

Self-assembly of periodic ZnO/C multilayers on Zn nanowires

K. W. Kwong and Quan Li^{a)}

Department of Physics, The Chinese University of Hong Kong, Shatin, New Territory, Hong Kong

(Received 21 June 2004; accepted 23 May 2005; published online 18 July 2005)

In a previous study, we observed periodic polycrystalline-ZnO/amorphous-C multilayers self-organized on the surface of Zn nanowires, which were dispersed on the amorphous carbon film at ambient conditions after 1500 h. Such self-assembled multilayers with individual layer thickness of ≈ 2 nm have been reproduced through a simple chemical reaction between the Zn nanowires and the CO₂ gas. Transmission electron microscopy is employed to investigate the evolution of the Zn nanowire during its reaction with the CO₂. A systematic study is carried out and a four-step mechanism—gas phase diffusion, interfacial chemical reaction, phase separation, and self-alignment—is proposed to explain the formation of such nanostructures. The parameters that affected the self-assembly process including the crystallinity of the original native zinc oxide sheath wrapping the Zn nanowires, the reaction temperature, and the reacting gases are discussed in detail based on the experimental observations. © 2005 American Institute of Physics.

[DOI: 10.1063/1.1957133]

I. INTRODUCTION

Self-assembled nanosized domain patterns have been observed^{1–19} or predicted^{11,20,21} in a variety of material systems. Plass *et al.* reported the formation of nanoscale domain patterns (clusters, stripes, etc.)¹ on material surfaces as driven by the periodic surface-lattice dislocations² or by the stress field in the substrate around each unit;^{3–6} Tober *et al.* achieved lateral multilayer superlattices utilizing the film/substrate interfacial strain-induced phase separation;^{7,8} several pseudosuperlattices were demonstrated in the growth direction of thin films as organized by growth-related driving force;^{9–11} and Springholz *et al.* observed three-dimensional quantum dot during the strained-layer epitaxial growth of superlattices.¹² In these systems, the mobility of atoms is a crucial factor in the self-assembly process, and the domain pattern formation is mostly driven by certain stress-related field(s). Another category of the self-assembly process usually involves specific chemical bonding between the target material and the anchoring molecule(s). Examples include self-assembled Langmuir-like monolayer with short chain organic molecules,^{13–16} well-defined ferroelectric nanograins on a substrate by self-assembly chemical solution deposition method,¹⁷ self-organized patterns (islands, intermediate, and continuous) based on the arrangement of alkyl chains on mica surface,¹⁸ and quasiequivalent monodendritic side groups attached to a flexible backbone as spherical and cylindrical polymers,¹⁹ etc.

These observations, together with theoretical predictions,^{11,20,21} have aroused tremendous amount of interest owing to the properties of these ordered nanosystems and their potential applications in mechanical, magnetic, electrical, and optical devices. With the urge of further increasing device density in limited space, and thus decreasing the size of the device, the self-assembly of nanosized domain patterns

becomes one of the most prospective means in achieving the final goal. Therefore, understanding the underlying physics of the materials' self-assembly process becomes critical in achieving various self-organized nanostructures in the era of nanotechnology.

In a previous study, we accidentally observed ordered multilayers of ZnO and C self-organized on the surface of Zn nanowires,²² where the Zn nanowires were fabricated by thermal evaporation and were covered with an epitaxial surface native oxide layer (≈ 5 nm).²³ These nanowires were then dispersed on amorphous carbon film and stored for over 2 months at ambient conditions, when well-organized polycrystalline zinc oxide (*p*-ZnO)/amorphous carbon (*a*-C) multilayers with individual layer thickness of ≈ 2 nm were found to form periodically outside the Zn cores, taking the place of the original surface ZnO. We refer to such ordered structures as self-assembled multilayers (SAMs) in the later sections.

Inspired by this observation, we carried out several experiments in order to understand such self-organization process. We have identified that solid phase diffusion of C is not the major driving force for the SAM formation outside the Zn nanowires, based on the experimental observation that no SAM was observed in the carbon-coated Zn nanowires after being stored for 2 months. The coating of the amorphous carbon, if not completely prevents, at least slows down the self-assembly process.²² As a comparison, we found that the reaction between carbon-containing gases (e.g., CO₂) and the Zn nanowires resulted in the formation of SAM structures.

In this study, we have carried out a systematic study in order to locate the critical parameters in the gas phase reaction experiments, which lead to the self-assembly of ZnO/C multilayers outside the Zn nanowire, so that the mechanisms can be better understood. The growth model of the SAM nanostructure is discussed in detail based on the experimental observations.

