

In situ x-ray diffraction study of the thermal expansion of the ordered arrays of silver nanowires embedded in anodic alumina membranes

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Thermal expansion of as-prepared and annealed ordered arrays of silver nanowires embedded in anodic alumina membranes (AAMs) was studied by *in situ* x-ray diffraction measurement in the temperature range from 25 to 800 °C. The axial thermal expansion coefficient (TEC) for the as-prepared nanowires is $6.35 \times 10^{-9}/^{\circ}\text{C}$ and $6.02 \times 10^{-6}/^{\circ}\text{C}$ below and above 650 °C, respectively. However, the TEC of the annealed sample turns from $2.32 \times 10^{-6}/^{\circ}\text{C}$ to $12.06 \times 10^{-6}/^{\circ}\text{C}$ when the temperature is above 350 °C. The collective effects of the intrinsic expansion, surface pressure, the limit effect of AAM, and the vacancies incorporated into the silver lattice were responsible for the thermal expansion. © 2006 American Institute of Physics.

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In recent years, there has been increasing interest in the one-dimensional (1D) nanostructures, such as nanowires and nanotubes, which may be the ideal building blocks for the nanoscale electronic and photonic structures. With the development of the nanodevices, the study of the thermal expansion properties of one-dimensional nanomaterials is becoming the focus of intensive research. The thermal expansion properties of the nanoparticles, such as Pd (Ref. 1) nanoparticles and Au nanoparticles² have been extensively studied; however, the research on the thermal expansion on 1D nanomaterials is scarce, though some research have been done on 1D nanowire.³⁻⁵

As a one-dimensional nanostructure, silver nanowires exhibit many unique physical properties and have found applications in many fields, such as optical devices,^{6,7} and antibacterial activity.⁸ However, the scarce research on the thermal properties of the silver nanowires has been a barrier for the practical use, especially in nanodevices. In this letter, we present the thermal expansion properties of ordered arrays of silver nanowires embedded in anodic alumina membranes (AAM) template with the testing temperature range from 25 to 800 °C.

The AAM plates used in this work were prepared via the two-step aluminum oxidation process proposed by Masuda and Satoh⁹ and the AAMs with the pore sizes of 55 nm were used to fabricate silver nanowires. Silver nanowires were deposited into the pores of AAM at room temperature. The electrolyte contained a mixture of $45 \text{ g l}^{-1} \text{ AgNO}_3$ and $45 \text{ g l}^{-1} \text{ H}_3\text{BO}_3$ in aqueous solutions, with *pH* of 2–3 by adding a HNO_3 solution. In our experiment, the as-prepared and annealed samples were used, and the annealed samples were annealed in the vacuum of 5×10^{-5} torr at 800 °C for 3 h.

In order to measure the thermal expansion of the silver nanowires and the bulk silver, high temperature and vacuum cell were attached to the x-ray diffractometer (Philips X'Pert), in which the vacuum can reach 5×10^{-5} mbar and the temperature can be controlled within ± 1 °C. The x-ray wavelength $\lambda_{\text{K}\alpha 1}$ is 1.5406 Å. The heating rate is 5 °C/min and at each testing point the temperature was hold on for 10 min before x-ray diffraction (XRD) measurement. In our experiment setup, we only measure the axial lattice parameters and their changes. Because the samples can hardly be put in the same position in the XRD experiment, the starting values of the axial lattice parameters for the nanowires are not the same. The axial lattice parameter *d* can be calculated from Bragg equation: $2d \sin \theta = \lambda$, where *d*, θ , and λ are the interplanar spacing, diffraction angle, and the x-ray incidence wavelength, respectively.

Positron-annihilation experiments were used to study the state of vacancies, which were carried out with a fast-slow coincidence ORTEC system with a time resolution of 190 ps (full width at half maximum). A 5×10^5 Bq source of ²²Na was sandwiched between two plates of AAM embedding silver nanowires. The measurements of the positron annihilation were performed at room temperature and the results were analyzed with POSITRONFIT-88 program in which variances of fit (*o*) between 1.105 and 1.101 were obtained.

Figures 1(a) and 1(b) show the field emission scanning electron microscopy (FESEM) (FEI Sirion 200) and transmission electron microscopy (TEM) (JEOL-2010) images of nanowires respectively. It can be observed from that the high ordered and uniform Ag nanowires were obtained. The XRD pattern of silver nanowires embedded in AAM is shown in Fig. 1(c). It can be observed that the nanowires are single crystalline and have a good orientation with the axis direction along the [220] crystallographic direction for the as-prepared nanowires.

