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J. Phys. Chem. C, **2008**, 112 (48), 18923-18926 • Publication Date (Web): 08 November 2008

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Enhancement of Oxide VLS Growth by Carbon on Substrate Surface

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Received: August 18, 2008; Revised Manuscript Received: October 3, 2008

Oxide nanowires formed via the vapor–liquid–solid (VLS) mechanism are potential candidates to incorporate the rich functionalities into the nanowire-based devices. However, the complex nature of oxide VLS mechanism has held back the formation of well-defined oxide nanowires. Here we report the enhancement of oxide VLS growth by carbon and discuss the underlying mechanism. In ZnO nanowire growth, the presence of carbon layers predeposited on the substrate surface strongly enhances the VLS growth. Spectroscopy analysis demonstrates that the carbon predeposited on the surfaces could only exist at the initial stage of the VLS growth, as also evidenced from the optical quality of the ZnO nanowires. Thus, the existence of carbon at the initial stage of the VLS growth plays an important role on enhancing the oxide VLS growth and might act as a seed material in addition to Au catalyst. Furthermore, the presence of carbon enhances various oxide VLS growths, including SnO₂ and MgO, indicating the universal effect on oxide VLS growth mechanism.

Introduction

Oxide nanowires formed via the vapor–liquid–solid (VLS) mechanism are potential candidates to incorporate the rich functionalities of the physical properties into nanowire-based devices.^{1–3} The VLS mechanism in oxide nanowires is very complex compared with conventional VLS mechanism, although the exact VLS mechanism in well-known Si–Au system remains under lively debate.^{4–6} Among various oxide nanowires, ZnO nanowires have been intensively investigated due to the fascinating optical and electric properties at nanoscale.^{7–10} Although ZnO nanowires can be formed even in the absence of metal catalysts via the self-catalyzed growth,^{11–13} the VLS growth of ZnO nanowires using metal catalysts has been shown to be very powerful due to the controllability of both the position and the size via the metal catalysts. In many previous reports, the mixed sources of ZnO and graphite powders have been commonly utilized to obtain ZnO nanowires.^{7–10} It is thought that this growth scheme is closely related to a carbothermal effect involving the reduction of ZnO to Zn metal, leading to the production of Zn–Au liquid particles as a starting point for nucleation formations of ZnO nanowires.^{7–10} However, the knowledge as to the details of the mechanism utilizing carbon atoms supplied on substrate surfaces is still scarce. Previously we have demonstrated the significant roles of various surface events on oxide VLS growths.^{14–20} As such, understanding the surface events in the presence of carbon would be invaluable. Here we investigate the effect of carbon predeposited on the substrate surface prior to the growth, instead of supplying continuously carbon from the source. We found the drastic effects of predeposited carbon on various oxide VLS growths.

Experimental Section

Oxide nanowires including ZnO, MgO, and SnO₂ were formed by an Au catalyst-assisted pulsed laser deposition (PLD) method, and the experimental details can be seen elsewhere.^{14–21} The oxide nanowires were grown on various single crystal substrates including Al₂O₃ (11–20), MgO (100), SrTiO₃ (100), Nb (0.75 wt %) doped SrTiO₃ (100) substrates, and amorphous Si₃N₄ coated Si wafers. Prior to the growths, the carbon layer with the thickness ranged from 2–8 nm was predeposited on the substrate surface. The carbon layer was deposited using arc-discharging method and the thickness was controlled by the deposition time. An ArF excimer laser pulse was used to ablate the target materials. The repetition rate, the laser energy, and the substrate-to-target distance were 10 Hz, 40 mJ, and 45 mm, respectively. The oxygen pressure and the growth temperature were 10 Pa and 800 °C, respectively. It is noted that for the nanowire growths the ablated mass of materials per unit area per unit time was controlled to be constant for all experiments using the same target material. A scanning electron microscopy with a field emission-type (FESEM, JEOL JSM-6330FT) was used to observe the surface morphology at an accelerating voltage of 30 kV. High-resolution transmission electron microscopy (HRTEM, JEOL JEM-3000F) coupled with energy dispersive spectroscopy (EDS) was used to evaluate the microstructure and the composition of the fabricated nanowires. The sample suspension was prepared by scratching the nanowires from the substrate within ethanol. Samples for HRTEM were prepared by placing a drop of the sample suspension on a copper microgrid (JEOL 7801-11613). HRTEM measurements were performed at an accelerating voltage of 300 kV. The X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) measurements were performed to examine the surface properties and the optical properties. Al K α (1486.6 eV) radiation was used for the XPS measurements. The photoelectrons were collected at room temperature by a conventional CHA analyzer (100 mm ϕ , VG Ltd.) with a pass energy of 50 eV. PL