^{a)}Author to whom correspondence should be addressed; electronic mail: liquan@phy.cuhk.edu.hk

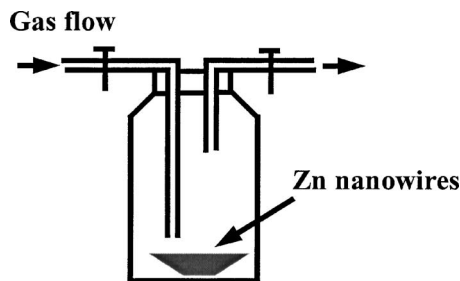


FIG. 1. Schematic diagram of the reaction gas cell consisting of a small chamber and gas feed throughs.

II. EXPERIMENT

Zn nanowires were synthesized by thermal reduction of zinc oxide using hydrogen in a vacuum tube furnace, the settings of which had been described elsewhere.²⁴ In brief, ZnO powders (99.9% purity, Fisher Chemicals) were placed in the center of tube as the source material, and Ar-5% H₂ gas mixtures were introduced as the carrier gas during the fabrication process. The tube was heated to 1000 and 1200 °C to produce Zn nanowires with different qualities. A total pressure of 300 mbars was maintained throughout the experiment. The final products were obtained in the low-temperature region of the furnace.

The gas phase reactions between the Zn nanowires and the carbon-containing gases are studied using a gas reaction cell. The gas cell consists of a small chamber and gas feed through (Fig. 1). Carbon-containing gases (e.g., CO₂) are allowed to flux through the chamber over the Zn nanowires, which were placed inside a small plastic container in the gas cell. Samples of nanowires were taken out from the gas cell for different reaction durations in order to study the evolution of the nanowires.

Several parameters were systematically examined in the gas phase reaction experiments to investigate their possible effect on the self-assembly process: (1) the crystallinity of the ZnO sheath outside the Zn core in the nanowires (referred to as series A in later sections), (2) the temperature (series B), and (3) the different reaction gases (series C). In series A, nanowires with different ZnO-sheath qualities (single crystalline versus polycrystalline) were placed in the reaction cell using CO₂ gas at room temperature. Series B was carried out using Zn nanowires with polycrystalline-ZnO sheath in the same gas reaction cell with a hot plate to provide elevated temperatures (100 vs 25 °C). Series C was carried out using Zn nanowires with polycrystalline-ZnO sheath at 100 °C with CO and CO₂ as the flux gases, respectively. The evolutions of the Zn nanowires were compared among the samples in each series.

Transmission electron microscopy (TEM, Philips CM120 and Tecnai 20 FEG) was employed to investigate the microstructure evolution of the nanowires at different experimental conditions. The chemical compositions of the nanowires were examined by the energy dispersive x-ray (EDX) spectrometer attached to the same microscope. Transmission electron diffraction (TED) is used to examine the crystallinity of ZnO in the native oxide sheath as well as that in the

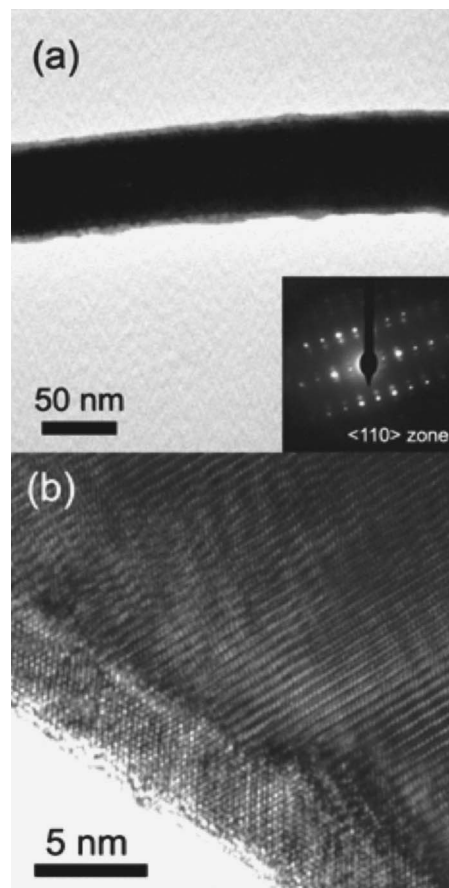


FIG. 2. (a) Low-magnification TEM image of a typical Zn nanowire synthesized at 1000 °C. The TED pattern in the inset was taken from the same nanowire, suggesting single-crystalline Zn and ZnO with epitaxial relationship between them. (b) High-resolution TEM image of the same nanowire showing the single-crystalline oxide sheath.

