Role of surrounding oxygen on oxide nanowire growth

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The ability to control oxide nanowires via vapor-liquid-solid (VLS) mechanism remains an important challenge to explore various applications of oxide nanowires. Here we demonstrate the crucial roles of surrounding oxygen on VLS grown SnO_2 nanowires. When the partial pressure of surrounding oxygen is relatively low, the oxygen mainly acts as an oxygen source, promoting VLS growth. While for relatively high oxygen partial pressures, vapor-solid (VS) growth emerges, suppressing nanowire growth. The findings as to the roles of surrounding oxygen on the inherent competition between VLS and VS growths are in principle rather universal for VLS grown nanowires of various oxides. © 2010 American Institute of Physics. [doi:10.1063/1.3474605]

Metal oxide nanowires formed by vapor-liquid-solid (VLS) mechanism are promising building blocks toward nanodevice applications due to their fascinating physical properties.[1–4] The VLS growth in principle allows us to design the size and location of oxide nanowires by controlling the metal catalysts. Within the framework of nanowire growth by VLS, controlling a competition between VLS and vapor-solid (VS) growths is quite important and suppressing VS growth realizes the growth of well-defined nanowire structures. Generally it has been controlled by the growth temperature and the partial pressure of the source gas. This means that oxygen gas in surroundings plays an important role on the formation of oxide nanowires because it is a major constitute of oxides. Thus understanding the roles of surrounding oxygen on VLS and VS growths of oxide nanowires is rather essential to design the microstructures and properties of oxide nanowires. Most previous studies[5–8] have dealt with various VLS grown oxide nanowires without controlling intentionally the surrounding oxygen, frequently only using the residual oxygen. Although a few reported the importance of oxygen partial pressure on oxide nanowire morphologies,[9–12] understanding the role of surrounding oxygen on VLS grown oxide nanowires is far from comprehensive. Here we demonstrate the crucial roles of surrounding oxygen on VLS grown oxide nanowires. We introduce the comparison between VLS grown nanowire experiments and conventional VS grown thin film experiments, which allows us to extract quantitatively each contribution of VLS and VS growths on oxide nanowires.

SnO_2 nanowires were grown on Al_2O_3 (110) oriented single crystal substrate by Au catalyst-assisted pulsed laser deposition technique.[13] The background pressure of the chamber was 10^{-6} Pa. Sn metal powders or SnO_2 powders were used as the target. Oxygen and argon mixed gas was introduced into the chamber to keep the ambient total pressure of 10 Pa with varying the ratio of oxygen and argon. The typical growth temperature was 700 °C. The nanowire

morphology was characterized by field emission scanning electron microscopy (FESEM). High-resolution transmission electron microscopy was used to evaluate the diameter, and the composition of the fabricated nanowires.

Figure 1 shows the FESEM images, the growth rate, and the number density of SnO_2 nanowires when varying the oxygen partial pressure P_{O_2} with the constant total pressure of 10 Pa. Sn metal target was used in these experiments. There are several interesting features in the results. Below 10^{-5} Pa of P_{O_2}, only droplets on the surface were observed. We confirmed by an electron probe microanalysis that the droplets consist of Au–Sn alloy. Such droplets were not detectable at all in the absence of Au catalysts. This is due to the lack of oxygen in surroundings. Above 10^{-5} Pa of P_{O_2}, nanowire morphology emerged, and the growth rate increased with increasing P_{O_2}. In this region, the partial pressure of surrounding oxygen enhances the VLS nanowire growth via supplying more oxygen. The trend was observed below P_{O_2} of 10^{-2} Pa, and then the growth rate showed the maximum around 10^{-2} Pa of P_{O_2}. Above P_{O_2} of 10^{-2} Pa,
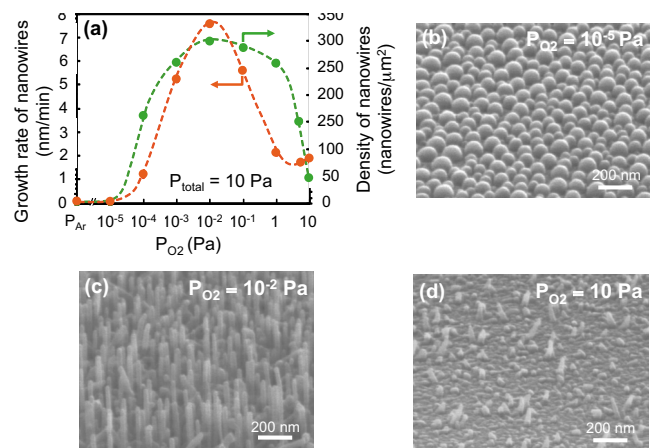

FIG. 1. (Color online) FESEM images, the growth rate, and the number density of SnO_2 nanowires when varying the oxygen partial pressure P_{O_2} with the constant total pressure 10 Pa.

