

Growth of Ternary Oxide Nanowires by Gold-Catalyzed Vapor-Phase Evaporation

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Zn_2SnO_4 nanowires and Zn_2SnO_4 diameter-modulated (DM) nanowires were successfully synthesized, accompanied by the formation of ZnO nanowires, via the thermal evaporation of a mixture of ZnO and SnO_2 powders, using gold as a catalyst. Their morphologies and structures were characterized by scanning electron microscopy, X-ray spectroscopy, and high-resolution transmission electron microscopy. The ZnO nanowires were single crystalline, with an axis of $[01\bar{1}0]$, which is different from the conventional $[0001]$ orientation and might be determined by the vapor components involved in the reaction. Zn_2SnO_4 nanowires and Zn_2SnO_4 DM nanowires were single crystalline, with $[302]$ and $[111]$ growth directions, respectively. A vapor–liquid–solid (VLS) growth mechanism is proposed, to interpret the growth of nanowires in the experiment. In regard to the formation of Zn_2SnO_4 DM nanowires, we suggest that the disturbance of vapor concentration is a major factor that changes the size of the catalyst alloy droplets and the growth velocity of nanowires, and ultimately results in the diameter-modulated feature.

Introduction

One-dimensional (1D) semiconductor nanowires have attracted much attention, because their novel properties make them potentially ideal functional components for nanometer-scale electronics and optoelectronics.^{1–3} Over the past decade, nanowires with different compositions have been synthesized via various methods, including vapor-phase evaporation,^{4,5} metallo-organic vapor-phase epitaxy,⁶ laser ablation,⁷ template-assisted synthesis,⁸ and solution synthesis.⁹ Among a variety of nanowires, metal oxide nanowires have shown unique optical, chemical, and electronic properties, attracting special interest. Thus, various types of 1D metal oxide nanostructures (such as nanowires of ZnO,^{10–12} MgO,¹³ In_2O_3 ,¹⁴ Ga_2O_3 ,¹⁵ and GeO_2 ¹⁶ and nanobelts of ZnO, In_2O_3 , SnO_2 , Ga_2O_3 , CdO, and PbO_2 ^{17–19}) have been successfully synthesized. However, the research of 1D metal oxide nanostructures is mainly focused on the binary oxides, and only a minor amount of attention has been focused on the ternary oxides.²⁰ It has been shown that some ternary oxides even have better properties than binary oxides in the application in electronics and gas sensors,^{21,22} and one advantage of ternary oxides is that their properties can be efficiently tuned by adjusting the ratio of components.

In this paper, we report that ternary oxide nanowires— Zn_2SnO_4 and Zn_2SnO_4 diameter-modulated (DM) nanowires—were successfully synthesized using a gold film as a catalyst and evaporating a mixture of ZnO and SnO_2 powders. The formation of the Zn_2SnO_4 DM nanowires is an interesting phenomenon, because these nanowires could possibly be more sensitive to surface phonon modes.²³

It is important to choose a suitable method for the synthesis of ternary oxide nanowires. After considering many types of

possible approaches, catalyst-assisted vapor-phase evaporation was chosen in our experiments. In the synthesis process, two types of metal oxides are simultaneously evaporated; their vapors then are transferred to the substrate and react with the catalyst, and, ultimately, ternary oxide nanowires can be formed based on a vapor–liquid–solid (VLS) growth mechanism.²⁴

Experimental Section

Our synthesis of the Zn_2SnO_4 nanowires is based on thermal evaporation of a mixture of ZnO and SnO_2 powders (molar ratio of 1:1), under controlled conditions with the assistance of a gold catalyst. A horizontal tube furnace was used as the evaporation apparatus, and the oxide powder was placed at the center of the alumina tube. Several silicon plates that were coated with 10 nm of gold were used as substrates and placed at the downstream positions of the source materials. The following parameters were adopted in our experiment: weight of the mixed powder, 0.5 g; evaporation temperature, 1400 °C; chamber pressure, 150 Torr; and argon flow rate, 50 standard cubic centimeters per minute (sccm). Before the evaporation occurred, the reaction chamber was cleaned three times using an argon gas flow, to exclude any remaining oxygen. The evaporation time was 30 min. In the synthesizing process, the substrate temperature was typically in the range of 850–950 °C. After the furnace had slowly cooled to room temperature, the substrates were removed from the furnace tube and white-colored products were observed on their surfaces.