SAM. Detailed microstructures and the interface(s) in the nanowires are studied by high-resolution electron microscopy (HREM).

III. RESULTS AND DISCUSSIONS

A. Freshly synthesized Zn nanowires

The chemical composition and the structure of the freshly synthesized Zn nanowires were investigated using TEM. The EDX results suggested that the as-synthesized nanowires are composed of Zn and O. Figure 2(a) is a low-magnification TEM image of a typical Zn nanowire synthesized at 1000 °C. Dark/light contrast is observed in the core/sheath region of the nanowires, suggesting the Zn-core/ZnO-sheath nanocable configuration. The TED pattern taken from the same nanowire in the inset of Fig. 2(a) suggests the presence of single-crystalline Zn and ZnO. Figure 2(b) is the corresponding HREM image of the same nanowire, which discloses the structure details at the Zn/ZnO interface. Together with the TED pattern, the high-resolution image reveals a good epitaxial relationship between Zn and ZnO with both lattices relaxed. As a comparison, Fig. 3 shows the TEM images of a typical nanowire synthesized at 1200 °C. The ring TED pattern in the inset of Fig. 3(a) suggests the polycrystalline nature of ZnO. This agrees well with the

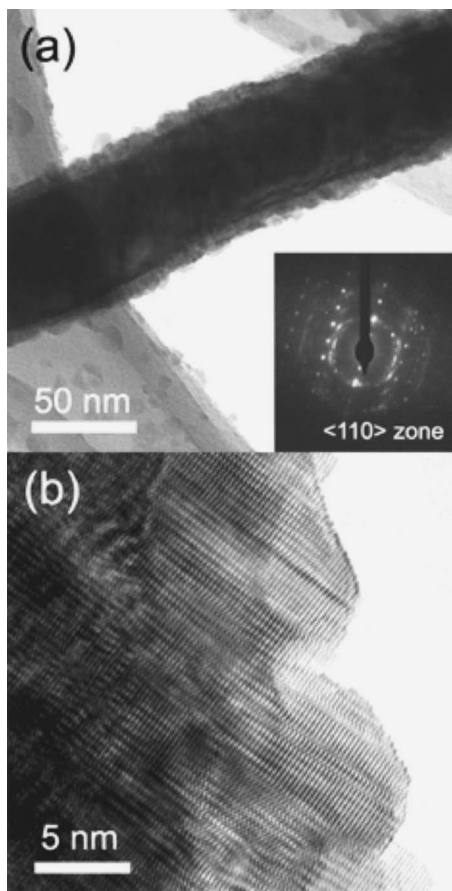


FIG. 3. (a) Low-magnification TEM image of a typical nanowire synthesized at 1200 °C. The TED pattern of the nanowire (in the inset) suggests the polycrystalline nature of the ZnO sheath. (b) High-resolution TEM image of the same nanowire.

HREM image taken from the same wire, where small grains of ZnO (~ 5 nm) without any specific orientation to the Zn core are observed in the sheath region.

B. Introducing carbon into the Zn nanowire: Gas phase reaction with CO₂

The ordered SAM started to appear in the sheath region of the Zn nanowires, which had been placed inside a CO₂ gas reaction cell at 100 °C for 168 h. This is much more effective compared to the over 2 months duration when the Zn nanowires were stored on the carbon film at ambient conditions. Figure 4 shows a typical SAM on the Zn nanowire as induced by exposure in CO₂ gas. EDX taken from the nanowire indicates the existence of Zn, O, and C. Figure 4(a) is a low-magnification TEM image of such structure revealing the light-dark-light striations in the sheath region of the wire. The corresponding high-resolution image in Fig. 4(b) shows the well-defined multilayer structures, where the dark layer (≈ 2 nm) appears to be polycrystalline and the light layer (≈ 2.5 nm) appears to be amorphous. The diffraction pattern of the same nanowire in the inset of Fig. 4(a) suggests the existence of single-crystalline Zn (one set of diffraction spots) and polycrystalline ZnO (diffraction rings). Similar

