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Size-dependent melting behavior of Zn nanowire arrays

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The melting behavior of Zn nanowires embedded in the holes of porous anodic alumina membrane with different diameters was studied by using the differential scanning calorimetry. The crystalline structure and morphology of Zn nanowire arrays were characterized by x-ray diffraction and transmission electron microscopy. The melting temperature of Zn nanowire arrays shows the strong dependence on nanowire sizes. The melting temperature was curvilinear with the reciprocal of the diameter of nanowires with the change of the diameter, which was discussed in terms of size-dependent heat of fusion change. © *2006 American Institute of Physics*.
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As one of the most important one-dimensional (1D) nanostructures, metal nanowires have attracted a great deal of research interest in recent years, because of their importance in fundamental low-dimensional physics research as well as in technological application.[1–3] To implement these nanowires' building blocks for nanoscale electronics,[4,5] their melting properties, which are one of the basic properties of materials, have to be carefully considered because of their extremely fine sizes and high surface areas. However, most studies on the melting properties of nanomaterials are focused on the nanoparticles, and only a few relate to the nanowires. The reported results show that the melting behavior of nanowires has exhibited dramatically different character from that of their bulk counterpart.[6–14] Using the molecular dynamics (MD) simulation method, Wang *et al.*[10] have investigated the melting behavior of ultrathin nanowires, which reveals that the melting of nanowires starts from the interior atoms. Wu and Yang *et al.*[12] reported the melting process of the single Ge nanowire using *in situ* transmission electron microscopy, which indicated that the melting of the Ge nanowire started at the two ends of the nanowire. Although these studies accounted for the general feature of the melting transition, the size-dependent melting behavior of the nanowire arrays with different diameters is still scarce. In this letter, we employed the direct current electrodeposition method to prepare the Zn nanowire arrays in the holes of the porous anodic alumina membrane (PAAM) with the diameter from 22 to 225 nm, respectively, and we also discussed the influence of the diameter on the melting point.

The PAAM templates were prepared according to the method proposed by Masuda and Fukuda[15] of using a two-step anodization process as described previously.[16] Prior to anodizing, high-purity aluminum foils (99.999%) were annealed in a vacuum of 10^{-3} Pa at 500 °C for 5 h to remove the mechanical stress and to obtain the homogenous structure. To prepare the PAAM with different diameters, anodization was first carried out in different acid solutions (0.3*M* H_2SO_4, 0.3*M* $H_2C_2O_4$, or 0.1*M* H_3PO_4) at 2 °C for 4 h, respectively. After removing the alumina layer formed at the above step in a mixture of phosphoric acid (6 wt %) and chromic acid (1.5 wt %), the aluminum foils were oxidized again in the same condition for 20 h. After the second anodization, the PAAM template was etched by a saturated $SnCl_4$ solution to remove the remaining aluminum. The alumina barrier layer was then dissolved in 5 wt % H_3PO_4 solution at 30 °C. Finally, a layer of Au film (about 200 nm in thickness) was sputtered onto one side of the PAAM template to serve as the working electrode. The Zn nanowires were electrodeposited into the holes of the PAAM from the electrolyte containing a mixture of 100 g/L $ZnSO_4 \cdot 7H_2O$, 40 g/L $ZnCl_2$, and 40 g/L H_3BO_3 solution. The *p*H value of the solution was adjusted to 5 with 1*M* $NH_3 \cdot H_2O$.

X-ray diffractometer (Philips X'Pert) with Cu $K\alpha_1$ radiation ($\lambda = 1.540\,56$ Å) and transmission electron microscopy (TEM, JEM-2010) were used to study the crystalline structure and morphology of nanowires. For x-ray diffraction (XRD) measurements, the overfilled nanowires on the surface of the PAAM template were mechanically polished away. For TEM observation, the PAAM was completely dissolved with 1*M* NaOH solution, and then the residual nanowires were rinsed with absolute ethanol for several times. Differential scanning calorimetry (DSC) experiments were carried out with a Perkin-Elmer Pyris Diamond DSC equipment. The measured DSC trace was the collective result of a bundle of Zn nanowires embedded in the holes of PAAM. The heat flow was recorded at the scanning rate of 10 °C/min.