As-deposited products were characterized and analyzed by X-ray diffractometry (XRD) (MAC Science, model MXPAHF with Cu K α radiation), field-emission scanning electron microscopy (FE-SEM) (JEOL model JSM-6700F), high-resolution transmission electron microscopy (HRTEM) (JEOL model 2000 at 200 kV), and energy-dispersive X-ray spectroscopy (EDS).

Results and Discussion

Figure 1 shows the morphologies and structures of the products. Scanning electron microscopy (SEM) observations

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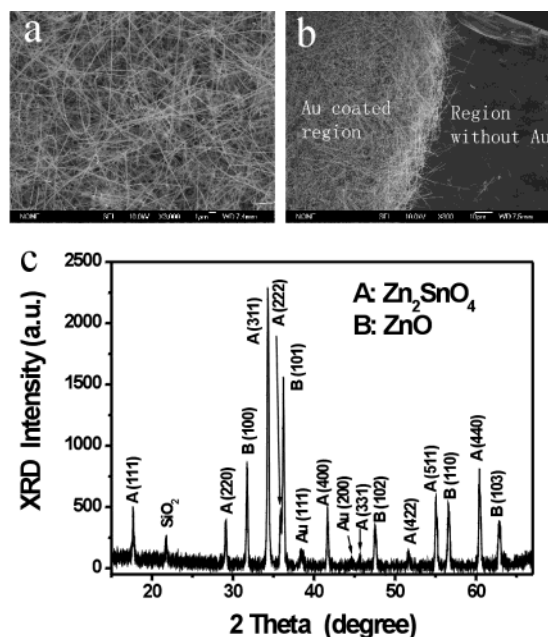


Figure 1. Morphologies and structure of as-deposited products prepared by thermal evaporation of mixed ZnO and SnO₂ powder (molar ratio of 1:1): (a) field-emission scanning electron microscopy (FE-SEM) image of the products on a silicon substrate with a 10-nm-thick gold coating; (b) the nanowire growth boundary, showing the role of the gold catalyst; and (c) X-ray diffraction (XRD) pattern of as-deposited products, demonstrating products that consist of Zn₂SnO₄ and ZnO nanowires (Au and SiO₂ peaks in the pattern come from the substrate).

reveal that the products consist of a large quantity of wirelike nanostructures with typical lengths in the range of several tens to several hundreds of micrometers and diameters normally in the range of 20–200 nm. In Figure 1b, we can see that no products can be formed in the region without a gold layer, demonstrating that the gold catalyst is necessary to synthesize the products in our experiments. The XRD pattern of an as-deposited sample (Figure 1c) shows that the product is a mixture of Zn₂SnO₄ and ZnO phases, and Au and SiO₂ peaks from the substrate also can be indexed. Analysis from the XRD pattern reveals that Zn₂SnO₄ has a cubic spinel structure with a lattice constant of $a = 8.665 \text{ \AA}$ and ZnO has a wurtzite (hexagonal) structure with lattice constants of $a = 3.253 \text{ \AA}$ and $c = 5.20 \text{ \AA}$, which is consistent with the standard values for bulk Zn₂SnO₄ and ZnO.

Figure 2a shows the cross section of a nanowire. We observed tens of nanowires, and their cross sections were all circular or almost circular; no nanowires with hexagonal or other cross-sectional shapes were observed in our products. As is well-known, the cross section of ZnO nanowires is usually hexagonal when it grows along the c -axis ([0001] crystal orientation) direction.⁶ SEM observations demonstrate that the ZnO nanowires in our product should have growth directions other than [0001]. Another phase in the products was recognized by XRD data as Zn₂SnO₄ with a cubic structure; the SEM observations also imply that the Zn₂SnO₄ nanowires have a circular cross section. A catalyst nanocluster was observed at the end of nanowire (see Figure 2b), suggesting that the nanowires grew via the well-known VLS mechanism. SEM images (see Figure 2c) also show some nanowires with an interesting structure; these are diameter-modulated (DM) nanowires, which are rarely observed in semiconductor oxide nanostructures. The DM nanowires were identified as a Zn₂SnO₄ compound in the following transmission electron microscopy (TEM) analysis.

