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Thermal expansion behavior of hexagonal Zn nanowires

Yinhai Wang[a],*, Hui Zhao[a], Yihua Hu[a], Changhui Ye[b], Lide Zhang[b]

[a]*School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Guangzhou 510090, People's Republic of China*
[b]*Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China*

Abstracts

The nanowires of hexagonal metal Zn were prepared in porous alumina membranes by an electrochemical deposition. Scanning electron microscope measurement shows the diameter of the nanowires is about 40 nm, in agreement with the pore diameter of the alumina membranes. X-ray diffraction (XRD) indicates the nanowires have a hexagonal structure and texture along c direction. The high-resolution (XRD), with high-temperature attachments, was employed to examine thermal expansion of the nanowires. The results show the Zn nanowires possess smaller thermal expansion compared with the conventional bulk Zn in c-axis direction, but almost is the same in a-axis direction.
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1. Introduction

One-dimensional nanostructures (such an nanowires, rods and tubes) have been the subject of intensive research due to their application in fabricated nanoscale electronic, photonic, and electrochemical devices [1–4]. Nanowires, in particular, have been recognized as the necessary functional components and interconnects in building nanocircuity [5]. Therefore, it is of vital importance to study the properties of nanowires. The electrical, optical, and magnetic properties have been investigated extensively. To our knowledge, the thermal expansion coefficient of metal nanowires, which is a key property in nanodevices, is still less reported. Recently, we reported the measurement of the thermal expansion of the Cu nanowires. The results show that the thermal expansion of the Cu nanowires is smaller than that of bulk Cu. Cu has a face-centered cubic structure, and exhibits the same thermal expansion in different directions. In this paper, we report the measurement results of hexagonal Zn nanowires for comparison

[6]. Usually, the diameters of metallic nanomaterials have a distribution and will change with the elevating temperature. It is a key factor to have a narrow distribution and control the variation of the diameter during the measurement of thermal expansion coefficient. Porous alumina possesses uniform and parallel nano-porous structures and hence has been used as an ideal template to prepare nanowires with a narrow diameter distribution [7,8]. In this paper, the porous alumina was employed as a template to synthesize the Zn nanowires, and in situ high-resolution X-ray diffraction (XRD) was employed to measure the thermal expansion coefficient of the Zn nanowires. The results were discussed in the framework of the defects of the grain boundaries.

2. Experimental details

The porous alumina membrane with ordered channel arrays was prepared from high-purity alumina foil in 0.3 M oxalic acid by the anodization process [9]. The Zn nanowires were deposited in the pores of alumina membrane by an electrochemical method [10], and these nanowires are polycrystalline. The as-prepared samples

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*Corresponding author.
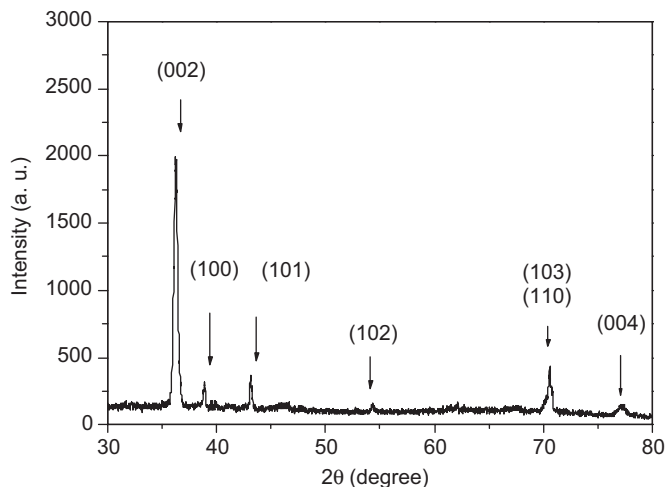E-mail address: yhwang@issp.ac.cn (Y. Wang).