Figure 1(a) shows the typical XRD pattern of the as-prepared sample with the diameter of 45 nm together with the standard diffraction peaks of hexagonal close packed (HCP) phase Zn (JCPDF 04-0831). It can be seen that all peaks of the samples can be indexed to the HCP phase. The intensity of (002) planes is higher than that of others, which indicates that the Zn nanowires have a preferred orientation along the [001] direction. Moreover, we have checked Zn nanowires with different diameters and found that they have the same HCP structure and the preferred orientation. Figure 1(b) shows a typical TEM image of Zn nanowires. It is clear that the nanowires have a high-aspect ratio and the diameter is uniform. In the electrodeposition process, Zn nucleates at the bottom of the pores and grows along the pores to the top. The diameter of nanowires is restricted by the diameter of pores of PAAM, and the length of the nanowires is the same as the thickness of the PAAM used. Meanwhile, the PAAM

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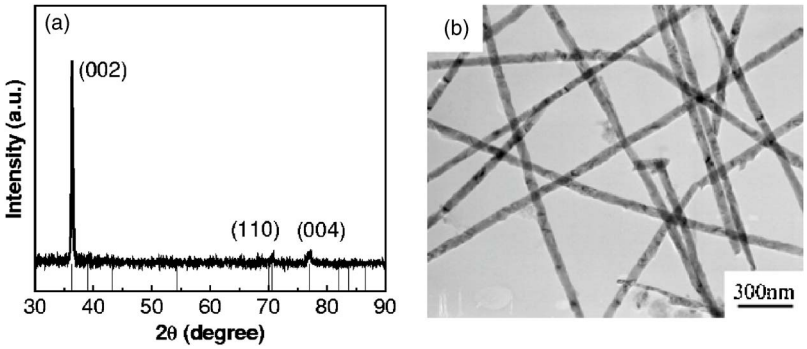

FIG. 1. The XRD pattern of Zn nanowire arrays (a) and TEM image of Zn nanowires with the diameter of 45 nm (b).

has the ordered pore arrangement and the uniform diameter of the pore. So, the diameter of nanowires is uniform.

Figure 2 shows the heating measurement DSC curves of Zn nanowire arrays with different diameters. There is one endothermic peak locating around the melting point of Zn that appears in each curve, and the peak is related to the melting fusion of Zn nanowires. One important fact is that the size-dependent endothermic peak of the nanowires is observed. It is clear that the onset point of the endothermic peak shifts to low temperature with the decrease of the diameter.

Figure 3(a) is the relation between the melting temperature and the diameter of Zn nanowires. The size-dependent nature of melting temperature for Zn nanowires is apparent in our experiments. One can see that the melting temperature decreases with the diameter of nanowires decreasing. Moreover, the smaller the diameter of nanowires becomes, the faster the melting temperature decreases. The mutative trend of the melting point for Zn nanowires resembles that for nanoscale particles which has been reported.[17–19]

The melting temperature depression for materials in confined geometry has been simulated with a confined 1D liquid model.[19–21] Within this model, the decrease of the melting point ΔT can be related to the diameter (D) of nanowires as follow:

$$\Delta T = T_0 - T_m(D) = 4\Delta\sigma\upsilon T_0/\Delta H_f D, \tag{1}$$

where ΔH_f is the heat of fusion, T_0 is the melting point of bulk material, $T_m(D)$ is the melting point of nanowires, υ is the molar volume of a liquid at the melting point $T_m(D)$, and $\Delta\sigma$ is the difference between the solid/wall interfacial energy and the liquid/wall interfacial energy. From Eq. (1), it can be seen that T_m should show a linear dependence on $1/D$ according to the viewpoint of classical thermodynamics. To explore the size dependence of the melting temperature for Zn nanowires, we plotted the melting temperature T_m versus the reciprocal diameter $(1/D)$ of Zn nanowires in Fig. 3(b) and found that the $T_m(D)$ obviously deviated from the linear relation with the diameter though they were a roughly linear relation when the diameter was lower than 65 nm [as curve a shown in Fig. 3(b)].

