Macroporous ZnO Films Electrochemically Prepared by Templating of Opal Films

Takayuki Sumida, Yuji Wada, Takayuki Kitamura, and Shozo Yanagida*
Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871

(Received October 13, 2000; CL-000936)

Highly ordered macroporous ZnO films were electrodeposited using polystyrene colloidal crystals as templates. The films prepared at –1.0 V vs Ag/AgCl had the long-range order of pores reflecting the templates.

Zinc oxide is an important material because of their wide applications in thin film devices such as chemical sensors, piezoelectric transducers, n-type semiconducting electrode, and luminescent devices.[1] A strategy to further enhance the performance of these devices would be to fabricate the highly ordered macropores within the ZnO films. From the viewpoint of the sensors and the semiconducting electrodes, the large internal surface area and improved mass transportation originated from size-controlled macropores would contribute to the performance. The structural order on an optical length scale should also give the films interesting photonic properties combined with the intrinsic luminescent and piezoelectric properties of the materials.

For this strategy of making the ordered macropores, colloidal crystal templating is a useful method.[2] The procedure of the method involves impregnation of the interstices of colloidal crystals as templates with desired precursors, followed by reactions, and removal of the templates. Since the first report,[3] the three-dimensionally interconnected macropores have been fabricated within oxide ceramics,[4] carbon,[5] polymers,[6] metals,[7]and semiconductors[8] by this method. However, with regard to the oxides including ZnO which have been mainly prepared via liquid-phase reactions such as sol–gel chemistry, the products have been generally fragile and powdery due to the cracks caused by significant shrinkage of materials during the synthesis. This has limited their further applications described above and has been an important problem to be overcome.

One effective approach to this problem should be the use of electrodeposition as an impregnation technique alternative to the sol–gel technique. The electrodeposition of oxides has several advantages over the sol–gel technique as follows. The properties such as doping[9] and thickness of oxides can be easily controlled through the electrochemical parameters (e.g., potential and current). Most deposits are grown as thin films adherent to the conductive surfaces under appropriate conditions, facilitating ready handling of the product solids for the film applications.

So far, in the colloidal crystal templating, the electrodeposition has been applied to chalcogenides (CdS and CdSe),[10] metals,[11] and polypyrrole.[12] But, there have been no reports on the electrodeposited macroporous oxides. Moreover, little has been reported on the basic relationship between the electrochemical conditions and the order of the final porous structures.

In this letter, we show not only the electrodeposited macroporous ZnO films by the colloidal crystal templating but also the effect of the deposition potential on the order of the product structures.

Monodisperse polystyrene (PS) spheres (diameter = 368 nm, polydispersity = 3.8%) were made by the published method.[13] As-prepared spheres in water were centrifuged and redispersed into ethanol giving PS spheres/ethanol dispersion with 1.2 vol%. According to the convective self-assembly technique[14] which relies on capillary forces,[15] we prepared PS colloidal crystals (PS-opal) supported on F-doped SnO_2 coated glasses (OTE) as described below. An OTE was vertically dipped into the PS spheres dispersion obtained above. Because the rapid evaporation of ethanol led to the poor uniformity of the thickness of the PS-opal, the dipped OTE was covered by a 200-mL beaker to slow the evaporation rate. After ethanol was evaporated for 5 days, an opalescent PS-opal with 3.0 μm average thickness was deposited on the OTE. The cathodic electrodeposition of ZnO was potentiostatically performed using 0.1 M zinc nitrate aqueous solution kept at 335 K with a BAS 100W (Bioanalytical Systems, Inc.) [Figure 1f].[16] The working electrode was a PS-opal/OTE (active area of 0.78 cm^2 exposed to the electrolyte). The counter electrode was a zinc sheet and the reference electrode was a Ag/AgCl in saturated KCl. After electrodeposition for 20 min at –1.0 V or for 5 h at –0.8 V, the templates were removed by dissolving in toluene for 48 h. The ZnO film/OTE was washed with deionized water and characterized by SEM and XRD.

