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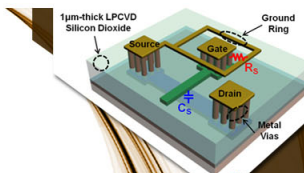Information for Authors: http://apl.aip.org/authors
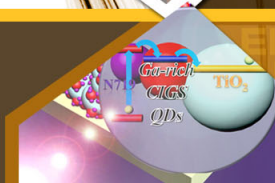
In situ x-ray diffraction study on AgI nanowire arrays

Yinhai Wang,[a] Changhui Ye, Guozhong Wang, and Lide Zhang
Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

Yanmei Liu and Zhongyan Zhao
Department of Physics, Anhui University, Hefei 230039, People's Republic of China

The AgI nanowire arrays were prepared in the ordered porous alumina membrane by an electrochemical method. Transmission electron microscopy observation shows that the AgI nanowires are located in the channels of the alumina membrane. *In situ* x-ray diffractions show that the nanowire arrays possess hexagonal close-packed structure (β-AgI) at 293 K, orienting along the (002) plane, whereas at 473 K, the nanowire arrays possess a body-centered cubic structure (α-AgI), orienting along the (110) plane. The AgI nanowire arrays exhibit a negative thermal expansion property from 293 to 433 K, and a higher transition temperature from the β to α phase. We ascribe the negative thermal expansion behavior to the phase transition from the β to α phase, and the elevated transition temperature to the radial restriction by the channels of alumina membrane. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1583856]

Silver iodide (AgI) is an important material mainly for two applications, in solid state batteries on the basis of superionic conductivity, and as a photographic film material based on the photochemical reactions occurring in it. AgI has a rich phase diagram with several different solid phases existing,[1] and it may exist in two phases β-AgI and γ-AgI, at room temperature and ambient atmosphere.[2] In β-AgI, the iodine ions are arranged in hexagonal close-packed (hcp) lattice with the silver ions being tetrahedrally coordinated to each of the iodides. Thus, in β-AgI, the system is in a wurtzite structure. In γ-AgI, the iodine ions are arranged in a face-centered cubic (fcc) lattice with the silver ions tetrahedrally coordinated to the iodine ions. At 420 K, β-AgI undergoes a first-order phase transition into the superionic α phase, in which iodine ions form a body-centered cubic (bcc) lattice. However, all of these works were performed on bulk AgI. It is still a challenge to synthesize aligned and well-distributed nanowire arrays of AgI. Anodic alumina possesses uniform and parallel porous structures and hence has been used extensively as an ideal template to prepare ordered nanowire arrays.[3,4] More recently, we have prepared the nano-AgI arrays in ordered porous alumina membrane,[5] in which nano-AgI is composed of a mixed phase of β-AgI and γ-AgI. In this letter, highly oriented β-AgI nanowire arrays are prepared in alumina membrane, and *in situ* x-ray diffraction (XRD) is employed to study the AgI nanowire arrays. The negative thermal expansion behavior and the elevated phase transition temperature (higher than the usual β to α phase transition temperature of 420 K) from β-AgI to α-AgI have been found.

The porous alumina membrane with ordered channel arrays was prepared from high-purity (99.999%) aluminum foil in 0.3 M oxidic acid by anodization.[6] A remaining aluminum layer at the bottom of the alumina membrane was removed in 1 M CuCl$_2$ solution. Subsequently, the pore bottoms were opened by chemical etching in 5 wt% phosphoric acid solution. The fabrication of AgI nanowire arrays was described in a previous publication.[7] In brief, the resulting porous alumina membrane was held on a hole (with diameter ~1 cm) located between two electrolytic cells. AgNO$_3$ and KI aqueous solution were filled into two electrolytic cells, respectively. After a direct voltage was applied between the two electrolytic cells, Ag$^+$ and I$^-$ ions move in the electric field and react in the channels of the alumina membrane. When the color of the alumina membrane changed into yellow, it indicated that the AgI was deposited in the channels.

Figure 1 shows a transmission electron microscopy (TEM, JEM200CM) image, from which it can be clearly seen that AgI nanowires were deposited in the channels of the alumina membrane. The diameter of the AgI nanowires is about 40 nm, in good agreement with the diameter of the channel.