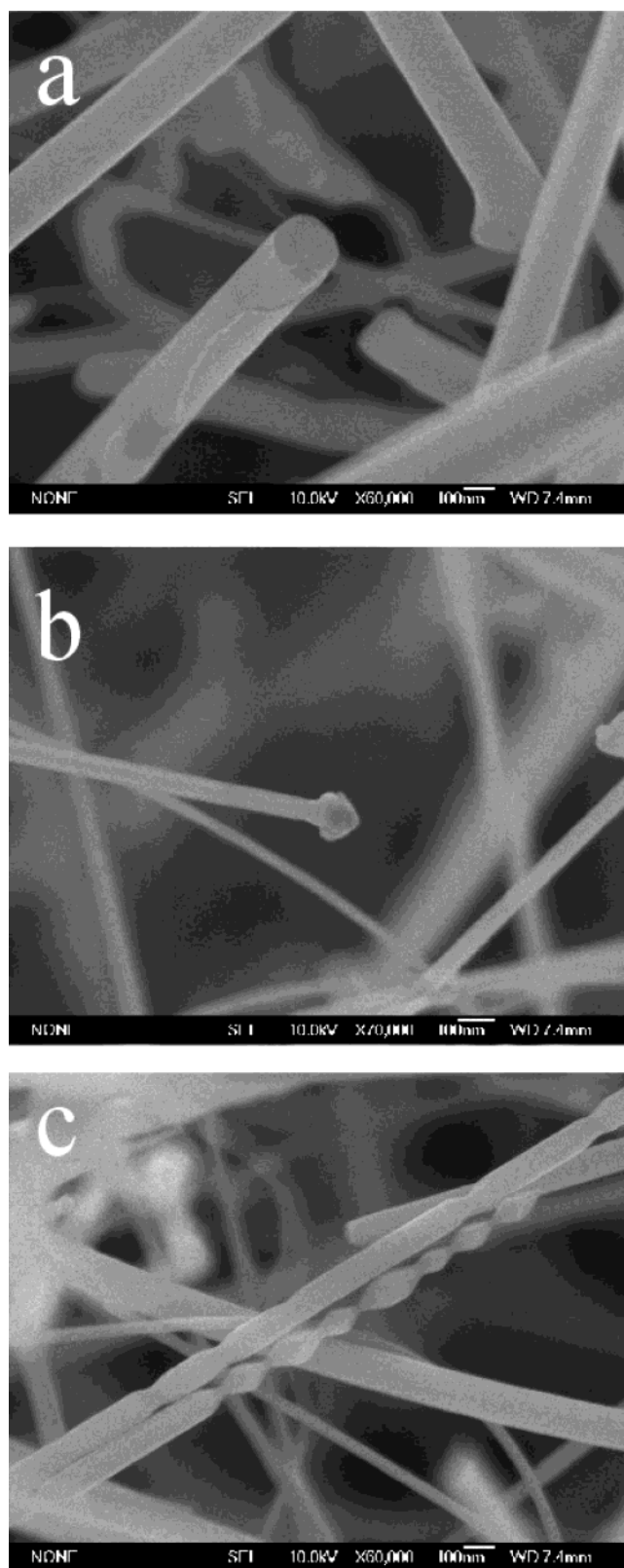


Figure 2. Enlarged FE-SEM images of the sample shown in Figure 1: (a) cross-sectional image of a nanowire, (b) a nanowire with a nanocluster catalyst at its end, and (c) diameter-modulated (DM) nanowires in the sample.

Additional structural characterization via TEM identified three types of nanostructures in our product: ZnO nanowires, Zn₂SnO₄ nanowires, and Zn₂SnO₄ DM nanowires. As shown in Figure 3a, the ZnO nanowire has a uniform diameter along its entire length. HRTEM and the corresponding selected area