Many works have discussed the melting mechanism of metal materials. On the one hand, Hui *et al.*[14] reported that the atomic structures of nanowires played a significant role on determining the melting behavior of nanowires. The differences of the interior structures for the nanowires could induce the change of melting point of nanowires because the melting of nanowires started from the interior atoms. On the other hand, it has been reported that with respect to the nanoscale particles, the heat of fusion ΔH_f is size dependent.[17,22,23] As for the linear deviation of the melting temperature, with the change of the diameter of nanowires in our case, we think that the heat of fusion ΔH_f change should be considered because Zn nanowires with different diameters have the same HCP structure and the same preferred orien-

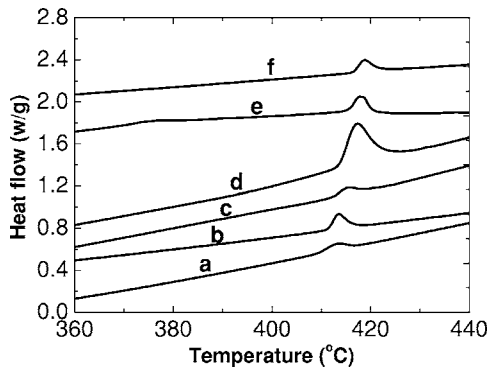

FIG. 2. DSC trace of Zn nanowire arrays with diameters of 25 nm (curve *a*), 45 nm (curve *b*), 65 nm (curve *c*), 90 nm (curve *d*), 145 nm (curve *e*), and 225 nm (curve *f*).

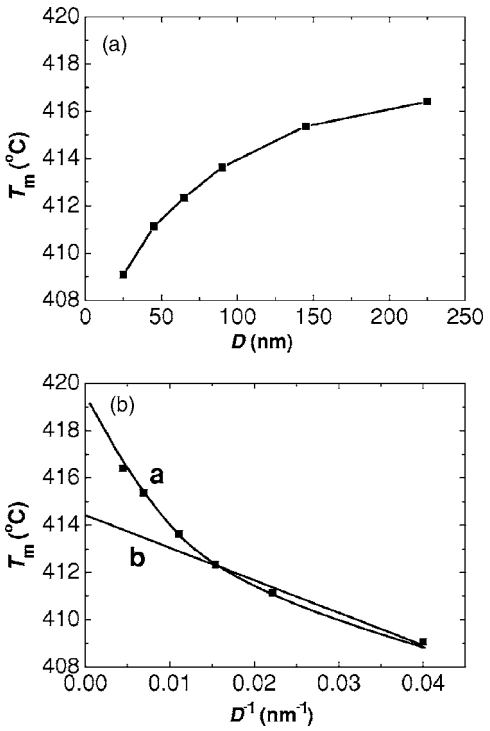

FIG. 3. Melting temperature T_m of Zn nanowire arrays as a function of the diameters (a) and as a function of the reciprocal of the diameters (b).

tation. According to the report of Lai *et al.*,[17] we can obtain the expression for the heat of fusion ΔH_f in terms of the diameter of nanowire D, as shown in the following equation:

$$\Delta H_f = \Delta H_0(1 - 2t_0/D)^2, \quad (2)$$

where ΔH_0 is the heat of fusion for bulk materials, and t_0 is the given critical thickness of liquid overlayer covering the cylindrical core at the melting temperature T_m. It can be seen from the Eq. (2) that with the increase of diameter D the value of t_0/D obviously decreases, which results in the obvious increase of the heat of fusion ΔH_f. Therefore, according to Eq. (1), the relation between $T_m(D)$ and $1/D$ should be curvilinear, and this is in agreement with the result of Fig. 3(b).

Moreover, if we linearly extrapolate the melting temperature from the small diameter to the bulk Zn, it is about 414.3 °C [as line *b* shown in Fig. 3(b)] lower than the experimental value of 419.58 °C.[24] There are two reports that give similar results. The first one is the MD simulation in the heating process of titanium nanowires by Wang *et al.*[10] The extrapolated bulk melting temperature of 1542 K is also remarkably lower than the experimental value of 1943 K for bulk titanium. The second one is also the MD simulation on the Ni nanowires by Wen *et al.*[25] All these studies have gotten significantly lower melting temperature of the bulk when linearly extrapolating from the nanowires studies. However, if we extrapolate the curve from the large diameter to the bulk Zn, we will find that the melting point is near the experiment value for the bulk [as curve a shown in Fig. 3(b)], which means that the ΔH_f change with the diameters should be considered.