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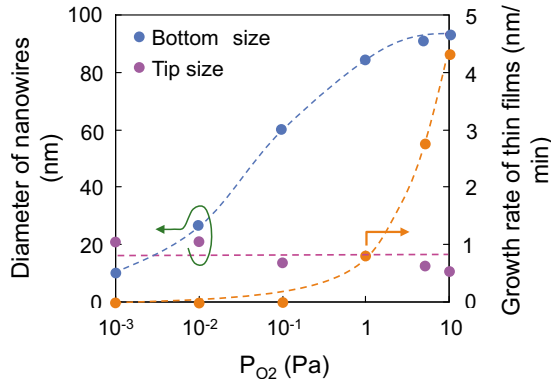
FIG. 2. (Color online) Sizes at the tip and the bottom of nanowire and the VS growth rate of thin films when varying P_{O_2}.
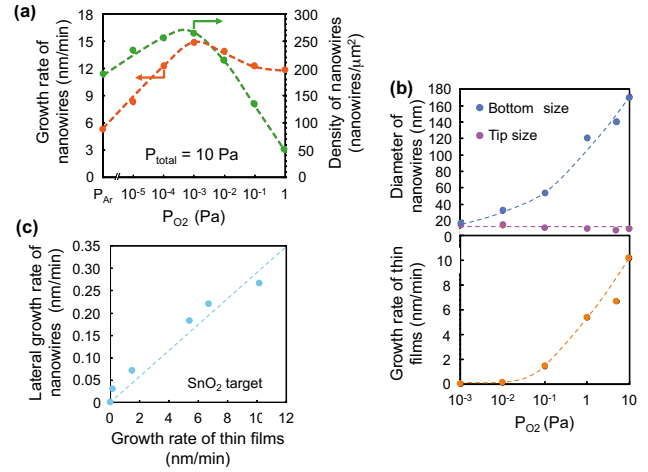

FIG. 3. (Color online) (a) Growth rate and the number density of nanowires when varying P_{O_2} with the constant total pressure 10 Pa. (b) Thin film VS growth rate and the data of nanowire sizes at the tip and the bottom when varying P_{O_2}. (c) Correlation between the VS growth rate of thin films and the lateral growth rate of nanowires in various oxygen partial pressures.

the growth rate decreased with increasing P_{O_2}. Here we examine what causes the maximum of the growth rate as a function of P_{O_2}. Within the framework of VLS, the precipitation rate at the liquid-solid (LS) interface underneath catalysts determines the growth rate of VLS nanowires. In other words, the ability to supply adatoms into metal catalysts plays an important role on VLS growth. In this scenario, a VS growth is detrimental because the supplied adatoms on the substrate tend to crystallize before incorporating into metal catalysts. Thus to know the behavior of the growth mode, it would be important to understand the competition between VLS and VS growths during nanowire formations. We have performed experiments as to SnO_2 thin films to measure the VS growth rate. Figure 2 shows the growth rate of SnO_2 thin films deposited under 700 °C (the same temperature of VLS experiments) as a function of P_{O_2}. It can be seen that below 10^{-2} Pa of P_{O_2}, the VS growth rate was found to be almost zero, indicating the absence of VS growth and the re-evaporation of supplied adatoms. On the other hand, above the threshold value, the VS growth rate increased with increasing P_{O_2}. There is a consistency between the maximum of VLS growth rate in Fig. 1 and the threshold value of VS growth in Fig. 2. This infers that the emergence of VS growth suppresses the VLS nanowire growth. Since the present VS growth experiments were performed for thin films in the absence of metal catalysts, it is necessary to validate the trend of VS growth in nanowire formations. Here we focus on the microstructural information of fabricated nanowires since it has been reported that the coexistence of VS and VLS growths makes the oxide nanowire morphology a tapered-shape due to the VS sidewall growth.[10] We have analyzed the nanowire sizes at the tip and the bottom (measured at 500 nm from the tip) when varying P_{O_2}. Figure 2 shows the data of sizes. The size at the bottom increased with increasing P_{O_2} while the tip size remained almost constant, indicating the presence of tapering. This indicates the occurrence of VS sidewall growth of nanowires above 10^{-2} Pa of P_{O_2}. In Fig. 1, the growth rate tends to be constant with increasing P_{O_2} above 1 Pa. This can be interpreted in terms of the competing two effects based on the following formula $R_{NW}(P_{O_2}) \propto [F_{total} - F_{eva}(P_{O_2})] \times \zeta_{VLS}(P_{O_2}) / N_{NW}(P_{O_2})$, where R_{NW} is the growth rate, F_{total} is a total impinging flux, F_{eva} is a re-evaporation flux, N_{NW} is a nanowire density, ζ_{VLS} is a percentage of VLS. The competing two effects, namely, "the increase in impinging flux for a

