lower figure shows the temperature dependence of critical vapor fluxes, above which a nucleation occurs, for both VS and LS interfaces.

This formula is based on the classical nucleation theory, where \( \gamma \) is the two-dimensional surface tension (energy) defined at the boundary of two-dimensional nuclear clusters at the solid surface, \( l_s \) is the lattice constant parameter of solid, which is set to be 1.145 in these calculations, \( k_B \) is the Boltzmann constant and \( T \) is temperature. \( \rho_{eq} \) is the saturated vapor density, whose value is obtained from preliminary simulations to be \( \rho_{eq} = 1.80 \times 10^{-4} \) at \( T = 0.307 \), and \( \rho_{eq} = 2.99 \times 10^{-5} \) at \( T = 0.270 \). \( \rho_{up} \) is the supplied vapor density. The values of surface tension for each of VS and VLS (LS interface) system, \( \gamma_{vs} \) and \( \gamma_{ls} \), as the fitting parameter, are estimated to be \( \gamma_{vs} = 0.37 \) and \( \gamma_{ls} = 0.25 \) at \( T = 0.307 \), and \( \gamma_{vs} = 0.42 \) and \( \gamma_{ls} = 0.20 \) at \( T = 0.270 \).

Eq 1 implies that the solid constantly grows when the flux density is higher than the following critical value \( \rho_c \), as expressed in the eq 2 (the maximum of the curvature of the theoretical curve),

\[
j_c \rho_{eq} \exp \left[ \frac{-l_s^2 \gamma^2}{(k_B T)^2 \ln(\rho_{up}/\rho_{eq})} \right]
\]

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This value tends to increase as temperature decreases ($W = 2.6$ at $T = 0.307$, and $W = 6.2$ at $T = 0.270$), as shown in Figure 2c. These MD simulation results and the analysis based on nucleation theory suggest that it should be experimentally possible to reduce the growth temperature of VLS nanowire growth by appropriately decreasing the vapor flux.

Figure 3 shows the experimental validation of above theoretical framework by utilizing the VLS growth of MgO nanowires with Au catalysts. The experimental details of nanowire growth can be seen in the Methods Section. Figure 3a shows the scanning electron microscopy (SEM) images of MgO nanowires formed via a VLS route. The growth temperatures were 400 and 800 °C, and the Mg metal fluxes were $8.8 \times 10^{17}$ cm$^{-2}$s$^{-1}$ and $34.1 \times 10^{17}$ cm$^{-2}$s$^{-1}$ with the constant oxygen partial pressure ($10^{-3}$ Pa). Although at the higher growth temperature, 800 °C, the nanowire structures could be formed at both vapor flux cases, there was the significant effect of vapor flux on the appearance of nanowire structures at the lower growth temperature, 400 °C. At the lower growth temperature, 400 °C, the nanowire shape was observable only for the lower vapor flux case, but not for the higher vapor flux case, where only grain-film structure was observed. To more quantitatively examine this effect of vapor flux on the VLS nanowire formation, we measured the nanowire density when varying the Mg vapor flux (ranged from $4.2$ to $34.1 \times 10^{17}$ cm$^{-2}$s$^{-1}$) and the growth temperature (ranged from 250 to 850 °C) with the constant oxygen partial pressure ($10^{-3}$ Pa), as shown in Figure 3b. When varying the growth temperature, there was a critical temperature, above which the nanowire structures were formed. For example, at the highest Mg vapor flux of $34.1 \times 10^{17}$ cm$^{-2}$s$^{-1}$, any nanowire structures were not observable below the critical temperature, 600 °C, and the nanowire structures emerged above the critical temperature. As shown in the inset figure, the critical temperature decreases with decreasing the growth temperature down to 350 °C. Furthermore, the similar trend was also confirmed even when varying only the oxygen partial pressure (e.g., oxygen vapor flux) with the constant Mg vapor flux, as seen in Figure 3c, which shows the nanowire density data when varying the oxygen partial pressures ranged from $10^{-3}$ Pa to 1 Pa and the growth temperature (ranged from 250 to 850 °C) with the constant Mg vapor flux ($8.8 \times 10^{17}$ cm$^{-2}$s$^{-1}$). Decreasing the oxygen partial pressure from 1 Pa to $10^{-3}$ Pa decreases the critical temperature for the VLS nanowire growth from 450 to 350 °C. Thus, the growth temperature for MgO nanowire growth via a VLS route can be reduced by decreasing the vapor flux, which is consistent with the theoretical framework.
predictions in Figure 2. Within the framework of “material flux window”, the successful reduction of growth temperature via controlling the vapor flux should originate from the suppression of a nucleation at VS interface. To confirm this, we measured the growth temperature dependence of thin film (VS) growth rate by varying Mg metal vapor flux, as shown in Figure 4. For comparison, the data of nanowire growth rates are also shown. Clearly, the VS thin film growth is significantly suppressed by decreasing the Mg metal vapor flux. For example, at the growth temperature of 500 °C, the VS thin film growth is almost zero for the lower vapor flux, 4.2 × 10^17 cm^{-2}s^{-1}, whereas for the higher vapor flux, 24.5 × 10^17 cm^{-2}s^{-1}, such VS thin film growth is significant (around 0.6 nm/min). Thus, the temperature dependent “material flux window” is a key phenomenon to successfully reduce the growth temperature of nanowires via a VLS route.