In summary, we have prepared Zn nanowire arrays using a direct current electrodeposition in the holes of PAAM templates with different diameters. Using the differential scanning calorimetry, the melting behavior of Zn nanowires has been investigated. The melting temperature of Zn nanowires has been found depending on the sizes of nanowires and being curvilinear with the reciprocal of the diameter of the nanowires due to the heat of fusion change with the change of the diameter. Therefore, after understanding the nature and the trend of the melting point change, it is possible to tune the melting point of nanomaterials by simply controlling the size of nanomaterials.

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[1] Y. Kondo and K. Takayanagi, Science **289**, 606 (2000).
[2] B. L. Wang, S. Y. Yin, G. Wang, and A. Buldum, Phys. Rev. Lett. **86**, 2046 (2001).
[3] J. Mallet, K. Y. Zhang, C. L. Chien, T. S. Eagleton, and P. C. Searson, Appl. Phys. Lett. **84**, 3900 (2004).
[4] M. S. Fuhrer, J. Nygard, L. Shih, M. Forero, Y. G. Yoon, M. S. C. Mazzoni, H. J. Choi, J. Ihm, S. G. Louie, A. Zettl, and P. L. Mceuen, Science **288**, 494 (2000).
[5] T. Rueckes, K. Kim, E. Joselevich, G. Y. Tseng, C. L. Cheung, and C. M. Lieber, Science **289**, 94 (2000).
[6] G. Bilabegovic, Solid State Commun. **115**, 73 (2000).
[7] P. S. Brancio and J. P. Rino, Phys. Rev. B **62**, 16950 (2000).
[8] Y. Gao, Y. Bando, and D. Golberg, Appl. Phys. Lett. **81**, 4133 (2002).
[9] Y. Xia, P. Yang, Y. Wu, B. Mayers, B. Gates, Y. Yin, and F. Kim, Adv. Mater. (Weinheim, Ger.) **15**, 353 (2003).
[10] B. L. Wang, G. H. Wang, X. S. Chen, and J. J. Zhao, Phys. Rev. B **67**, 193403 (2003).
[11] S. Link, Z. L. Wang, and M. A. El-Sayed, J. Phys. Chem. B **104**, 7867 (2000).
[12] Y. Y. Wu and P. D. Yang, Adv. Mater. (Weinheim, Ger.) **13**, 520 (2001).
[13] L. Hui, B. L. Wang, J. L. Wang, and G. H. Wang, J. Chem. Phys. **120**, 3431 (2004).
[14] L. Hui, F. Pederiva, B. L. Wang, J. L. Wang, and G. H. Wang, Appl. Phys. Lett. **86**, 011913 (2005).
[15] H. Masuda and K. Fukuda, Science **268**, 1466 (1995).
[16] M. S. Sander, R. Gronsky, T. Sands, and A. M. Stacy, Chem. Mater. **15**, 335 (2003).
[17] S. L. Lai, J. Y. Guo, V. Petrova, G. Ramanatch, and L. H. Allen, Phys. Rev. Lett. **77**, 99 (1996).
[18] E. A. Olson, M. Yu. Efremov, M. Zhang, Z. Zhang, and L. H. Allen, J. Appl. Phys. **97**, 034304 (2005).
[19] K. M. Unruh, T. E. Huber, and C. A. Huber, Phys. Rev. B **48**, 9021 (1993).
[20] D. D. Awschalom and J. Warnock, Phys. Rev. B **35**, 6779 (1987).
[21] E. V. Charnaya, C. Tien, K. J. Lin, and Y. A. Kumzerov, Phys. Rev. B **58**, 11089 (1998).
[22] F. Ercolessi, W. Andreoni, and E. Tosatti, Phys. Rev. Lett. **66**, 911 (1991).
[23] H. S. Lim, C. K. Ong, and E. Ercolessi, Z. Phys. D: At., Mol. Clusters **26**, S45 (1993).
[24] R. C. Eeast, D. R. Lide, M. J. Astle, and W. H. Beyer, *CRC Handbook of Chemistry and Physics*, 70th ed. (CRC, Boca Raton, FL, 1989).
[25] Y. H. Wen, Z. Z. Zhu, R. Zhu, and G. F. Shao, Physica E (Amsterdam) **25**, 47 (2004).