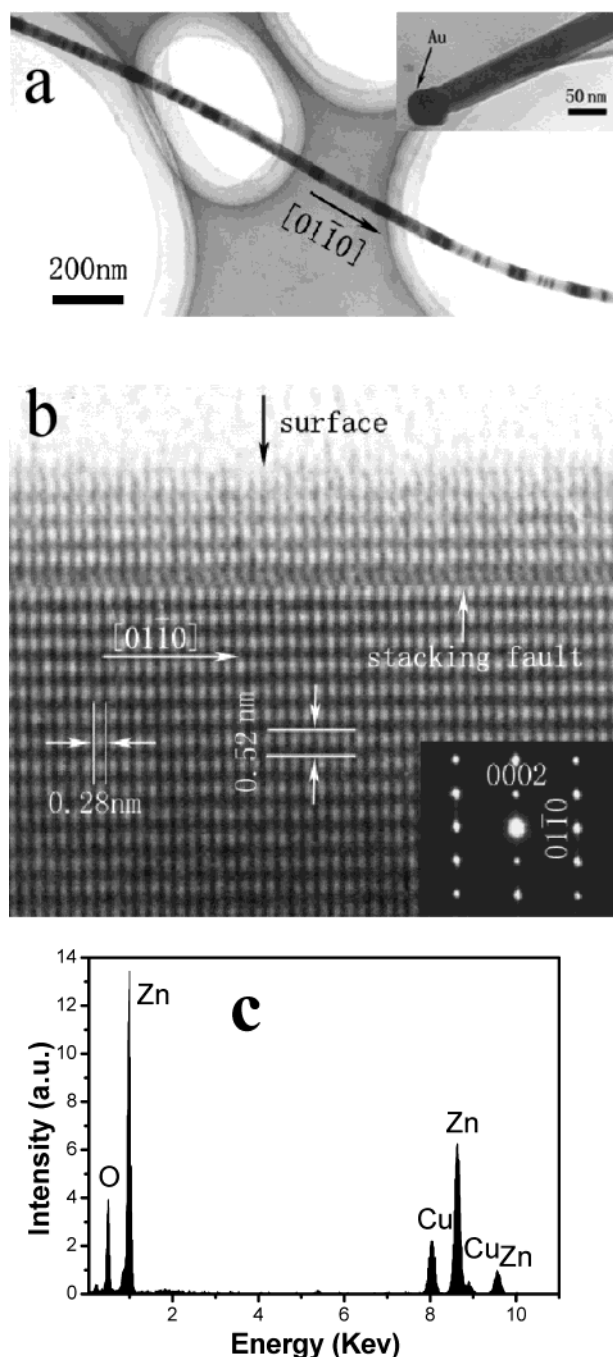


Figure 3. TEM and HRTEM images of ZnO nanowires: (a) morphology of a ZnO nanowire, showing that the diameter is uniform along its entire length (inset shows a nanowire with a gold catalyst tip); (b) HRTEM image of the ZnO nanowire shown in panel a, revealing that the nanowire grows along the $[01\bar{1}0]$ direction (a stacking fault is found in the nanowire, and the inset shows the electron diffraction pattern); and (c) EDS spectra of the nanowire (Cu peaks are caused by the surface of the copper grids used in the TEM measurement).

electron diffraction (SAED) analysis (Figure 3b) show that the ZnO nanowire is single crystalline with a uniform structure, but growing along the $[01\bar{1}0]$ direction, which is different from the conventional $[0001]$ orientation. In the work of Huang, Yang, and other researchers,^{5,25,26} gold catalysts were also used to synthesize ZnO nanowires, and the substrate temperature was similar to that in our experiment; however, only nanowires with a $[0001]$ growth orientation were reported. Therefore, it is difficult to relate the change of the growth direction to the gold catalyst and temperature used in the experiment; thus, other

reasons should be considered. It is suggested that the vapor phases involved in the reaction may seriously influence the products obtained. In the experiment of Huang et al., gas-phase zinc, CO, and CO₂ were included in the vapor, and the zinc would be oxidized to ZnO in the subsequent reaction. However, in present work, three main types of gas-phase ZnO, SnO, and O₂ are involved, with the two latter phases coming from the decomposition of SnO₂ at high temperature. The $[01\bar{1}0]$ growth direction of ZnO nanowires might be due to the influence of SnO in the vapor phases. More evidence comes from an additional experiment: pure ZnO powder is vaporized under the same conditions, and only ZnO nanobelts were obtained on the substrate. This fact suggested that the vapor components could seriously influence the morphologies and structures of the final nanostructures. The HRTEM image also reveals that the ZnO nanowire is almost free of dislocations: only a single stacking fault that is parallel to the axis and runs throughout the entire length of the nanowire was observed (see Figure 3b). The appearance of the stacking fault is due to the slippage of the (0001) face, and it is reasonable, because the (0001) crystal face is the gliding plane of the hexagonal-structured crystal. EDS analysis of the ZnO nanowire (see Figure 3c) reveals a Zn:O atomic ratio of 1:(~1.1–1.4), in which the large measurement error of oxygen is due to its small atomic number, indicating that excess oxygen is present in the nanowire. The inset in Figure 3a is a TEM image of a nanowire with an alloy tip, which was confirmed as pure gold through EDS analysis. All the alloy tips found in the TEM analysis gave the same result. The presence of the alloy tip is a clear indication of the VLS growth mechanism.