Next we examine the applicability of above strategy to reduce the growth temperature for VLS nanowire growths of various metal oxides. Figure 5 shows the SEM images of SnO_2 and ZnO nanowires formed via the VLS route with Au catalysts. The growth temperatures were 400 and 750 °C, and the Sn and Zn metal fluxes were ranged from 3.3 × 10^{17} cm^{-2}s^{-1} to 39.1 × 10^{17} cm^{-2}s^{-1} with the constant oxygen partial pressure (10^{-3} Pa). The other experimental details of nanowire growths can be seen in the Methods Section. At the higher growth temperature, 750 °C, the nanowire structures of both SnO_2 and ZnO were observable independent of the vapor flux cases. On the other hand, at the lower growth temperature, 400 °C, the nanowire structures were observable only for the lower vapor flux, 3.3 × 10^{17} cm^{-2}s^{-1} (SnO_2) and 4.3 × 10^{17} cm^{-2}s^{-1} (ZnO). Thus, decreasing the metal vapor flux successfully enhances the VLS nanowire growths of both SnO_2 and ZnO even at the lower growth temperature, 400 °C, and these results highlight the universality of the present strategy for VLS nanowire growth of various metal oxide materials.

Figure 6 shows the microstructures, optical and electrical properties of SnO_2 nanowires fabricated at both relatively high (750 °C) and low (500 °C) temperatures. Figure 6a shows the transmission electron microscopy (TEM) images of SnO_2 nanowires. The smooth surfaces of nanowires can be seen in both samples. In addition, the single crystallinity of SnO_2 nanowires with the growth direction perpendicular to [011] orientation was commonly observed in the high-resolution TEM (HRTEM) images and the selective area electron diffraction (SAED) pattern. Figure 6b shows the electron energy loss spectroscopy (EELS) of SnO_2 nanowires at Sn−M_{4.5} edge and O−K edge. The reference data of SnO_2 and SnO bulks are also shown for comparison. Since the EELS peaks at Sn−M_{4.5} edge are not clear, the O−K edge peaks are used for the discussion. The O−K edge peaks indicate that the valence state of 750 °C sample and 500 °C sample are similar to SnO_2 bulk and the significant difference between the two spectra cannot be seen, indicating the similar defect density in both samples. Next we performed the photoluminescence (PL) spectroscopy as shown in Figure...
The emission peaks were commonly observed at around 635 nm, which are associated with the bridging oxygen vacancies at SnO$_2$ nanowire surface. The peak intensity of 750 °C sample is higher than that of 500 °C sample, however, we cannot simply interpret this result in terms of the higher defect density of 750 °C sample since the peak intensity can be varied by the volume fraction of SnO$_2$ nanowires. Since the nanowire density grown at 750 °C is higher than that at 500 °C as shown in Figure 5, the PL intensity of 750 °C sample should be higher than 500 °C sample. To directly compare the nanowire property, we performed the electrical conduction measurement using single nanowire device. Figure 6d shows the current–voltage ($I$–$V$) characteristics of single SnO$_2$ nanowire measured at room temperature in vacuum condition ($10^{-3}$ Pa). The nanowire diameters of 750 °C sample and 500 °C sample are 25 and 13 nm, respectively. The SEM image of the single SnO$_2$ nanowire device and the resistivity data are shown as the insets in Figure 6d. The resistivity of 750 °C sample and 500 °C sample are $15.2 \times 10^3$ Ωcm and $5.0 \times 10^3$ Ωcm, respectively. These resistivity values are much higher than that of previous work. Since the electrical conduction of SnO$_2$ is associated with the defect density, these results imply the low defect density of our SnO$_2$ nanowires. Comparing the two growth temperature conditions, the resistivity value of 500 °C sample is slightly lower than that of 750 °C sample. This indicates the higher defect density of 500 °C sample. Presumably, this might be related to the surface defect rather than the defect density within nanowires since the surface-to-volume ratio of 500 °C sample is almost twice of 750 °C sample. Thus, these results of measured physical properties highlight that we can fabricate relatively high quality metal oxide nanowires even at low temperature by utilizing the present temperature dependent “material flux window” principle.