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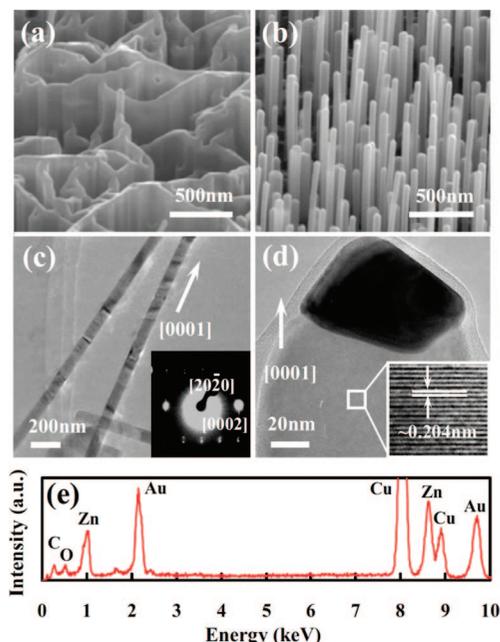


Figure 1. Effect of carbon on ZnO nanowire growth: (a) FESEM image in the absence of carbon, (b) FESEM image in the presence of carbon predeposited on the substrate surface, (c) and (d) HRTEM images of ZnO nanowire and the insets show the ED pattern and the lattice fringe, (e) EDS data of the ZnO nanowire.

measurements were conducted at room temperature using a He–Cd laser (325 nm) with an excitation power of 20 mW and a 1.0 m double spectrometer equipped with a 1200 grooves/cm grating blazed at 500 nm.

Results and Discussion

Figure 1a and b show FESEM images of ZnO samples grown on Al_2O_3 (11–20) substrates. Clearly the presence of carbon predeposited on the substrate surface strongly enhanced the nanowire growth. In the absence of the carbon layer, the resulting surface morphology tended to have a ridge and valley structure. On the other hand, fine ZnO nanowires were obtained by combining the ultrathin carbon layer with the Au-catalyst. The ZnO nanowires were only found within the Au-catalyst-patterned area, indicating the significant role of metal catalysts and also the VLS growth mechanism. Figures 1c–e show the HRTEM images and the EDS data, revealing the presence of Au catalyst on the tip and the preferential growth along the *c*-axis [0001] direction. Selected area electron diffraction (SAED) patterns also demonstrated the single crystalline nanowires. It is worth noting that the present experiments using the predeposited carbon essentially differ from previous investigations, in which the carbon was continuously supplied from the source.^{7–10} In general, the VLS growth is related to the incorporation of adatoms from surroundings into a metal catalyst droplet.^{7–10} There are several possible scenarios to explain above remarkable growth enhancement in the presence of carbon predeposited on the substrate surface.