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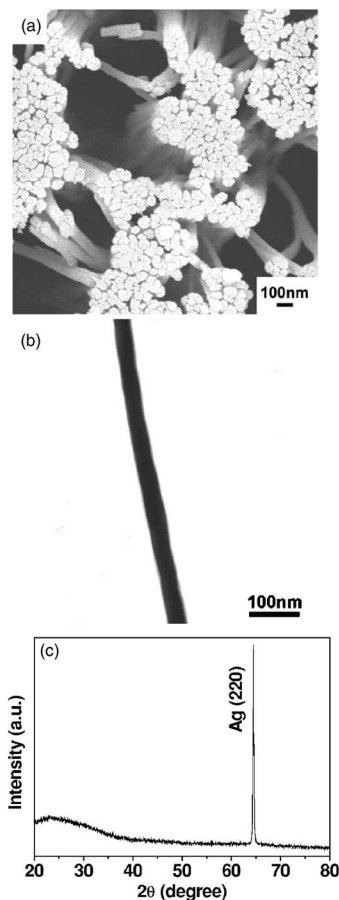


FIG. 1. (a) FESEM micrograph of the Ag nanowire arrays; (b) TEM image of a single Ag nanowire; (c) XRD pattern of the Ag nanowire arrays embedded in AAM.

The variation of axial lattice parameters versus temperature for the as-prepared and annealed silver nanowires are shown in Fig. 2(a), in which the corresponding data of bulk silver are also included. It can be found that in the studied temperature range, the variation of the axial lattice parameters for the as-prepared silver nanowires can be divided into

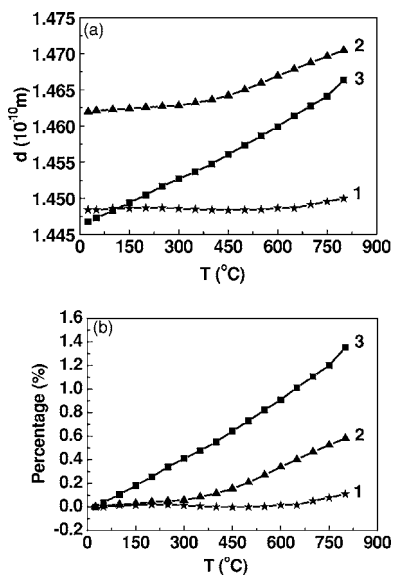


FIG. 2. The plots of silver axial lattice parameters (a) and the percentage of the thermal expansion (b) vs temperature. Curve 1, as-prepared nanowires; curve 2, annealed nanowires; curve 3, bulk silver. [Calculated from Ag (220).]

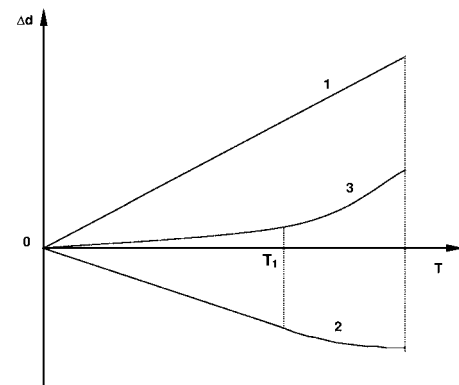


FIG. 3. The illustration of axial lattice parameter changes with the temperature. Curve 1, the collective effects of thermal expansion of intrinsic expansion and surface pressure together with the limit effect of AAM; curve 2, the contraction induced by vacancies; curve 3, the collective effects by curve 1 and curve 2.

two parts. When the temperature is below 650 °C, the axial lattice parameter keeps nearly constant, but has a slight increase when the temperature is above 650 °C. We can thus obtain that the lattice thermal expansion coefficients are $6.35 \times 10^{-9}/^{\circ}\text{C}$ and $6.02 \times 10^{-6}/^{\circ}\text{C}$, respectively, for the two ranges, which is nearly two-fifths that of bulk silver ($16.74 \times 10^{-6}/^{\circ}\text{C}$).

For the annealed sample, the axial lattice parameters begin to increase from the beginning of the testing temperature, which can also be divided into two parts at the temperature of 350 °C. The thermal expansion coefficient (TEC) turns from $2.32 \times 10^{-6}/^{\circ}\text{C}$ to $12.06 \times 10^{-6}/^{\circ}\text{C}$ when the temperature is above the point. At the higher temperature, the TEC is about twice that of as-prepared nanowires and two-thirds that of the bulk silver.

Figure 2(b) shows the relative variation of the axial lattice parameters as the function of the temperature, calculated from the values in Fig. 2(a). We can clearly see that the axial lattice parameter increase is less than 0.1% totally for the as-prepared samples and 0.6% totally for the annealed samples. For the bulk silver the corresponding value is 1.4%.

The results of positron-annihilation experiments show that the lifetime components τ_1 are 227.5 and 247 ps for the as-prepared and annealed silver nanowires, and the lifetime components τ_1 are 188.2 and 241.2 ps for the as-prepared and annealed AAMs, respectively.

Besides the intrinsic expansion, the thermal expansion of the nanowires observed in our experiment may be determined by two factors. One is the axial expansion resulted from the radial contraction induced by surface pressure, together with the limit effect of the AAM. The collective effects of intrinsic expansion, surface pressure and the limit effect of AAM are shown as curve 1 in Fig. 3. Another is the contraction caused by the vacancies, as curve 2 shown in Fig. 3. The curve 3 depicts the collective effects of curves 1 and 2.