Finally, we apply the present concept to VLS nanowire growths of metal oxides onto various substrates, which require relatively low growth temperatures due to their thermal stability. Figure 7 shows the photo shots and SEM images of VLS nanowires of both SnO$_2$ and ZnO grown on ITO glass and PI substrates. The lowest growth temperature of SnO$_2$ and ZnO nanowires was 350 °C which was achieved by controlling the vapor flux. Successful formations of nanowires on these substrates can be clearly seen. Thus, the present strategy based on the temperature dependent “material flux window” concept would expand the application range of VLS nanowire growth of metal oxides.
functional metal oxides, where existing VLS process has not been applicable due to the temperature limitation.

In summary, we proposed a rational concept to reduce the growth temperature of the VLS nanowire growth of various metal oxides. MD simulations theoretically predicted the possibility to reduce the growth temperature of VLS nanowire growth by precisely controlling the vapor flux. This concept is based on the temperature dependent "material flux window" that the appropriate vapor flux for VLS nanowire growth decreases with decreasing the growth temperature. Experimentally, we found the applicability of this concept for reducing the growth temperature of VLS processes for various metal oxides including MgO, SnO$_2$, and ZnO. In addition, we showed the successful applications of this concept to ITO glass and PI substrates.

**Methods. Nanowire Growths.** Pulsed laser deposition (PLD, ArF excimer laser, $\lambda = 193$ nm, repetition rate =10 Hz) method was utilized to grow metal oxide nanowires, as described previously. $^{36-38}$ SnO$_2$ and ZnO nanowires were grown on a sapphire Al$_2$O$_3$ (110) substrate, and MgO nanowires were grown on a MgO (100) substrate (Crystal Base Co. Ltd.). As the metal catalysts, Au thin layer ($\sim$1 nm) was deposited onto the substrates by direct current (dc) sputtering. The vapors of material species were supplied by ablating metal tablets or metal oxide tablets (purity over 99.99%; Koujundo Chemicals Co. Ltd.). MgO, SnO$_2$ and Zn targets were used for MgO, SnO$_2$, and ZnO nanowire growths, respectively. The materials 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. The oxygen partial pressure was altered from 10$^{-3}$ to 1 Pa. The temperature of substrate was varied from 250 to 850 °C, and the typical growth time was 30 min. After nanowire growth, the substrate was cooled down to room temperature in the chamber within 30 min.