single nanowire" and "the decrease in VLS rate due to the occurrence of VS growth," should be responsible to result in the observed constant R_{NW}. The impinging flux for a single nanowire corresponds to $[F_{total} - F_{eva}(P_{O_2})] / N_{NW}(P_{O_2})$, and the VLS rate is related to $\zeta_{VLS}(P_{O_2})$. If the increase in impinging flux: $[F_{total} - F_{eva}(P_{O_2})] / N_{NW}(P_{O_2})$ is cancelled by the decrease in VLS growth rate: $\zeta_{VLS}(P_{O_2})$ for certain P_{O_2} region, R_{NW} can be constant.

Compared with previous studies as to VLS grown oxide nanowires, the major feature of the present study is an intentional control of surrounding oxygen with the low backpressure of 10^{-6} Pa, which allows us to identify the competing effects of VLS and VS growths. One of unique trends in the data of Fig. 1 is the presence of the lower limit of surrounding oxygen to emerge VLS growth, which is around between $10^{-5} - 10^{-4}$ Pa of P_{O_2}. This indicates that the present SnO_2 VLS growth requires only $10^{-5} - 10^{-4}$ Pa of P_{O_2} in surroundings, which can be supplied from residual oxygen in the cases of low vacuum circumstance. This might also explain some previous reports[5–8] as to the occurrence of oxide VLS growth even without supplying an oxygen source. We have examined this issue by using oxygen contained source material-SnO_2 target instead of Sn metal target. Since the supplied flux contains oxygen in this case, the threshold value of P_{O_2} for SnO_2 VLS growth and the P_{O_2} pressure with the maximum VLS rate are expected to become lower. Figure 3(a) shows the growth rate and the number density of nanowires with varying P_{O_2} with the constant total pressure of 10 Pa. Except for target material, these experiments was performed under the same conditions of experiments in Fig. 1. As expected, the VLS growth occurred even in pure Ar atmosphere due to supplying oxygen from the source, and the maximum of the VLS growth rate was shifted to lower P_{O_2} around 10^{-3} Pa from 10^{-2} Pa in Fig. 1. In the same manner as Fig. 2, we have extracted the VS growth effects by performing thin film experiments and analyzing nanowire sizes at the tip and the bottom. Figure 3(b) shows the thin film VS growth rate and the data of nanowire sizes at the tip and the bottom when varying P_{O_2}. The growth rate of nanowires in Fig. 3(a) was found to be nearly double of the cases

in Fig. 1, and this is due to the increase in impinging flux when using SnO_2 target as seen in the data of thin film growth rate. The VS growth rate and the nanowire size at the bottom consistently increased above around 10^{-3} Pa of P_{O_2}. These results are clearly consistent with the maximum of the VLS growth rate in Fig. 3(a). Thus the role of surrounding oxygen on both VLS and VS growths is rather universal even varying the source materials. The trend of P_{O_2} dependence of the nanowire density seems to be closely related to the occurrence of VLS growth, e.g., both the maximum nanowire density and the maximum nanowire growth rate were found at the same P_{O_2}. We consider several factors to explain this phenomenon, including a distribution of the nanowire growth rates and a competition between VLS and VS growths. Below P_{O_2} at the maximum nanowire density, where VLS growth dominates and VS growth is negligible, the nanowire density can increase by increasing P_{O_2} due to the increase in the nucleation probability for VLS growth. Above P_{O_2} at the maximum nanowire density, VS growth tends to dominate and the competition between VLS and VS becomes significant. Since there is a distribution of nanowire growth rate, the nanowire density can decrease by increasing P_{O_2} if the growth rates of some nanowires are less than the VS growth rate. In addition, the universality of this mechanism can be seen in some previous experimental trends of various oxide nanowires, including MgO,[10] In$_2$O$_3$,[11] and ZnO,[12] where the tapered shape of nanowires due to the VS sidewall growth emerged when the oxygen partial pressure increased. The present approach is also capable of designing and controlling the tapering of nanowires (i.e., the sidewall growth). We analyzed the lateral growth rate of nanowire R_L via $R_L = (D_{bottom} - D_{tip})/(2t_d)$, where D_{bottom} is the nanowire size measured at 500 nm from the tip, D_{tip} is the nanowire size at the tip and t_d is the deposition time. As shown in Fig. 3(c), there is a good correlation between the VS growth rate of thin films and the lateral growth rate of VLS grown nanowires, indicating the possibility to predict and control the tapering prior to nanowire formation experiments, which had been unfeasible. The approach proposed herein, which compares the VLS nanowire growth with thin film VS growth, suggests a strategy to explore and design oxide VLS growths. Since the competition between VLS and VS growths inherently exists in any oxides, an oxygen partial pressure must be an important controlling factor to realize a nanowire growth for various oxides. This study proposes that such appropriate atmospheric conditions can be estimated by performing thin film experiments prior to nanowire formation experiments. Since the occurrence of VS growth is detrimental for VLS growth, it is essential to find the conditions where only VLS growth occurs. In most of the oxides where the nanowire growths occur (SnO_2, MgO, ZnO, and so on), metal elements in their oxides have high vapor pressure or low melting temperature compared with the oxides. For this reason, we can expect that VS growth of such oxides is sup-pressed under lower oxygen pressure and appropriate substrate temperature, where the metal elements just on the substrate can solidify only accompanied by oxidization and nonoxidized metal atom must re-evaporate. In order to proceed with VLS nanowire growth under such condition, the oxygen partial pressure required for crystal growth at LS interface should be lower than that for the growth at VS interface. Such conditions to promote preferentially VLS growth might be realized by the higher concentration of metal atoms within liquid catalysts compared with that in vapor phase.