In order to investigate the phase transition behavior of the AgI nanowire arrays, *in situ* high temperature x-ray dif-
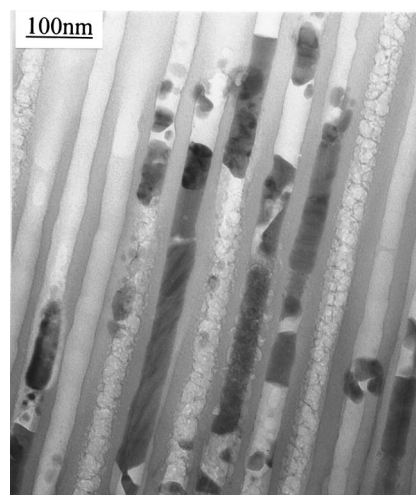

FIG. 1. TEM image of the AgI nanowires located in the channels of the ordered porous alumina membrane.

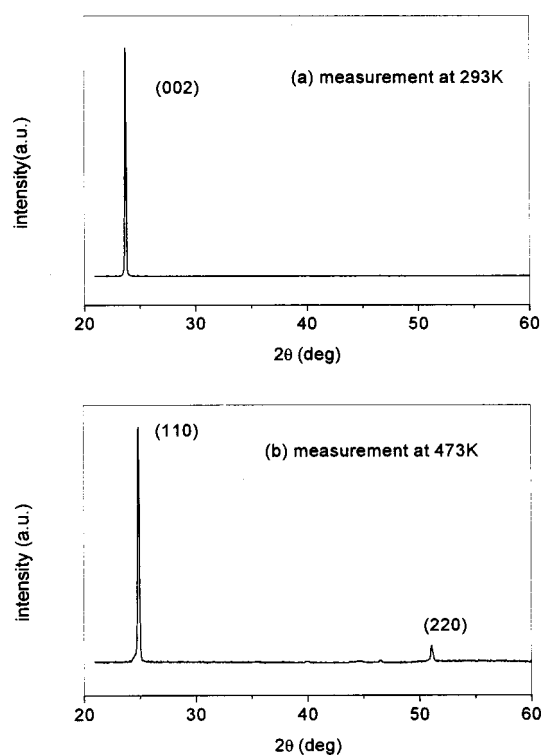[a]Author to whom correspondence should be addressed; electronic mail: yhwangahu@hotmail.com

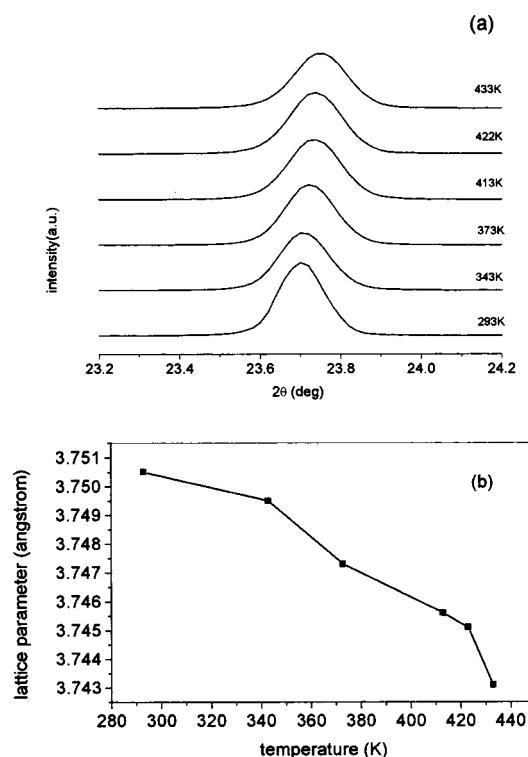FIG. 2. XRD patterns of the AgI nanowire arrays, oriented along (002) plane.

FIG. 3. (a) XRD patterns of the (002) plane of the β-AgI measuring from 293 to 433 K. (b) Temperature dependence of the lattice parameters of AgI nanowires from 293 to 433 K.

fraction (XRD, MXP 18AHF) was performed in the range from 293 to 473 K under the ambient atmosphere. Temperatures were kept constant ($\pm 1°$) for 30 min before each measurement, and scans were carried out for $20° < 2\theta < 60°$. Figure 2(a) shows one XRD pattern of the AgI nanowire arrays at 293 K. Only one diffraction peak was observed, which indexed to the (002) plane of β-AgI and the (111) plane of γ-AgI. In accordance with the commonly accepted conclusion,[8] one always gets γ-AgI in the presence of excess silver ions, whereas a large excess of iodine concentration produces β-AgI. In the present experiment, iodine concentration was bound to be in the excess because the AgI nanowires were formed by diffusion of Ag^+ from $AgNO_3$ to KI solution.[9] Thus, we come to the conclusion that highly oriented β-AgI nanowire arrays were prepared in the channels of the alumina membrane. From 293 to 433 K, the x-ray diffraction patterns, ascribed to (002) plane of β-AgI, show no significant difference. At 473 K, only α-AgI was found [see Fig. 2(b)], orienting along the (110) plane, which indicates the AgI nanowires transition from the β to α phase. Furthermore, with increase of temperature, the peak positions of the (002) plane of β phase shift toward higher angle direction [see Fig. 3(a)], suggesting a negative expansion property. The lattice parameters of β-AgI as a function of the temperature were shown in Fig. 3(b), which clearly shows the variation of the lattice constants with temperature.