Figure 1 shows SEM images of the original PS-opal and the macroporous ZnO. Figures 1b and 1c demonstrated that the ZnO films prepared at –1.0 V had honeycomb macroporous structures mirroring the ordered interstices of the templates (Figure 1a) and ZnO observed as bright spots at the interstices (Figure 1a, inset). Similar structured films could also be obtained at –1.1 V and –1.2 V. The smaller holes inside each macropore, which formed at the contact points between PS spheres, were clearly observed. And also, these holes were open at nearly all the contact parts of the macropores as judged by other SEM images taken at different five regions. The inset in Figure 1b is the Fourier transform of the image, in which the sharp peaks confirmed long-range order of the macropores. The frameworks around the macropores were confirmed to consist of wurtzite ZnO grains with ca. 65 nm crystallite size by XRD. The mean center-to-center distance between the macropores was smaller by 1.4% than the diameters of the original PS spheres. This shrinkage was very low compared to that of ca. 30 % of macroporous oxide ceramics obtained by sol–gel routes.[4a,4b] The low shrinkage should be due to the densely electrodeposited ZnO, which would not experience the significant shrinkage as observed for the sol–gel routes, in the interstices. As shown in Figure 1d, the complete filling was supported by the fact that even cracks in the template were filled with ZnO. As a result, thus obtained ZnO films were not broken into the smaller particles, which could be caused by the cracks formed in ZnO, and preserved the filmy form supported on OTE. From these results, it is concluded that the electrodeposition provides the oxide film with the long-range ordered macropores adhered to the substrates.

The long-range ordered porous ZnO films were obtained at

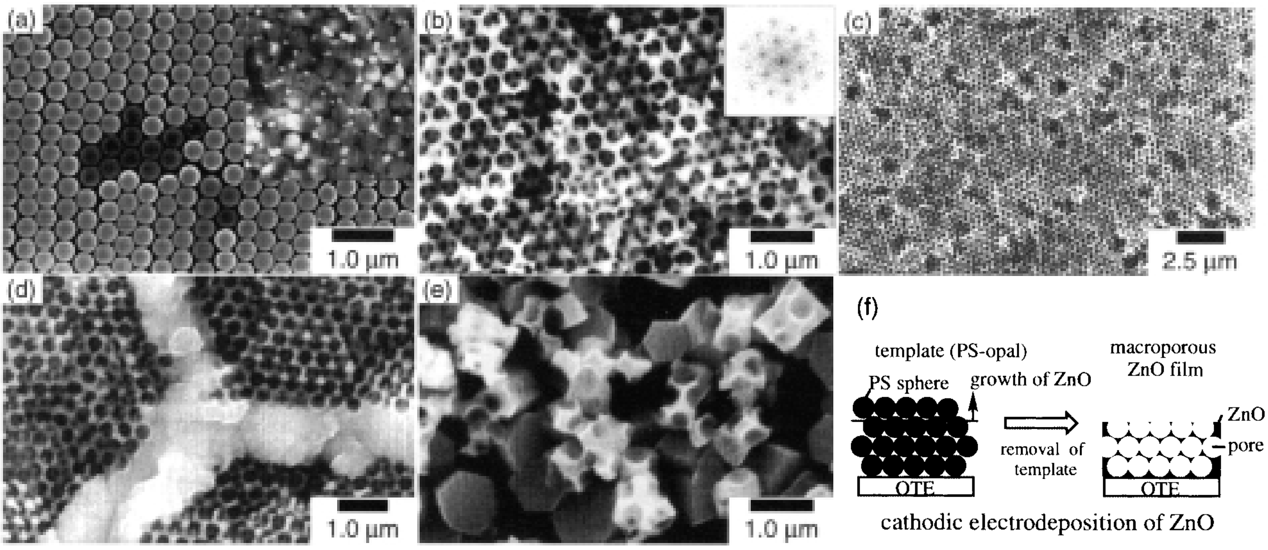

Figure 1. SEM images of the macroporous ZnO films made from polystyrene spheres of 368 nm diameter; (a) original template, (b) macroporous ZnO films obtained at -1.0 V, (c) lower magnification image of (b), (d) cracks filled with ZnO in the sample obtained at -1.0 V, (e) ZnO films prepared at -0.8 V and (f) schematic representation of the electrochemical colloidal crystal templating. The inset of (a) is the image of ZnO / PS-opal composite before removing the template by dissolving in toluene. The inset of (b) is the Fourier transform corresponding to the image (b).

–1.0 V as described above, while the large hexagonal ZnO grains disrupted the ordered structure at some areas in the case of –0.8 V (Figure 1e). It was reported in the literature[16] that the preferred growth of (002) plane of the larger hexagonal grains in ZnO film was obtained at anodic potentials from –0.7 to –0.9 V, though the degree of orientation decreased with decreasing the potentials, and that this preferred orientation was lost at –1.0 V. This explains well the behaviors of ZnO growth depending on the potentials in our system. That is, the PS-opal was not enough robust to confine the excess growth of the ZnO grains at –0.8 V in the interstices. The similar loss of the long-range order was also observed in the system of electrodeposited gold using PS-opal by Wijnhoven et al.[11b] In their report, it occurred because the surface tension of gold was larger than the van der Waals forces between the PS spheres, and therefore they successfully prepared the ordered macroporous gold using the robust sintered silica opal as a template, which was finally removed by HF aqueous solutions. However, considering that the HF solutions might damage both the substrate and the oxides, the PS-opals would be more suitable than the silica opals for oxides. Thus, when using the soft PS-opal as templates, the electrochemical conditions would be particularly important to prepare well ordered samples.