With the decrease of particle size, the surface effect will get more and more significant, and the external pressure will induce the variation of lattice parameter. For the spherical particle, using the definition of the compressibility, $\kappa = -\Delta V/PV$, we can get¹⁰

$$\frac{\Delta a}{a} = -\frac{\kappa P}{3}, \quad (1)$$

where a is the lattice parameter, Δa is the variation in lattice parameter a due to the external pressure P , and κ is the compressibility. It can be found that the external pressure can induce the lattice parameter contraction for the nanoparticle. For the nanowires studied here, the diameters are on the order of tens of nanometers, and the axial dimension is on the order of tens of microns, so the external pressure may induce the contraction along the radius direction of the nanowires. In addition, the thermal expansion of AAM is positive ($7.7 \times 10^{-6}/^\circ\text{C}$),¹¹ so the hole of AAM will be smaller with the temperature increase, which will limit the nanowire expansion perpendicular to the axial direction. Furthermore, Nelson and Riley suggested that the expansion of the graphite materials in the out-of-plane direction resulted in a lateral contraction due to Poisson's effect,¹² so we think in our case that the contraction of the nanowires in their radial may induce a larger axial expansion along their axial direction.

Fukai *et al.*¹³ and Fukai¹⁴ have found superabundant vacancy formation in the process of electrodeposition. And during the preparation process, some vacancies will inevitably lump with the silver atoms. As we know, the existence of the vacancies in materials makes the adjacent atoms a slight shift to them instead of staying at their equilibrium position, which causes the lattice parameters slightly larger. When vacancies congregate into voids or escape from the samples, Ag atoms then go back to their equilibrium position, which makes the lattice parameters contract.

As far as the as-prepared samples are concerned, the positron-annihilation experiments show that the lifetime component τ_1 is 227.5 ps, which is different from τ_1 of the AAM (188.2 ps). It is much larger than that of the bulk silver we measured (134 ps) and the reported value (136 ps).¹⁵ So the τ_1 of 227.5 ps is the lifetime of positron in silver nanowires. The τ_1 for the as-prepared samples is also larger than that of positrons trapped in monovacancies (186 ps) (Ref. 16) in silver. So we attribute the lifetime constant τ_1 to positron trapping and annihilation in nanovoids consisting of several vacancies. With the temperature increase, these vacancies gradually congregate into voids or escape from the samples, so the lattice parameters contract. The contraction caused by the vacancies is comparable with the collective effects of the axial expansion and intrinsic expansion at the beginning of the testing, so the macroscopic expansion behavior of the nanowires is indistinct, even the value of the TEC along the wire axis is nearly zero, as the part below 650°C shown in Fig. 2(a). With the temperature further increases, the effect of the vacancies weakens, as illustrated by curve 2 after T_1 point in Fig. 3; then the axial expansion caused by the radial contraction and the intrinsic expansion will become dominant. Both effects of vacancies and radial contraction result in the lattice parameter change as curve 3 shown in Fig. 3. And the contraction caused by the escape or the congregation of the vacancies makes the axial expansion of nanowires smaller than that of counterpart bulk materials.

For the annealed sample, τ_1 turns to be 247 ps, which is larger than that of the as-prepared samples. It means that after annealing, vacancies congregate into larger voids. If the number of the vacancies is fixed, when the vacancies exist in the form of large voids, the number of the atoms close to these voids is less than that of the atoms close to small voids.

So, the effect of the vacancies is smaller, compared with that for the as-prepared sample. In this case, the macroscopic expansion behavior is that the axial TEC for the annealed sample will be larger than that for the as-prepared sample, which is consistent with the experimental results shown in Fig. 2(a). Though most vacancies escaped in the annealed process, some vacancies were still left in the nanowires, so the TEC ($2.32 \times 10^{-6}/^\circ\text{C}$) for the annealed sample is still smaller than that of bulk silver ($16.74 \times 10^{-6}/^\circ\text{C}$). It is found that the τ_1 of annealed AAM is also larger than that of the as-prepared AAM, which indicates that after annealing the vacancies in AAM also congregate into larger voids.

In summary, for the as-prepared sample, the axial lattice parameter keeps nearly constant when the temperature is lower than 650°C , and the value of the coefficients of the thermal expansion is $6.35 \times 10^{-9}/^\circ\text{C}$. The axial lattice parameter begins to increase when the temperature is above 650°C , and the TEC is $6.02 \times 10^{-6}/^\circ\text{C}$, which is nearly two-fifths that of the bulk silver ($16.74 \times 10^{-6}/^\circ\text{C}$). As far as the annealed sample is concerned, the axial lattice parameter increases in the whole testing temperature range, which can also be divided into two parts at the temperature of 350°C . The TEC value turns from $2.32 \times 10^{-6}/^\circ\text{C}$ to $12.06 \times 10^{-6}/^\circ\text{C}$ when the temperature is above 350°C . The collective effects of the intrinsic expansion together with surface pressure and the vacancies incorporated into the silver lattice were responsible for the thermal expansion. The study could be of importance for the structural design, thermal stability, and reliability of the future nanodevices.

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