First, a chemical reaction between the predeposited carbon and the substrate material might alter the surface potential and possibly the surface migration of adatoms. If such chemical reactions proceed under a high growth temperature and affect the VLS events, the material dependence of substrates should be observable. Thus we performed ZnO nanowire growths in the presence of predeposited carbon on various substrates, including MgO (100), SrTiO_3 (100), oriented single crystalline

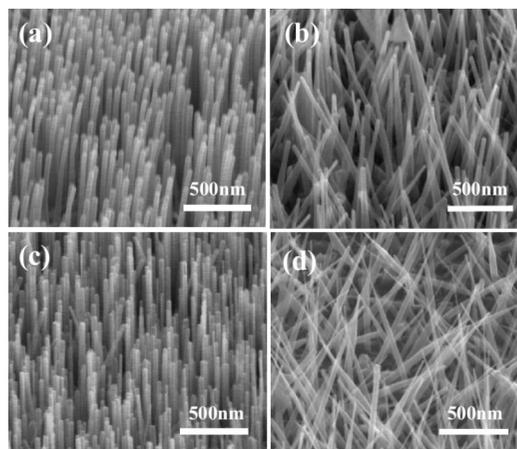


Figure 2. Effect of substrate materials on ZnO nanowire growth in the presence of predeposited carbon: (a) MgO (100) substrate, (b) SrTiO_3 (100) substrate, (c) Nb (0.75 wt %) doped SrTiO_3 (100) substrate and (d) amorphous Si_3N_4 -coated Si (100) substrate.

Nb (0.5 wt %) doped SrTiO_3 (100) with the metallic conductivity, and Si wafers with an amorphous Si_3N_4 buffer. Figure 2 shows the FESEM images of nanowires for various substrates. It can be clearly seen that the formation of well-defined ZnO nanowires is almost independent of the substrate material properties including the elements, the conductivities and the crystalline structures. Thus the insensitivity of substrate material properties on the carbon effect does not support the scenario based on only the chemical reactions between the substrate material and the predeposited carbon.

The second possible scenario is based on a carbothermal effect between carbon and zinc oxides, which might explain the VLS growth enhancement. Zn adatoms reduced strongly by carbon can be easily incorporated into the metal catalyst, operating as a driving force toward the fabrication of ZnO nanowires.¹⁰ The carbothermal effect requires the carbon supplied continuously from sources for a relatively long time during the VLS growth. However, the growth time of ZnO nanowires in this study was approximately 2 h. If the carbothermal scenario is suitable for the formation of ZnO nanowires, the predeposited carbon layer must be retained on the surface during the growth. Figure 3 shows the XPS spectra of six different samples using Nb– SrTiO_3 substrates, and the experimental details of samples can be seen in Table 1. Sample I was an as-received substrate without any treatments. The spectra of Sample I shows the peaks, which can be assigned to Sr, Ti, Nb, and O atoms,^{22,23} and C (1s) peak originating from absorbed hydrocarbons by air.^{22,23} After predepositing the carbon layer, samples V and VI, the strong C (1s) peak clearly appeared compared with the as-received substrate. This implies that the substrate surface was almost covered by the carbon. The C (1s) peak was almost retained after the thermal treatment for 10 min (sample IV). However, the intensity of the C (1s) peak drastically decreased due to the violent evaporation of carbon during the thermal treatment at 800 °C for 120 min in an O_2 atmosphere (sample III). As shown in Figure 3b, the spectrum of sample III was almost comparable with that of the C (1s) peak for sample II, which is caused by hydrocarbons absorbed naturally on the substrate surface by atmospheric exposure. Figure 3c shows the deconvoluted data of Figure 3b and the calculated area ratio data of C(1s)/ $\text{Sr}(3p_{3/2})$ in the inset. The quantitative data of Figure 3c are consistent with above qualitative implications. Thus, the predeposited carbon layers can exist only at the initial process, which is indeed consistent with previous study.²⁴ We then evaluated the