As previously presented, AgI undergoes a phase transition from β to α phase at 420 K.[10,11] However, in our experiment the phase transition occurs at above 433 K at least, which clearly indicated the AgI nanowire arrays in the alumina membrane have a higher phase transition temperature. At this temperature, the β phase orienting along the (002) plane of hexagonal close-packed structure transformed to the

α phase orienting along the (110) plane of body-centered cubic structure.

With the elevation of temperature, most materials usually show a positive thermal expansion property. This behavior can be understood by considering the effects of the anharmonic potential on the equilibrium lattice separations and is usually characterized by Gruneisen parameter.[12] The negative thermal expansion, which represents lattice contraction with the elevation of temperature, was also observed among anisotropic systems,[13,14] where contraction along one crystallographic direction was usually accompanied by expansion along the others.[15]

The close-packed structure transforms into body-centered cubic structure in the AgI nanowires, which can be interpreted according to the Burgers mechanism.[16] In Fig. 4, for the transition from the (002) plane of hexagonal close-packed structure to the (110) plane of body-centered cubic structure, the iodine ions will have a glide, implying that it will expand along Y direction, resulting in the distance between the iodine ions changing from 4.59 to 5.04 Å, and contract along X direction [see Fig. 4(a)], resulting in the distance between the iodine ions changing from 7.95 to 7.12 Å. Meanwhile, the plane spacing contracted from 3.75 Å of the (002) plane of the β phase to 3.53 Å of the (110) plane of the α phase. Due to the fact that AgI nanowires are located in the channels of alumina membrane, the expansion in radial direction will be hindered, resulting in a rising phase transition temperature. This indicated that the channels could enhance the stability of β-AgI. So far, it has not reached a consensus what is responsible for the β to α phase transition. Madden and his co-workers[17] argued that the disordering tendency of the Ag^+ ions in the β phase could be taken as
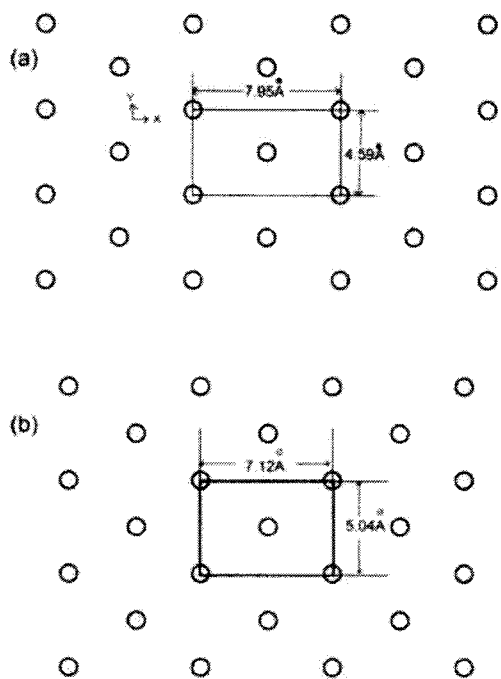
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FIG. 4. Iodine ions arrangement of the (002) plane of β phase (a) and (110) plane of α phase (b).

the driving force for the β to α phase transition. However, Seok and Oxtoby[18,19] argued that the structure change of the I$^-$ lattice and the disordering of Ag$^+$ ions are correlated processes, rather than the disordering of Ag$^+$ ions driving the β to α phase transition. In any case, our experimental results suggested that the channels of the alumina membrane hindered the ordering–disordering transition of the Ag$^+$ ions, henceforth, raised the transition temperature for the β- to α-phase transition.

In summary, the AgI nanowire arrays, highly oriented along the (002) plane of the β-AgI, were prepared by an electrochemical method in the porous alumina membrane.

From 293 to 433 K, the AgI nanowire arrays have a negative thermal expansion property, which derives from the phase transition that occurred at above 433 K. The phase transition temperature from the hexagonal close packed to body-centered cubic is raised because of the restriction of the channels of alumina membrane.

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