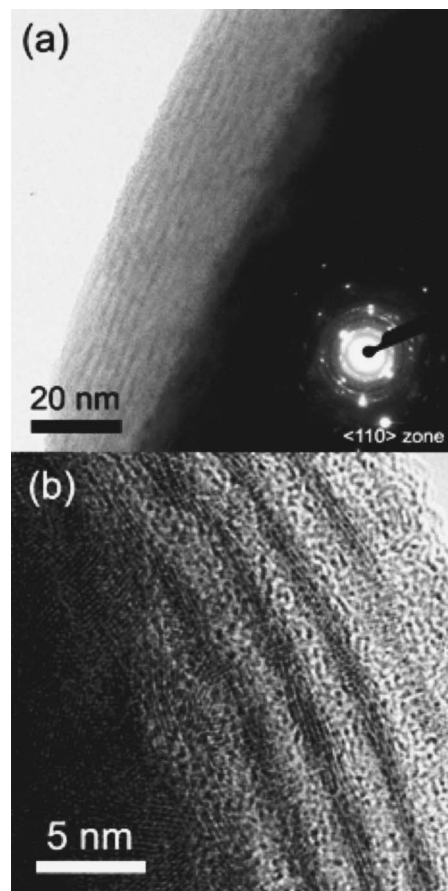


FIG. 4. (a) Low-magnification TEM image of a nanowire with typical SAM structure, which is induced by CO₂ exposure. The TED pattern of the nanowire in the inset shows one set of diffraction spots (single-crystalline Zn) and several diffraction rings (corresponding to polycrystalline ZnO). (b) HREM image of the nanowire showing the ordered layer structure of SAM.

results were obtained when using CO as the fluxing gas. The difference between using CO₂ and CO will be discussed later.

The evolution of the SAM structure as a function of the exposure time to the gas phase has been previously described; details can be found in the published work.²² After examining a large number of nanowires, it is found that the outmost surface of the sheath could be terminated by either ZnO or carbon [Figs. 5(a) and 5(b), respectively]. The discontinuity of the multilayer along the axial direction of the nanowire (as marked by arrows in Fig. 6) is commonly observed in the SAM.

The above results suggest that the carbon phase in the ZnO/C multilayers can be effectively introduced into the Zn nanowires by gas phase reaction with CO₂. In general, the carbon-containing gas could diffuse to the Zn/ZnO interface, where it reacts with the metal Zn to produce ZnO and C, which finally leads to the self-organized ZnO/C multilayers outside the Zn nanowires.

A four-step mechanism—gas phase diffusion, interfacial chemical reaction, phase separation, and self-alignment—has been proposed to explain the formation of such nanostructures.²² Briefly, the diffusion of CO₂ to the core/sheath interface may resemble that of O₂ during the further oxidation process of an already oxidized Zn surface.²⁵ The

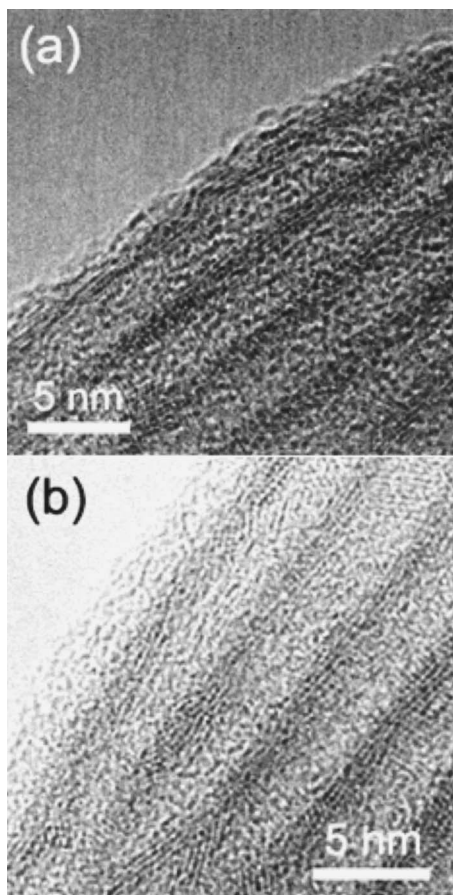


FIG. 5. SAM with (a) ZnO and (b) carbon as the termination surface layers.

fact that the native oxide layer is usually oxygen deficient, together with the possible defects associated with the nanowire cylindrical configuration, serves as the driving force for O_2 (CO_2 in this case) to diffuse through the original oxide sheath to the Zn core for reaction.