The morphology of an individual Zn₂SnO₄ nanowire was shown in Figure 4a, from which we could find that the diameter of the nanowire is not very uniform along its length. The HRTEM image and SAED pattern (see Figure 4b) recorded along the $[21\bar{3}]$ zone axis reveal that the nanowire is single crystalline with a uniform structure. As shown in Figure 4b, the lattice fringes are spaced 0.493 ± 0.005 nm apart, corresponding to the d -spacing of the (111) planes of the Zn₂SnO₄. However, $[302]$ instead of $[111]$ is the growth direction of the nanowire, according to the SAED pattern. For the crystal with face-centered cubic (fcc) structure, only the crystal faces with full-odd or full-even indices can be recorded in XRD and SAED patterns. That is the reason we cannot observe the (302) face of Zn₂SnO₄ in XRD analyses or via electron diffraction in the TEM analysis. Further compositional analysis by EDS (see Figure 4f) reveals that the Zn₂SnO₄ nanowire has a Zn:Sn:O atomic ratio of 1.75:1:(~2.6–3.5), which is a departure from the stoichiometric ratio 2:1:4 of Zn₂SnO₄. Taking into account the error of measurement, this result still reveals that a deficiency of zinc and oxygen exists in the nanowire.

Zn₂SnO₄ DM nanowire is also studied by TEM (see Figure 4c). HRTEM and SAED (Figure 4d, e) results confirm that the DM nanowire is single crystalline and that the spacing between adjacent lattice planes is 0.494 ± 0.005 nm, corresponding to the distance between two (111) planes, which indicates that $[111]$ is the growth direction for the Zn₂SnO₄ DM nanowires. Further observation reveals the fringes are continuous in the region of joint, demonstrating that the DM nanowire has a uniform structure, except for the variety of diameters along the length. EDS analysis (Figure 4g) reveals that this DM nanowire has a Zn:Sn:O atomic ratio of 1.74:1:(~6.6–8.9). The ratio of Zn:Sn is similar to the ratio in Zn₂SnO₄ nanowire, as mentioned