In conclusion, we have prepared the ordered macroporous ZnO by electrodeposition using the colloidal crystals. The electrodeposited ZnO was a film with large area of ~1 cm^2, which was more suitable for various applications than many particulate oxides previously reported.[4a,4b] And also, it was found that their range of order depended on the potentials related to the growth of the ZnO grains.

This work was supported in part by the Japan Society for the Promotion of Science as part of the "Research for the Future Program" and also by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

References

1 S. Peulon and D. Lincot, *Adv. Mater.*, **8**, 166 (1996).

2 a) C. G. Göltner, *Angew. Chem. Int. Ed.*, **38**, 3155 (1999). b) O. D. Velev and E. W. Kaler, *Adv. Mater.*, **12**, 531 (2000).

3 O. D. Velev, T. A. Jede, R. F. Lobo, and A. M. Lenhoff, *Nature*, **389**, 447 (1997).

4 a) B. T. Holland, C. F. Blanford, and A. Stein, *Science*, **281**, 538 (1998). b) J. E. G. J. Wijnhoven and W. L. Vos, *Science*, **281**, 802 (1998). c) G. Subramania, K. Constant, R. Biswas, M. M. Sigalas, and K. Ho, *Appl. Phys. Lett.*, **74**, 3933 (1999). d) G. Subramanian, V. N. Manoharan, J. D. Thorne, and D. J. Pine, *Adv. Mater.*, **11**, 1261 (1999). e) H. Yan, C. F. Blanford, B. T. Holland, W. H. Smyrl, and A. Stein, *Chem. Mater.*, **12**, 1134 (2000).

5 A. A. Zakhidov, R. H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. O. Dantas, J. Marti, and V. G. Ralchenko, *Science*, **282**, 897 (1998).

6 a) B. Gates, Y. Yin, and Y. Xia, *Chem. Mater.*, **11**, 2827 (1999). b) K. Yoshino, S. B. Lee, S. Tatsuhara, Y. Kawagishi, M. Ozaki, and A. A. Zakhidov, *Appl. Phys. Lett.*, **73**, 3506 (1998). c) P. Jiang, K. S. Hwang, D. M. Mittleman, J. F. Bertone, and V. L. Colvin, *J. Am. Chem. Soc.*, **121**, 11630 (1999). d) S. A. Johnson, P. J. Ollivier, and T. E. Mallouk, *Science*, **283**, 963 (1999).

7 a) O. D. Velev, P. M. Tessier, A. M. Lenhoff, and E. W. Kaler, *Nature*, **401**, 548 (1999). b) P. Jiang, J. Cizeron, J. F. Bertone, and V. L. Colvin, *J. Am. Chem. Soc.*, **121**, 7957 (1999). c) H. Yan, C. F. Blanford, B. T. Holland, M. Parent, W. H. Smyrl, and A. Stein, *Adv. Mater.*, **11**, 1003 (1999).

8 a) Y. A. Vlasov, N. Yao, and D. J. Norris, *Adv. Mater.*, **11**, 165 (1999). b) A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader, and H. M. van Driel, *Nature*, **405**, 437 (2000).

9 J. A. Switzer, C.-J. Hung, B. E. Breyfogle, M. G. Shumsky, R. van Leeuwen, and T. D. Golden, *Science*, **264**, 1573 (1994).

10 P. V. Braun and P. Wiltzius, *Nature*, **402**, 603 (1999).

11 a) L. Xu, W. L. Zhou, C. Frommen, R. H. Baughman, A. A. Zakhidov, L. Malkinski, J.-Q. Wang, and J. B. Wiley, *Chem. Commun.*, **2000**, 997. b) J. E. G. J. Wijnhoven, S. J. M. Zevenhuizen, M. A. Hendriks, D. Vanmaekelbergh, J. J. Kelly, and W. L. Vos, *Adv. Mater.*, **12**, 888 (2000). c) P. N. Bartlett, P. R. Birkin, and M. A. Ghanem, *Chem. Commun.*, **2000**, 1671.

12 T. Sumida, Y. Wada, T. Kitamura, and S. Yanagida, *Chem. Commun.*, **2000**, 1613.

13 J. W. Goodwin, J. Hearn, C. C. Ho, and R. H. Ottewill, *Colloid Polym. Sci.*, **252**, 464 (1974).

14 P. Jiang, J. F. Bertone, K. S. Hwang, and V. L. Colvin, *Chem. Mater.*, **11**, 2132 (1999).

15 N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, and K. Nagayama, *Nature*, **361**, 26 (1993).

16 M. Izaki and T. Omi, *Appl. Phys. Lett.*, **68**, 2439 (1996).