Once the carbon-containing gas diffuses to the Zn/ZnO interface, carbon may be produced from the following chemical reaction:

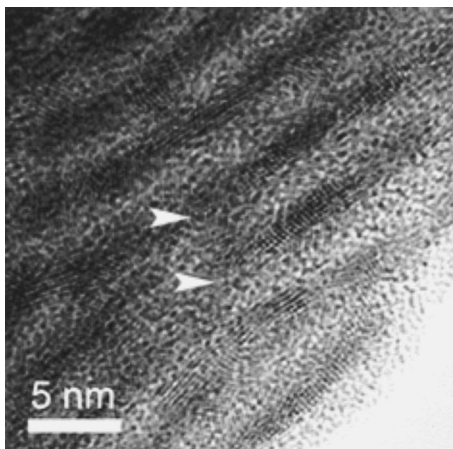
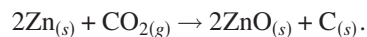


FIG. 6. Discontinued ZnO layers (pseudodislocations) observed along the axial direction of the nanowire (as marked by arrows).

The change in Gibbs free energy for such a reaction (at room temperature) is calculated to be negative,²⁶ which implies that the reaction is thermodynamically favorable. The small size of the Zn nanowire may promote the reactivity of the above reaction. More importantly, ZnO is the other product of the same reaction, which, in fact, suggests an ever-increasing amount of ZnO as the reaction continues. This is consistent with the experimental observation that the total thickness of the ZnO layers in the SAM can be much larger than that of the original ZnO sheath.²² Nevertheless, the above reaction does not represent the possible intermediate processes, in which other chemical reactions among Zn, ZnO, and different carbon-containing species may be involved (may include ZnO itself, defect formation, and various intermediate species),²⁷⁻²⁹ which cannot be directly observed experimentally.

As ZnO and carbon would be continuously generated at the original Zn/ZnO interface by the above chemical reaction, one would expect phase separation of ZnO and C owing to the immiscibility of the two phases. At the same time, these newly formed C and ZnO at the core/sheath interface would push the original oxide layer laterally, being away from the core region. This would lead to the fracture of the original oxide sheath due to the stress that resulted from the sheath's lateral expansion.

Thermodynamically, the system does not favor the small ZnO particles/amorphous carbon configuration, which is associated with high interfacial energy. This serves as one of the major driving forces of the self-organization of the ZnO and C into layered structures, which can be achieved by short-range migration of the two phases and resulting interfacial energy reduction in the system. The dynamic process of continuous ZnO and C formation at the interface and the inner-out motion of the sheath materials make it difficult for an ordered layer structure formation in regions close to the interface, and suggests that the equilibrium is first reached in the outmost surface of the nanowire, which becomes the first site for the ordered multilayer to appear on. Once the multilayers are formed at the outmost surface region, further "pushing" process can be realized through pseudodislocation (discontinuous ZnO layers throughout the multilayer structures) movements without destroying the already formed multilayer structures. The observation that both ZnO and C act as the termination surface layer in SAM [Figs. 5(a) and 5(b)] agrees with the proposed model, which must involve the "damage" of the original native oxide layer, the migration of different phases, and the establishment of the short-range equilibrium.

Several factors that affect the SAM formation processes were investigated systematically.

1. Crystallinity of original oxide sheath (series A)

The as-synthesized Zn nanowires with different oxide sheath crystallinities (single crystalline versus polycrystalline; details can be found in part of the freshly synthesized Zn nanowires) are used to study the effect of the ZnO crystallinity on the SAM formation. Similarly, samples were taken out from the gas reacting cell at room temperature for different durations. In general, ordered SAMs are observed

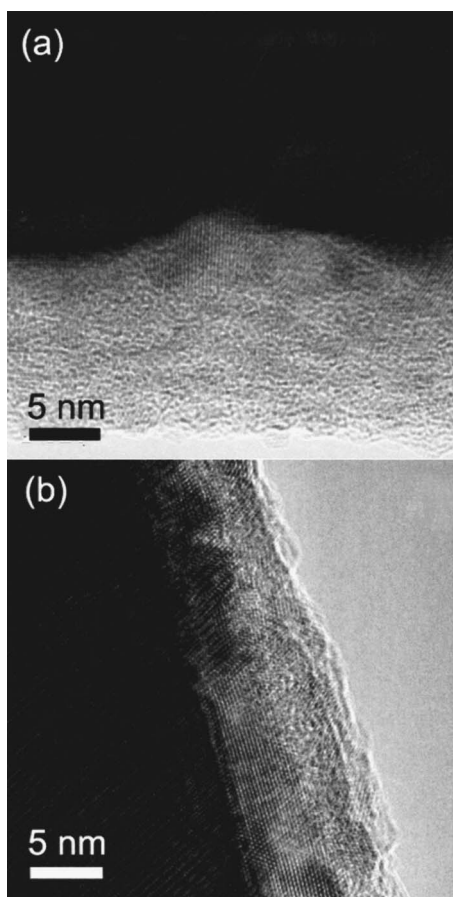


FIG. 7. HREM images of the Zn nanowire originally with (a) polycrystalline native oxide sheath and (b) single-crystalline sheath. Both were taken from the CO_2 reacting cell at 25 °C after 168 h.