**Characterizations.** Fabricated nanowires were characterized by field emission scanning electron microscope (FESEM, JEOL JSM-7610F) at an accelerating voltage of 15 kV. The materials flux was estimated from the thickness of oxide films deposited in pure oxygen ambient (10 Pa) and at room temperature, because the evaporation rate on the substrate is negligible at such low temperature. $^{39,40}$ The thickness of film was measured by surface profiler (Alpha-Step IQ). Nanowire density was extracted by counting the number of nanowires per unit area (1 $\mu$m$^2$) in the top view SEM images. Ten unit areas were randomly selected to ensure the accuracy and the reliability. The crystallinity and the growth direction of fabricated nanowires were characterized by scanning transmission electron microscopy (STEM, JEOL JEM-ARM200F) at an accelerating voltage of 200 kV. Electron energy loss spectroscopy (EELS) equipped with TEM and photoluminescence (PL, JASCO FP-8500) spectroscopy was utilized to evaluate the valence state and the crystal defects of fabricated nanowires. The PL measurement was performed at room temperature. The electrical conduction measurement was performed in the form of single nanowire device. $^{31}$ The single nanowire device was constructed onto 100 nm SiO$_2$ coated Si (100) substrate by the electron beam (EB) lithography at an accelerating voltage of 30 kV. Briefly, the fabricated oxide nanowires were first dispersed into 2-propanol by applying the sonication with 28 kHz for 5 min. Then the nanowire suspension was dropped onto the substrate where the contact electrodes are prepatterned. Then the EB lithography was performed to make the nanowire-electrode contact, followed by Ti 1 nm/Pt 100 nm electrode deposition using RF sputtering (50 W, Ar 0.3 Pa). The electrical conduction measurement was carried out using 4-probe method at room temperature in vacuum condition (10$^{-3}$ Pa).

**Molecular Dynamics (MD) Simulation.** The molecular dynamics simulation can express time-evolution of motion (position and translation speed) for each particles which interact each other through short-range Lenard-Jones (L-J) potential. $^{41}$ In this simulation system, three types of particles (A, B, and C) were utilized to model the vapor–liquid–solid (VLS) growth process. Here, A and C can make AC compound in solid phase expressing oxide formation, and B is always assigned as solvent liquid.

Following L-J type potential was used as 2-body interaction potential except the interaction between A–A and C–C.

$$\phi(r_{ij}) = 4\epsilon \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} + \phi_{corr}(r_{ij})$$

where, $r_{ij}$ means a distance between the interacted two particles (center–center distance), $\sigma_{ij}$ is sum of the respective particles’ radii and $\epsilon$ expresses the bonding energy constant defined for respective particle combinations, $\epsilon_{AB}, \epsilon_{AC}$, and $\epsilon_{BC}$ independently. To accelerate the calculation speed, a long-range interaction was neglected in this program code by inducing cutoff distance, $R_C$ and $\phi(r_{ij})$ was set to be zero for $r_{ij}>R_C$. The correction term $\phi_{corr}$ was set to satisfy the continuity of $\phi$ and $d\phi/dr$ at $r_{ij} = R_C$. $^{25}$

For the potential between A–A and C–C, other modified L-J potential was used.

$$\phi(r_{ij}) = 4\epsilon \left( \frac{\sigma_{ij}}{r_{ij}-l_0} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}-l_0} \right)^{6} + \phi_{corr}(r_{ij}-l_0)$$

where, $l_0$ is offset distance and $\epsilon_{AC} =$ ($\epsilon_{AA}$) is energy constant. Potential (2) and $l_0$ were introduced to stabilize the rock-salt structure of AC solid phase. $l_0$ was set to be $l_0 \equiv l_c/(\sqrt{2} - 1)$, where $l_c$ is the lattice constant of AC rock-salt crystal.

The simulation box was set to be $L \times L \times \alpha L$, where $\alpha L$ is the system height (set $\alpha = 2$ in this article). Here the typical system size was set to be $L = 32l_c$. Initially, the substrate with eight layer-thick solid consisting of A and C particles with rock-salt order was fixed on the bottom wall. A flat layer of B-particle solvent was placed on the substrate for the simulation of the VLS process, while no solvent was added or the VS process. The sidewalls have a periodic boundary condition. The temperature of the system was controlled on the top and bottom walls. The particle bath densities of A particles $\rho_A^{\text{ss}}$ and of C particles $\rho_C^{\text{ss}}$ were set independently, and each species was supplied from the top wall. $^{25}$

All physical parameters used in this program are normalized by $\epsilon_{AC}, \sigma_{AC}$ and the particle mass $m$. This normalization leads to dimensionless temperature and time parameters of $k_B T/\epsilon_{AC}$ and $t \sqrt{\epsilon_{AC}/m}/\sigma_{AC}$, respectively.

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