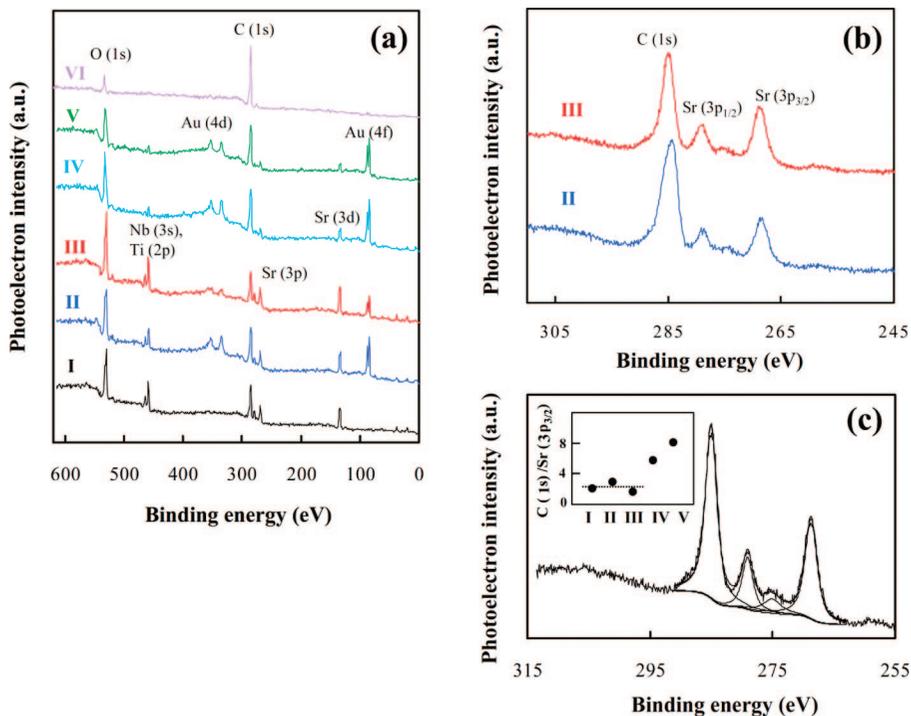


Figure 3. XPS data: the heating effect on carbon predeposited on the substrate surface. (a) XPS data in the binding energy 0–600 eV, (b) XPS data around C (1s) region, (c) deconvoluted spectra of (b) and the inset shows the area ratio of C (1s)/Sr(3p_{3/2}) estimated from the deconvoluted data. The details of samples are shown in Table 1.

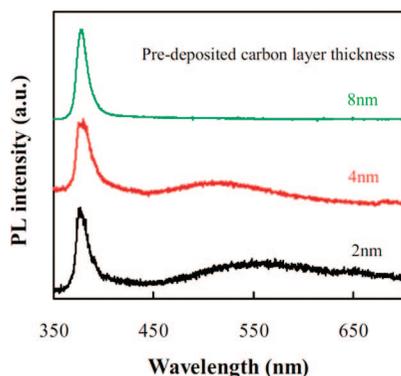


Figure 4. PL spectra of ZnO nanowires grown in the presence of predeposited carbon on the substrate surface. The thickness of predeposited carbon was ranged from 2–12 nm.

TABLE 1: Details of Samples Employed for XPS Measurements

sample	heat treatment at 800 °C (heating time)	Au catalyst	predeposited carbon (thickness)
I	×	×	×
II	(120 min)	○	×
III	(120 min)	○	○ (2 nm)
IV	(10 min)	○	○ (2 nm)
V	×	○	○ (2 nm)
VI	×	○	○ (8 nm)

optical quality of the ZnO nanowires using PL spectroscopy, as shown in Figure 4. The PL technique is a very sensitive tool for extrinsic impurities doped into the host. The PL spectra consists of two components; one is a ultraviolet (UV) emission peak around 380 nm originating from excitonic-related transitions, and the other comprises visible emissions observed from 500 to 550 nm, which are closely attributed to lattice defects formed in the host such as ionized oxygen vacancies.¹² In the case of Ga-doped ZnO, luminescence efficiency in ZnO gener-