in both types of nanowires when the reaction time in the gas cell is long enough (usually after 240 h). Nevertheless, the SAM formation appears to be faster in the samples with the polycrystalline native oxide sheath. A representative comparison is shown in Figs. 7(a) and 7(b), which shows the morphologies of two types of Zn nanowires after a 168-h duration in the gas cell. It is observed that one or two of ZnO/C alternating layers have formed in the case of the nanowires originally with the polycrystalline sheath, while in the case of nanowires originally with the single-crystalline sheath only ZnO particle/carbon matrix configuration or some ill-defined layers appear.

The above observations suggest that the SAM formation favors the Zn nanowires with polycrystalline oxide sheath. This is explained by the diffusion process of CO_2 through the original oxide layer. CO_2 can only diffuse through the bulk ZnO crystal in the case of Zn nanowires with single-crystalline ZnO sheath. In the case of ZnO nanowires with the polycrystalline oxide sheath, grain-boundary diffusion is another route. It is known that grain-boundary diffusion has much lower activation energy, and thus a faster rate, which contributes to the faster SAM formation in the polycrystalline case.

2. Temperature (series B)

The effect of temperature on the SAM formation is studied by performing the same experiment (Zn nanowires with

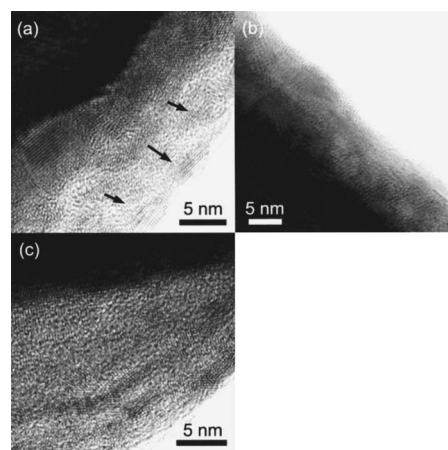


FIG. 8. HREM images of Zn nanowire (originally with polycrystalline native oxide sheath) exposed in CO_2 reacting cell at (a) 100 °C after 72 h, (b) 25 °C after 72 h, and (c) 100 °C after 168 h. The arrows indicate the position of ZnO particles.

polycrystalline native oxide sheath and CO_2 gas) at different temperatures (100 vs 25 °C). Samples were collected after different reaction durations to investigate the formation process of the SAM structure. The SAM structure formed faster at 100 °C compared to that at 25 °C. Representative TEM images that demonstrate the differences of the SAM formation at the two temperatures are shown in Fig. 8. Figs 8(a) and 8(b) show the two samples after a 72-h exposure; small ZnO particles embedded in the carbon matrix are observed in the sample reacted at 100 °C, and the total outer layer thicknesses also increase from the original ≈ 5 to ≈ 15 nm; while in the case of the reaction at 25 °C, only a slight increase in the outer layer thickness is observed without any obvious morphology change. Figures 8(c) (100 °C) and 7(a) (25 °C) show the two samples after a 168-h duration. Several ordered ZnO/C alternating layers are formed at the outer sheath region of the nanowire reacted at 100 °C, with an average outer-layer thickness increase to ≈ 20 nm. As a comparison, the sample reacted at 25 °C only demonstrates one or two less-ordered alternating layers.

Based on the above observations, we found that the SAM formation favored an elevated temperature. It is intuitive that the gas diffusion process would be enhanced at elevated temperatures, especially in the early stage while the sheath layer is thin. Nevertheless, the Zn core in the nanowire is extremely active, which would evaporate at higher temperatures. This makes further investigation at higher temperatures inappropriate.