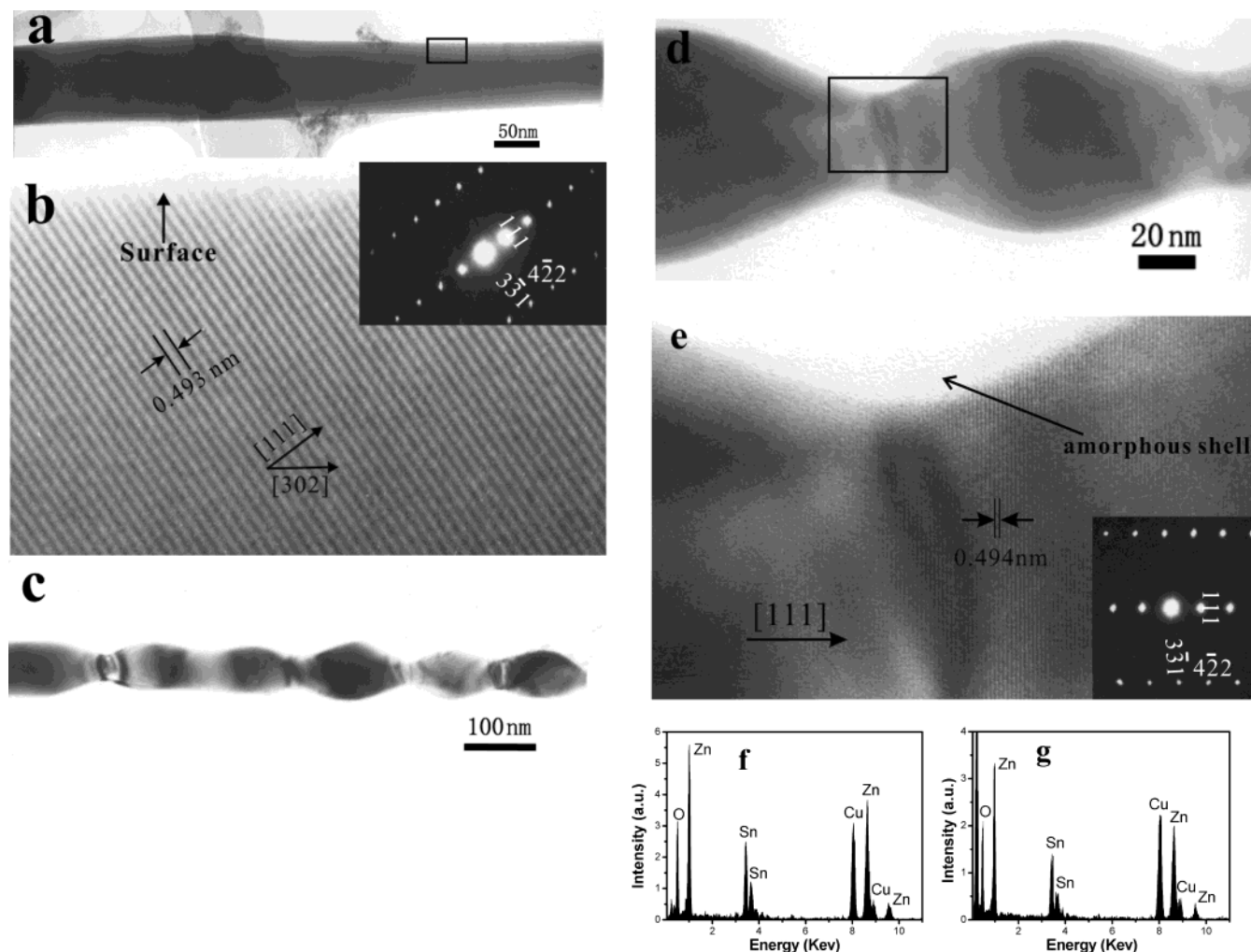


Figure 4. TEM and HRTEM images, and EDS patterns, of a Zn_2SnO_4 nanowire and a Zn_2SnO_4 DM nanowire: (a) TEM image of a Zn_2SnO_4 nanowire, showing that its diameter is not very uniform; (b) HRTEM image from the box in panel a (the electron diffraction (ED) pattern is shown in the inset, revealing that the nanowire grows along the [302] direction); (c) TEM image of a Zn_2SnO_4 DM nanowire; (d) enlarged view of the image presented in panel c; (e) HRTEM image from the box in panel d, indicating that [111] is the growth direction of the Zn_2SnO_4 DM nanowire (the dark arrow indicates the amorphous shell out of the DM nanowire, and the inset shows the ED pattern of the Zn_2SnO_4 DM nanowire); (f) EDS spectra of the Zn_2SnO_4 nanowire in panel a; and (g) EDS spectra of the Zn_2SnO_4 DM nanowire shown in panel c.

previously, although the oxygen content is much higher, even exceeding the stoichiometric ratio of Zn_2SnO_4 . The presence of an excess amount of oxygen in the DM nanowire cannot be simply explained as instrument error. One possible explanation might be attributed to the existence of an amorphous shell outside of the DM nanowire, as shown in Figure 4e. The growth direction of Zn_2SnO_4 DM nanowires is [111], which is different from [302] of Zn_2SnO_4 nanowires. Two types of Zn_2SnO_4 with different morphologies and structures were formed at the same time, which might be attributed to the variety of microcosmic growth conditions.

The VLS crystal growth mechanism proposed by Wagner and Ellis²⁷ has been widely used for the growth of semiconductor nanowires such as silicon,⁷ GaN,²⁸ and InAs.²⁹ Oxide nanowire could be successfully synthesized using a VLS growth mechanism in the presence of oxygen.²⁵ In our experiment, ZnO and SnO_2 were vaporized in the higher-temperature zone of furnace and transported to the substrates located downstream at a lower temperature zone. The vapor, which is composed of ZnO, SnO, and O_2 , would react with the gold solvent and form alloy droplets. For the Zn–Sn–O ternary system, a stable Zn_2SnO_4 phase would form in the droplets, under suitable conditions. When more ZnO and SnO vapor were dissolved in the droplets,