[1] B. S. Kwak, A. Erbil, B. J. Wilkens, J. D. Budai, M. F. Chisholm, and L. A. Boatner, Phys. Rev. Lett. **68**, 3733 (1992).
[2] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature (London) **426**, 55 (2003).
[3] J. P. Locquet, J. Perret, J. Fompeyrine, E. Mäechler, J. W. Seo, and G. Van Tendeloo, Nature (London) **394**, 453 (1998).
[4] K. Nagashima, T. Yanagida, K. Oka, and T. Kawai, Appl. Phys. Lett. **94**, 242902 (2009); K. Oka, T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai, J. Am. Chem. Soc. **131**, 3434 (2009); K. Nagashima, T. Yanagida, K. Oka, M. Taniguchi, T. Kawai, J. S. Kim, and B. H. Park, Nano Lett. **10**, 1359 (2010); K. Oka, T. Yanagida, K. Nagashima, T. Kawai, J. S. Kim, and B. H. Park, J. Am. Chem. Soc. **132**, 6634 (2010).
[5] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, and H. Choi, Adv. Funct. Mater. **12**, 323 (2002).
[6] K. H. Woo, S. S. Hyun, and L. J. Woo, J. Nanosci. Nanotechnol. **7**, 4434 (2007).
[7] P. Nguyen, H. T. Ng, J. Kong, A. M. Cassell, R. Quinn, J. Li, J. Han, M. McNeil, and M. Meyyappan, Nano Lett. **3**, 925 (2003).
[8] Q. Wan, E. N. Dattoli, and W. Lu, Appl. Phys. Lett. **90**, 222107 (2007).
[9] S. Kodambaka, J. B. Hannon, R. M. Tromp, and F. M. Ross, Nano Lett. **6**, 1292 (2006).
[10] K. Nagashima, T. Yanagida, K. Oka, H. Tanaka, and T. Kawai, Appl. Phys. Lett. **93**, 153103 (2008).
[11] C.-P. Chu, T.-S. Ko, Y.-C. Chang, T.-C. Lu, H.-C. Kuo, and S.-C. Wang, Mater. Sci. Eng., B **147**, 276 (2008).
[12] J. Song, X. Wang, X. Wang, E. Riedo, and Z. L. Wang, J. Phys. Chem. B **109**, 9869 (2005).
[13] K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai, Appl. Phys. Lett. **90**, 233103 (2007); T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai, *ibid.* **91**, 061502 (2007); K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai, J. Appl. Phys. **101**, 124304 (2007); A. Marcu, T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai, *ibid.* **102**, 016102 (2007); T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai, *ibid.* **104**, 016101 (2008); K. Nagashima, T. Yanagida, H. Tanaka, S. Seki, A. Saeki, S. Tagawa, and T. Kawai, J. Am. Chem. Soc. **130**, 5378 (2008); A. Marcu, T. Yanagida, K. Nagashima, K. Oka, H. Tanaka, and T. Kawai, Appl. Phys. Lett. **92**, 173119 (2008); T. Yanagida, A. Marcu, H. Matsui, K. Nagashima, K. Oka, K. Yokota, M. Taniguchi, and T. Kawai, J. Phys. Chem. C **112**, 18923 (2008); K. Oka, T. Yanagida, K. Nagashima, H. Tanaka, S. Seki, M. Ishimaru, A. Hirata, and T. Kawai, Appl. Phys. Lett. **95**, 133110 (2009); A. Klamchuen, T. Yanagida, K. Nagashima, S. Seki, K. Oka, M. Taniguchi, and T. Kawai, *ibid.* **95**, 053105 (2009); K. Nagashima, T. Yanagida, A. Klamchuen, M. Kanai, K. Oka, S. Seki, and T. Kawai, *ibid.* **96**, 073110 (2010).