3. Different reaction gases (series C)

CO and CO_2 are two of the common carbon-containing gases which can induce the SAM formation. Their effect on the self-organized process is compared in series C by investigating the SAM formation on polycrystalline-sheathed nanowires in the two mediums at 100 °C. Similar to the other two series of experiments, samples were taken out from the gas cell after different reacting durations and CO_2 is found to be more effective in terms of SAM formation. Figure 9(a) shows the morphology of the nanowires reacted in CO_2 for

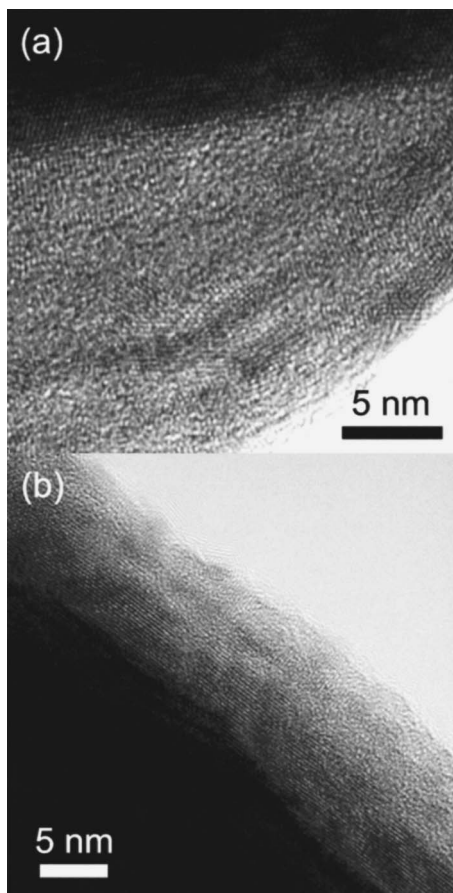
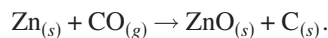


FIG. 9. HREM images of Zn nanowire (originally with polycrystalline native oxide sheath) exposed in (a) CO_2 for 168 h and (b) CO for 500 h. Both were reacted at 100°C .

168 h, where a couple of ZnO/C alternating layers already formed in the sheath region. As a comparison, only one or two ZnO/C layers are formed on nanowires reacted in the CO medium after a long reaction time of 500 h [Fig. 9(b)].

Similar to CO_2 , CO gas would react with the Zn at the core/sheath interface, generating ZnO and C,



The above reaction is thermodynamically favorable due to the negative Gibbs free energy.³⁰ Nevertheless, the result is somewhat surprising as CO is expected to diffuse faster through the sheath region to the core/sheath interface due to its smaller size compared to that of CO_2 . However, similar to those mentioned previously, the simple reaction mechanism between CO and Zn nanowire does not take any possible intermediate process into consideration. In fact, Moller *et al.* had evidenced the CO oxidation on the ZnO (0001) surface and the formation of (CO_2^-) chemisorption complex during the photodesorption process of CO and CO_2 .²⁷ These reactions may also contribute to the final overall chemical reactions. On the other hand, the cylindrical configuration of the nanowire (defects are expected in the sheath in order to maintain the cylindrical configuration) provides an easy path for the gas phase diffusion, which makes the size of the gas molecule a less important parameter in the diffusion process.

In addition, the SAM formation rate may be affected by other kinetic factors.

IV. CONCLUSIONS

In conclusion, periodic polycrystalline--ZnO/amorphous-C multilayers can be self-assembled on the surface of the Zn nanowires via a simple chemical reaction between Zn and CO_2 (CO). Such self-assembly process is governed by a four-step mechanism—gas phase diffusion, interfacial chemical reaction, phase separation, and self-alignment process. The chemical reaction that takes place in the core-sheath interface of the nanowires results to an inner-out pushing force. Together with the immiscible nature of ZnO and C phases and the large interfacial energy associated with the ZnO-particle/C-matrix configuration, the inner-out dynamic process leads to the formation of the periodic multilayers. We also found that the SAM formation favors nanowires with polycrystalline native oxide sheath, elevated temperature, and CO_2 as the reaction gas.

ACKNOWLEDGMENT

The authors acknowledge the financial support from the RGC direction allocation in the Chinese University of Hong Kong, under Project No. 2060261.