Zn_2SnO_4 would reach the supersaturated state and solid Zn_2SnO_4 subsequently precipitates from droplets in the form of nanowires. Continuous feeding of ZnO and SnO into the liquid droplets sustains the growth of the Zn_2SnO_4 nanowires. Finally, when the system is slowly cooled to room temperature, Zn_2SnO_4 precipitate absolutely and only gold remained at the tips of the nanowires. Meanwhile, different vaporization speeds of ZnO and SnO_2 result in excess ZnO vapor to form ZnO nanowires coexisted with Zn_2SnO_4 in the product. The Zn_2SnO_4 DM nanowires are believed to be grown via the VLS process, but the reason for the modulation of the diameter along the axis is not clear yet. As we try to understand the formation mechanism of the Zn_2SnO_4 DM nanowires, the following fact should be considered: Only Zn_2SnO_4 nanowires have diameter-modulated features; ZnO nanowires synthesized at the same time do not have this feature, which means that the appearance of a DM structure is related to the growth character of the reaction product. We suggest that the disturbance of the vapor concentration is a major factor that changes the diameter of the catalyst alloy droplets and the growth velocity of nanowires, and ultimately results in the diameter-modulated feature. As shown in Figure 5, a gold nanoparticle absorbs Zn and Sn atoms from the vapor and forms an alloy droplet, and the oxidation of the

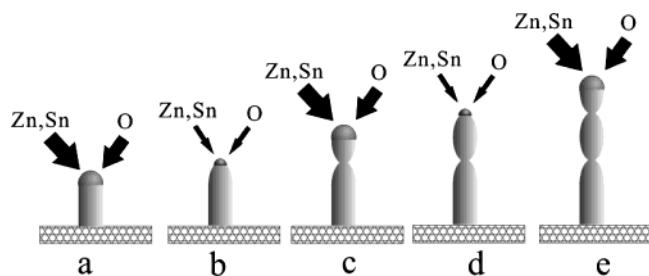


Figure 5. Schematic illustration of the growth process of a DM Zn_2SnO_4 nanowire: (a) a Au nanoparticle absorbs Zn and Sn atoms from the vapor and forms an alloy droplet, then the oxidation of the Zn and Sn atoms initiates the growth of a Zn_2SnO_4 nanowire; (b) a disturbance-induced decrease of the zinc and (or) tin concentration near the alloy droplet reduces the size of the droplet and results in a decrease of the nanowire diameter; (c) a small size alloy droplet absorbs fewer atoms from the vapor, which induces the increase of the zinc and tin concentration near the alloy droplet and finally results the increase of the droplet size and nanowire diameter; (d) the size-resumed alloy droplet draws more atoms from the vapor, which reduces the zinc and tin concentration and the nanowire diameter again; and (e) continuation of the steps depicted in panels c and d forms a Zn_2SnO_4 DM nanowire.

Zn and Sn atoms initiates the growth of a Zn_2SnO_4 nanowire. When a vapor disturbance induces a change in the zinc and (or) tin concentration near the alloy droplet, the size of the droplet shrinks and the nanowire diameter decreases. A small-sized alloy droplet absorbs less atoms from the vapor, which induces an increase of the zinc and tin concentration near the alloy droplet and finally results the increase of the droplet size and nanowire diameter. The size resumed alloy droplet draws more atoms from the vapor, which reduces the zinc and tin concentration and the nanowire diameter again. This mechanism suggests that a disturbance of the vapor concentration triggers a vapor density oscillation near the alloy droplet and finally forms a Zn_2SnO_4 DM nanowire.

Accurate control of the evaporation of source materials is important in the synthesis of ternary oxide nanowires. The ratio of ternary and binary oxide nanowires in the final product is dependent on the ratio of source materials, the evaporation temperature, and the growth temperature. Pure-phase ternary oxide nanowires might be obtained under strict conditions.

Conclusion

In conclusion, we report here a method to synthesize ternary oxide nanowires via a vapor–liquid–solid (VLS) growth mechanism, using gold as a catalyst. Zn_2SnO_4 nanowires and Zn_2SnO_4 diameter-modulated (DM) nanowires were successfully synthesized, accompanied by the formation of ZnO nanowires. Their morphologies and structures were characterized by SEM, XRD, and HRTEM. The diameters of Zn_2SnO_4 nanowires were not very uniform along their length, but were single crystalline, with [302] as their growth direction. However, the Zn_2SnO_4 DM nanowires had a [111] growth direction. The production of the Zn_2SnO_4 DM nanowires is an interesting finding, because this type of nanowire could possibly be more sensitive to surface phonon modes.²³ A VLS growth mechanism is proposed to

understand the formation of the Zn_2SnO_4 , Zn_2SnO_4 DM, and ZnO nanowires. We suggest that the disturbance of the vapor concentration is a major factor that changes the growth velocity of nanowires and ultimately results in the formation of Zn_2SnO_4 DM nanowires. The synthesis process used in our experiment, which is based on the technique of catalyst-assisted vapor-phase evaporation, is expected to be applicable to the preparation of other ternary oxides.