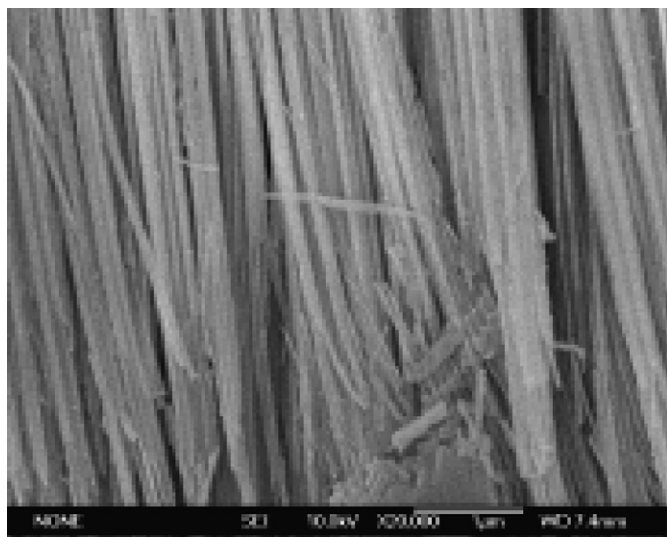Fig. 1. XRD pattern of the Zn nanowires embedded in alumina membrane, measurement at room temperature.

Fig. 2. SEM image of the Zn nanowires removing the alumina membrane.
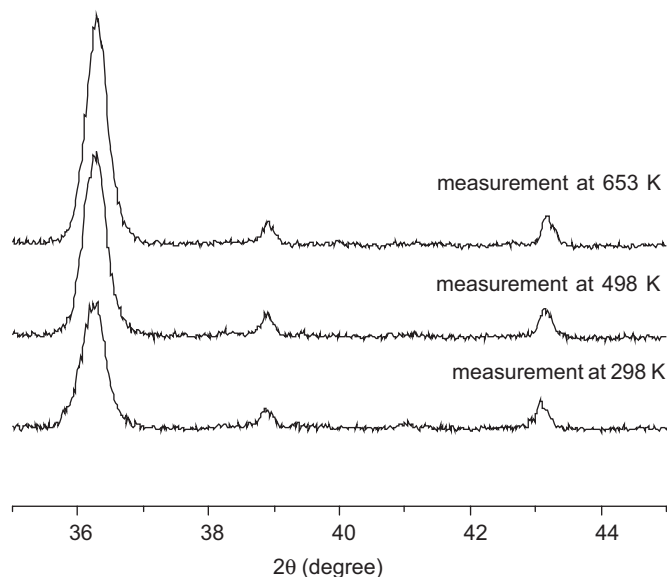

Fig. 3. XRD patterns of the Zn nanowires measuring at 298, 498, and 653 K respectively.

$0.016°$. The XRD patterns were obtained in a vacuum environment, and the temperature was kept at constant for about 10 min before XRD measurement at each temperature. Fig. 3 shows three XRD patterns measured in 298, 498, and 653 K, respectively. It can be seen that XRD patterns show no significant difference, and only the peak positions shift toward lower angle side suggesting a thermal expansion property of lattice parameters with elevating temperature. For comparing with Zn nanowires, the lattice parameters of the bulk Zn, were measured at the same condition. The lattice parameters as a function of the measuring temperature are shown in Fig. 4 for the Zn nanowires and bulk Zn, respectively. It can be seen that the increment of the lattice parameters with elevated temperature exhibits the thermal expansion property. From Fig. 4, we can find: (1) the lattice parameters of the nanowires are slightly increased with respect to the equilibrium lattice constants for bulk materials; and (2) the thermal expansion coefficient of the Zn nanowires is more smaller than that of the bulk Zn at [0 0 1] direction and is slightly smaller than that of bulk Zn at [1 0 0] direction.

3. Discussion

Lattice parameters in a number of nanomaterials have been measured by means of the XRD technique, and they were found to be slightly increased with respect to the equilibrium lattice parameters for bulk materials [11,12]. Very recently, based on X-ray and electron diffraction results, the nanocrystalline Nb film exhibits a significantly large lattice expansion with reduction in the crystallite size [13]. In our experiment, the Zn nanowires showed about 0.6% increase in the lattice parameters at room temperature, that can be ascribed to nonlinear effects caused by the existence of the microstrain field [14], originated from

were characterized by XRD (X'pert PRO) (Fig. 1). It can be seen that all peaks can be indexed to hexagonal metal Zn. However, the intensity of the diffraction peak of the (0 0 2) plane is much stronger than the others that indicate the Zn nanowires located in the pores have a texture along [0 0 1] direction. Fig. 2 shows the field emitting scan electron microscope (FESEM; JSM-6700F) image of the Zn nanowire arrays after removing the alumina membrane. It can be seen that the Zn nanowires are uniform and nearly parallel. The diameters of the Zn nanowires are about 40 nm, in good agreement with the pore diameter of alumina membrane [8].