- ¹R. Plass, J. A. Lasst, N. C. Bartelt, and G. L. Kellogg, *Nature (London)* **412**, 875 (2001).
- ²D. D. Chambliss, R. J. Wilson, and S. Chiang, *Phys. Rev. Lett.* **66**, 1721 (1991).
- ³D. J. Egelsham and M. Cerullo, *Phys. Rev. Lett.* **64**, 1943 (1990).
- ⁴K. Pohl, M. C. Bartelt, J. de la Figuera, N. C. Bartelt, J. Hrbek, and R. Q. Hwang, *Nature (London)* **397**, 238 (1999).
- ⁵K. O. Ng and D. Vanderbilt, *Phys. Rev. B* **52**, 2177 (1995).
- ⁶P. Zeppenfeld, *et al. Surf. Sci.* **342**, L1131 (1995).
- ⁷E. D. Tober, R. F. C. Farrow, R. F. Marks, G. Witte, K. Kalki, and D. D. Chambliss, *Phys. Rev. Lett.* **81**, 1897 (1998).
- ⁸E. D. Tober, R. F. Marks, D. D. Chambliss, K. P. Roche, M. F. Toney, A. J. Kellock, and R. F. C. Farrow, *Appl. Phys. Lett.* **77**, 2728 (2000).
- ⁹H. J. Osten, E. Bugiel, and P. Zaumseil, *J. Appl. Phys.* **82**, 231 (1997).
- ¹⁰A. Claverie, J. Faure, J. L. Balladore, L. Simon, A. Mesli, M. Diani, L. Kubler, and D. Aubel, *J. Cryst. Growth* **157**, 420 (1995).
- ¹¹H. Rucker, M. Methfessel, E. Bugiel, and J. H. Osten, *Phys. Rev. Lett.* **72**, 3578 (1994).
- ¹²G. Springholz, V. Holy, M. Pinczolits, and G. Bauer, *Science* **282**, 734 (1998).
- ¹³A. N. Parikh, D. L. Allara, I. B. Azouz, and F. Rondelez, *J. Phys. Chem.* **98**, 7577 (1994).
- ¹⁴K. W. Wong, H. L. Yip, Y. Luo, K. Y. Wong, and W. M. Lau, *Appl. Phys. Lett.* **80**, 2788 (2002).
- ¹⁵J. E. Malinsky, G. E. Jabbour, S. E. Shaheen, J. D. Anderson, A. G. Richter, T. J. Marks, N. R. Armstrong, B. Kippelen, P. Dutta, and N. Peyghambarian, *Adv. Mater. (Weinheim, Ger.)* **11**, 227 (1999).
- ¹⁶C. Ganzorig, K. K. Kwak, K. Yagi, and M. Fujihira, *Appl. Phys. Lett.* **79**, 272 (2001).
- ¹⁷A. Roelofs, T. Schneller, K. Szot, and R. Waser, *Nanotechnology* **14**, 250 (2003).
- ¹⁸H. Heinz, H. J. Castelijns, and U. W. Suter, *J. Am. Chem. Soc.* **125**, 9500 (2003).
- ¹⁹V. Percec, C. H. Ahn, G. Ungar, D. J. P. Yearley, M. Moller, and S. S. Sheiko, *Nature (London)* **391**, 161 (1998).
- ²⁰C. Ratsch and A. Zangwill, *Surf. Sci.* **293**, 123 (1993).
- ²¹M. I. Larsson, R. F. Sabiryanov, K. Cho, and B. M. Clemens, *Surf. Sci.* **536**, L389 (2003).
- ²²Q. Li, K. W. Kwong, D. Ozkaya, and D. J. H. Cockayne, *Phys. Rev. Lett.* **92**, 186102 (2004).
- ²³J. Q. Hu, Q. Li, X. M. Meng, C. S. Lee, and S. T. Lee, *Chem. Mater.* **15**, 305 (2003).

- ²⁴Q. Li and C. R. Wang, *Appl. Phys. Lett.* **82**, 1398 (2003).
- ²⁵O. Kubaschewski and B. E. Hopkins, *Oxidation of Metals and Alloys* (Butterworths, London, 1962).
- ²⁶*Thermochemical Properties of Inorganic Substances*, edited by O. Knacke, O. Kubaschewski, and K. Hesselmann, (Springer, Hong Kong, 1991).
- ²⁷P. J. Moller, S. A. Komolov, E. F. Lazneva, and E. H. Pedersen, *Surf. Sci.* **323**, 102 (1995).
- ²⁸W. Gopel, R. S. Bauer, and G. Hansson, *Surf. Sci.* **99**, 138 (1980).
- ²⁹P. J. Moller, S. A. Komolov, and E. F. Lazneva, *Surf. Sci.* **290**, L677 (1993).
- ³⁰D. A. Porter and K. E. Easterling, *Phase Transformations in Metals and Alloys* (Chapman and Hall, New York, 1992).