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References and Notes

- (1) Gudiksen, M. S.; Lauhon, L. J.; Wang, J. F.; Smith, D. C.; Lieber, C. M. *Nature* **2002**, *415*, 617.
- (2) Park, W. I.; Jun, Y. H.; Jung, S. W.; Yi, G. C. *Appl. Phys. Lett.* **2003**, *82*, 964.
- (3) Duan, X.; Huang, Y.; Agarwal, R.; Lieber, C. M. *Nature* **2003**, *421*, 241.
- (4) Wu, Y.; Yang, P. *Chem. Mater.* **2000**, *12*, 605.
- (5) Huang, M. H.; Wu, Y.; Feick, H.; Weber, E.; Yang, P. *Adv. Mater.* **2001**, *13*, 113.
- (6) Park, W. I.; Kim, D. H.; Jung, S.-W.; Yi, G.-C. *Appl. Phys. Lett.* **2002**, *80*, 4232.
- (7) Duan, X.; Lieber, C. M. *Adv. Mater.* **2000**, *12*, 298.
- (8) Li, Y.; Meng, G. W.; Zhang, L. D.; Philipp, F. *Appl. Phys. Lett.* **2000**, *76*, 2011.
- (9) Holmes, J. D.; Johnston, K. P.; Doty, R. C.; Korgel, B. A. *Science* **2000**, *287*, 1471.
- (10) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897.
- (11) Kong, Y. C.; Yu, D. P.; Zhang, B.; Fang, W.; Feng, S. Q. *Appl. Phys. Lett.* **2001**, *78*, 407.
- (12) Yao, B. D.; Chan, Y. F.; Wang, N. *Appl. Phys. Lett.* **2002**, *81*, 757.
- (13) Yang, P.; Lieber, C. M. *Science* **1996**, *273*, 1836.
- (14) Liang, C. H.; Meng, G. W.; Lei, Y.; Philipp, F.; Zhang, L. D. *Adv. Mater.* **2001**, *13*, 1330.
- (15) Wu, X. C.; Song, W. H.; Huang, W. D.; Pu, M. H.; Zhao, B.; Sun, Y. P.; Du, J. J. *Chem. Phys. Lett.* **2000**, *328*, 5.
- (16) Bai, Z. G.; Yu, D. P.; Zhang, H. Z.; Ding, Y.; Wang, Y. P.; Gai, X. Z.; Hang, Q. L.; Xiong, G. C.; Feng, S. Q. *Chem. Phys. Lett.* **1999**, *303*, 311.
- (17) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947.
- (18) Dai, Z. R.; Pan, Z. W.; Wang, Z. L. *Solid State Commun.* **2001**, *118*, 351.
- (19) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Appl. Phys. Lett.* **2002**, *80*, 309.
- (20) Qi, H.; Wang, C.; Liu, J. *Adv. Mater.* **2003**, *15*, 411.
- (21) Young, D. L.; Williamson, D. L.; Coutts, T. J. *J. Appl. Phys.* **2002**, *91*, 1464.
- (22) Wang, A.; Dai, J.; Cheng, J.; Chudzik, M. P.; Marks, T. J.; Chang, R. P. H.; Kannewurf, C. R. *Appl. Phys. Lett.* **1998**, *73*, 327.
- (23) Gupta, R.; Xiong, Q.; Adu, C. K.; Kim, U. J.; Eklund, P. C. *Nano Lett.* **2003**, *3*, 627.
- (24) Morales, A. M.; Lieber, C. M. *Science* **1998**, *279*, 208.
- (25) Yang, P.; Yan, H.; Mao, S.; Russo, R.; Johnson, J.; Saykally, R.; Morris, N.; Pham, J.; He, R.; Choi, H.-J. *Adv. Funct. Mater.* **2002**, *12*, 323.
- (26) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897.
- (27) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.
- (28) Duan, X. F.; Lieber, C. M. *J. Am. Chem. Soc.* **2000**, *122*, 188.
- (29) Yazawa, M.; Koguchi, M.; Muto, A.; Hiruma, K. *Adv. Mater.* **1993**, *5*, 557.