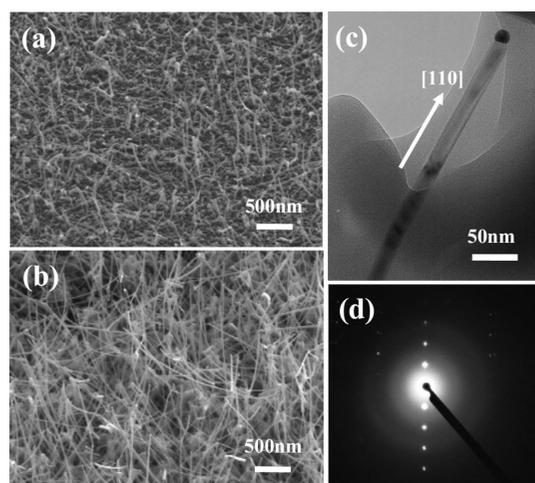


Figure 5. Effect of predeposited carbon on SnO₂ nanowire growth. (a) FESEM image in the absence of predeposited carbon, (b) FESEM image in the presence of predeposited carbon, (c) HRTEM image of SnO₂ nanowires, and (d) SAED pattern.

ally decreases with an increase in Ga concentration, which is related to potential fluctuations induced by a random distribution of donor impurities and causes a broadening of the band-edge emission as a result of excitonic-related transitions. The results shown in Figure 4 demonstrate that the UV peak position and the line width remain unchanged with increasing the layer thickness of carbon, and the PL spectra were almost the same as those obtained with previous data for undoped ZnO layers (Figure 4).^{11–13} The results of PL measurements indicate that the doping concentration of carbon atoms into the host is close to unintentional impurity levels, and therefore, this does not cause a degradation of the optical quality of the ZnO nanowires. Because the predeposited carbon cannot be continuously supplied, it does not act as a reducing agent of ZnO from the beginning to the end of nanowire growth. Thus, the scenario

based on only the carbothermal effect due to the presence of carbon on the substrate surface alone cannot explain the observed VLS growth enhancement for long time range.

The third possible scenario proposes that the carbon layers only act as a seed and/or catalyst, contributing to an initial nucleation stage within the metal catalysts. Although the direct experimental evidence as to the carbon on the substrate surface were not available, in principle this mechanism should be applicable not only for ZnO VLS growth but also for various oxide VLS growths. In order to confirm this implication, we performed SnO₂ and MgO nanowire growths using the predeposited carbon. Figure 5 shows the FESEM, HRTEM, and SAED data of SnO₂ nanowires fabricated. SnO₂ nanowires were grown on TiO₂ (001) substrate without and with the carbon layer possessing the thickness of 2 nm at the substrate temperature of 750 °C under an O₂ gas flow of 10 Pa. Surprisingly, the remarkable improvement of VLS growth in the presence of predeposited carbon was observed for SnO₂. HRTEM and SAED observations showed that SnO₂ nanowires were single crystalline structures oriented along the [110] direction, and Au droplets were located on the tip. A similar effect was also confirmed even for MgO nanowire growth. It is thought that carbon influences catalyst droplets at the initial stage of VLS growth and determines the scheme of crystal growth. Thus, these results highlight that the effect of carbon on the oxide VLS growth is rather universal phenomenon. Further investigations using various direct experimental techniques as such in situ HRTEM need to be undertaken to clarify the exact role of carbon at the initial stage of VLS growth.

Conclusion

This work revealed the enhancement of oxide VLS growth by carbon predeposited on the substrate surface and discussed the underlying mechanism. In ZnO nanowire growth, the presence of carbon layers on the substrate surface strongly enhances the VLS growth. Spectroscopy analysis demonstrated that the carbon layers on the surface could only exist at the initial stage of VLS growth due to the evaporation. The results of PL measurements indicated that the doping concentration of carbon atoms into the host was close to unintentional impurity levels, and therefore, this did not cause a degradation of the optical quality of the ZnO nanowires. Interestingly, the presence of carbon enhances various oxide VLS growths, including SnO₂

and MgO, indicating the universality of this effect on oxide VLS growth mechanism. These findings would be invaluable for further understanding and controlling of the complex oxide VLS growth phenomena.