To study the thermal expansion of the Zn nanowires, the sample was measured by high-resolution XRD with high-temperature attachments capable of controlling temperature within ± 1 K, the temperature range from 298 to 653 K. The XRD data were collected by a step scanning method in 2θ range from $35°$ to $45°$ with a step width of
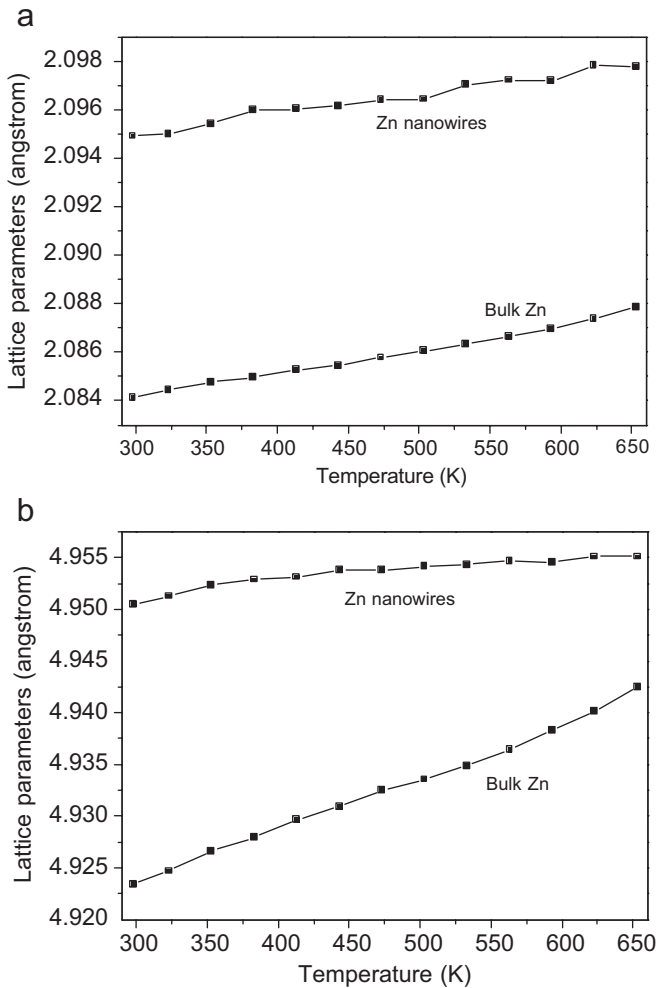
Fig. 4. Temperature dependences of lattice parameters of the Zn nanowires and bulk Zn: (a) and (b) show the *a*- and *c*-axis of the hexagonal structure, respectively.

defect of surface, as vacancies and vacancy clusters. The crystal lattice expansion mainly exists near and in the grain boundaries. The vacancies and vacancy clusters in the grain boundaries of nanomaterials are the main source of the crystal lattice expansion of nanomaterials.

Surprisingly, the thermal expansion coefficient, α, of the Zn nanowires along *c* direction is far smaller than that of bulk Zn, and α is slightly smaller than that of bulk Zn along *a*-axis direction (see Fig. 3). The thermal expansion coefficient defined by $\alpha_{\perp} = (da/dT)(1/a)$ and $\alpha_{\parallel} = (dc/dT)$ $(1/c)$, where $\alpha_{\perp}$ and $\alpha_{\parallel}$ are thermal expansion coefficient along *a*- and *c*-axis, respectively and T is temperature. It can be obtained that $\alpha_{\perp} = 5.2 \times 10^{-6} \, \text{K}^{-1}$ for the Zn nanowires and $18.4 \times 10^{-6} \, \text{K}^{-1}$ for bulk Zn, and $\alpha_{\parallel} = 5.4 \times 10^{-6} \, \text{K}^{-1}$ for the nanowires and $5.7 \times 10^{-6} \, \text{K}^{-1}$ for bulk Zn. In general, the nanomaterials have a larger thermal expansion coefficient in respect to the bulk materials. Birringer and Gleiter observed that the linear thermal expansion coefficient of nano-Cu bulk samples with a mean grain size of 8 nm is about 1.94 times that of its

conventional polycrystalline counterpart [15]. Similarly, Zhao et al. [16] found that α of the nano-Fe bulk sample determined by means of the XRD analysis increases monotonically with a decrease of grain size. Zhang and Mitchell found that α of the bulk nanocrystalline Se increased with a reduction of grain size, from which they deduced thermal expansion coefficient of the interface decreased with the refinement of the grain size [17]. They think that high thermal expansion coefficient derived from the grain boundaries due to the nanomaterials consists of a high density of grain boundaries.

Why the thermal expansion coefficient, α, of the Zn nanowires at the *c*-axis direction is much smaller than that of conventional bulk Zn? As we know, the thermal expansion depends mainly on the nonlinear crystal lattice vibration [18]. The more obvious the vibration, the bigger the α is. The contribution of nonlinear crystal lattice vibration in the grain boundary component is apparently larger than that in the grain component because of random atom arrangement in grain boundaries, which arises from the existence of a large number of vacancies and vacancy clusters in the grain boundaries. For one-dimensional Zn nanowires the grain diameter is about 40 nm, which is obtained from XRD peaks by using Scherrer's formula [19]. The grain diameter is almost the same as the Zn nanowire diameter. This implies that for every Zn nanowires the all grain boundaries with the nanowire surface are almost crossed. During the increasing temperature, for nanowires vacancies and vacancy clusters move easily along the grain boundaries onto the surfaces of the nanowires and disappear fast. As a result, atoms in grain boundaries rearrange rapidly, resulting in the increase of the order degree of grain boundary structure. This makes nonlinear vibration contribution in grain boundaries to α decrease fast. Moreover, the nonlinear vibration of crystal lattice in grain boundaries becomes the main contribution to α. The fast decrease of grain boundary contribution to α causes the Zn nanowires to have a very small α. For Zn nanocrystalline bulk samples with a large volume fraction of grain boundaries it is difficult for vacancies and vacancy clusters to move fast along the grain boundary towards the sample surface and then fast disappear. Therefore, with increasing temperature, the nonlinear vibration of crystal lattice becomes more and more obvious in both grain boundaries and grains. This gives rise to highly thermal expansion. This is why the nanocrystalline bulk has a high α. As we know, because conventional Zn bulks contain very few grain boundaries the nonlinear vibration of crystal lattice in grains is the main contribution to α with elevating temperature, the nonlinear vibration of crystal lattice in grains with very small vacancies and vacancy clusters becomes more and more obvious because the atom rearrangement process in grains is not obvious caused by annihilation of defects. Conversely, as mentioned above for the Zn nanowires with a large volume fraction of grain boundaries, the grain boundary atom rearrangement process becomes very rapid with the increase of

temperature due to fast annihilation of vacancies and vacancy clusters on nanowires surface, the nonlinear vibration of crystal lattice in grain boundaries becomes rapidly weak, so that their contribution to thermal expansion decreased substantially. And at the same time, the nanowire grain boundary is the main contribution to α. Therefore, the α of Zn nanowires becomes lower than that of conventional Zn bulks.

4. Conclusion

In summary, the lattice parameters and thermal expansion coefficient of the Zn nanowires were measured by high-revolution XRD. The results show that the thermal expansion coefficient along c-axis is far smaller than that of the bulk counterpart, and that is almost equivalent at a-axis direction, suggesting an anisotropy of the thermal expansion of the Zn nanowires. The vacancies and vacancy clusters existing at the boundaries of the nanowires cause the atomic random arrangement. For Zn nanowires with a large volume fraction of grain boundaries, the contribution of nonlinear in grain boundaries to α is dominant. However, these grain boundaries are crossed with the surfaces of Zn nanowires. With rise of temperature, vacancies and vacancy clusters in grain boundaries shift more easily along grain boundaries towards the surfaces and then disappear rapidly. As a result, the atomic arrangement trends fast towards a order arrangement and thus nonlinear vibration of crystal lattice becomes fast weak, resulting in the substantial decrease of α. This is why the Zn nanowires have small α.

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