References and Notes

- (1) Han, S.; Li, C.; Liu, Z.; Lei, B.; Zhang, D.; Jin, W.; Liu, X.; Tang, T.; Zhou, C. *Nano Lett.* **2004**, *4*, 1241.
- (2) Zhang, D.; Liu, Z.; Han, S.; Li, C.; Lei, B.; Stewart, M. P.; Tour, J. M.; Zhou, C. *Nano Lett.* **2004**, *4*, 2151.
- (3) Lei, B.; Li, C.; Zhang, D.; Han, S.; Zhou, C. *J. Phys. Chem. B* **2005**, *109*, 18799.
- (4) Hannon, J. B.; Kodambaka, S.; Ross, F. M.; Tromp, R. M. *Nature* **2006**, *440*, 69.
- (5) Kodambaka, S.; Tersoff, J.; Reuter, M. C.; Ross, F. M. *Phys. Rev. Lett.* **2006**, *96*, 096105.
- (6) Hofmann, S.; Sharma, R.; Wirth, C. T.; Cervantes-Sodi, F.; Ducati, C.; Kasama, T.; Dunin-Borkowski, R. E.; Drucker, J.; Bennett, P.; Robertson, J. *Nat. Mater.* **2008**, *7*, 372.
- (7) Banerjee, D.; Jo, S. H.; Rem, Z. F. *Adv. Mater.* **2002**, *22*, 2028.
- (8) Banerjee, D.; Lao, J. Y.; Wang, D. Z.; Huang, J. Y.; Rem, Z. F.; Steeves, D.; Kimball, B.; Sennett, M. *Appl. Phys. Lett.* **2003**, *83*, 2061.
- (9) Dalal, S. H.; Baptista, D. L.; Teo, K. B. K.; Lacerda, R. G.; Jefferson, D. A.; Milne, W. I. *Nanotechnology* **2006**, *17*, 4811.
- (10) Perez, J. Z.; Gahm, A.; Czekalla, C.; Lenzner, J.; Lorenz, M.; Grundmann, M. *Nanotechnology* **2007**, *18*, 195303.
- (11) Sun, Y.; Fuge, G. M.; Ashfold, M. N. R. *Chem. Phys. Lett.* **2004**, *396*, 21.
- (12) Choopun, S.; Tabata, H.; Kawai, T. *J. Cryst. Growth* **2005**, *274*, 167.
- (13) Wei, M.; Zhi, D.; Driscoll, J. L. M. *Nanotechnology* **2005**, *16*, 1364.
- (14) Nagashima, K.; Yanagida, T.; Tanaka, H.; Kawai, T. *J. Appl. Phys.* **2007**, *101*, 124304.
- (15) Nagashima, K.; Yanagida, T.; Tanaka, H.; Kawai, T. *Appl. Phys. Lett.* **2007**, *90*, 233103.
- (16) Marcu, A.; Yanagida, T.; Nagashima, K.; Tanaka, H.; Kawai, T. *J. Appl. Phys.* **2007**, *102*, 016102.
- (17) Yanagida, T.; Nagashima, K.; Tanaka, H.; Kawai, T. *Appl. Phys. Lett.* **2007**, *91*, 016502.
- (18) Nagashima, K.; Yanagida, T.; Tanaka, H.; Seki, S.; Saeki, A.; Tagawa, S.; Kawai, T. *J. Am. Chem. Soc.* **2008**, *130*, 5378.
- (19) Marcu, A.; Yanagida, T.; Nagashima, K.; Oka, K.; Tanaka, H.; Kawai, T. *Appl. Phys. Lett.* **2008**, *92*, 173119.
- (20) Yanagida, T.; Nagashima, K.; Tanaka, H.; Kawai, T. *J. Appl. Phys.* **2008**, *104*, 016101.
- (21) Nagashima, K.; Yanagida, T.; Oka, K.; Tanaka, H.; Kawai, T. *Appl. Phys. Lett.* **2008**, *93*, 153103.
- (22) Vasquez, R. P. *J. Electron Spectrosc. Relat. Phenom.* **1991**, *56*, 217.
- (23) Yoshikawa, T.; Bowker, M. *Phys. Chem.* **1999**, *1*, 913.
- (24) Azuma, Y.; Fujimoto, T.; Kojima, I. *Jpn. J. Appl. Phys.* **2005**, *44*, 8256.