Highly ordered TiO₂ nano-pore arrays fabricated from a novel polymethylmethacrylate/polydimethylsiloxane soft template

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A novel soft polymer template containing a double-layer structure, which includes a thin layer of polymethylmethacrylate (PMMA) used as a pattern layer and a thicker layer of polydimethylsiloxane (PDMS) used as a back layer, was fabricated from a replica molding process. Anodic aluminum oxide (AAO) template was used as the replica mold to be replicated to the polymethylmethacrylate layer by a thermal infiltration process under a vacuum condition. Results indicate that PMMA/PDMS soft templates with different sizes could be easily fabricated from the as-prepared AAO replica mold. The PMMA/PDMS soft templates were then employed to imprint a TiO₂ gel for achieving TiO₂ nano-pore arrays. After the imprinting process, the PDMS layer was firstly peeled off and the PMMA layer was then removed into acetonitrile, which can avoid any demolding problems like damages or distortions. The TiO₂ nano-pore arrays with the crystalline of anatase could be obtained at a heat treatment temperature of 450°C.

Since the concept of nanoimprint was first proposed by Chou and his coworkers [1], this unique way of fabricating micro- and nanoscale patterns has attracted more and more attentions in recent years. As compared to conventional lithography methods of fabricating micro- or nanopatterns, such as electron-beam lithography [2], X-ray lithography [3], and extreme ultraviolet lithography [4], nanoimprint has the advantages of high throughput, high resolution, the simplicity and capability to replicate nanostructures into various kinds of materials by mechanical contact and three dimensional material displacement [5]. Among a variety of nanoimprint solutions, soft lithography technique employs rubber-elastic stamps or masks with a pattern defined in their surface topography. The soft technique has the advantages that it can avoid brittle failure and permanent deformation as compared to hard template imprinting and the soft template can contact substrate conformably, that is to say, it can achieve an intimate contact without voids between the elastomeric stamp and the substrate [6]. However, up to now, the fabrication of the soft template still relies on the opposite hard template obtained by the traditional photolithography ways mentioned above, which are expensive and low-throughput process. Namely, the fabrication of the soft template is still limited by conventional micro-nano fabrication methods. Therefore, it is of great interest and significance to find a simple and low-cost way to obtain the soft template for nanoimprinting applications.

Currently, a well-known self-organized material called anodic aluminum oxide (AAO) has been used to prepare one-dimension (1-D) nanowires, nanopillars, nanotubes of different materials for various applications [7-10]. As one knows, AAO is a mature material, the nano-size of which can be adjustable by changing the anodization conditions [11-14]. Here, we describe a novel and simple method to fabricate a soft template for nanoimprinting. The fabricated soft template contains a double-layer structure, for which a thin layer of polymethylmethacrylate (PMMA) is used as the nanopattern layer and a thicker layer of polydimethylsiloxane (PDMS) is used for the back layer. Anodic aluminum oxide AAO template

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is used as the replica mold to be replicated to the PMMA layer by a thermal infiltration process under a vacuum condition. It should be stressed here that the bi-layer structure can make full use of the advantages of the two different materials [15], which PMMA can achieve a high resolution since the compression modulus is as high as 2~3 GPa and PDMS is soft enough to ensure the conformal contact between the template and the substrate during the imprinting process. Then, the as-fabricated novel PMMA/PDMS polymer soft template was employed by a nanoimprint process to fabricate highly ordered TiO_2 nano-pore arrays on substrates, which are potential in applications of photovoltaic, photo-catalysts and biomedicine [16-19].

Two kinds of AAO templates were fabricated by employing different acid electrolytes. One was fabricated in 0.3 M oxalic acid, and the other was fabricated in 10 wt% phosphoric acid. A two-step anodization method was then employed to fabricate the AAO templates. Namely, the first anodization lasted 1 h in 0.3 M oxalic acid at an anodization voltage of 40 V at 5°C or in 10 wt% phosphoric acid at an anodization voltage of 160 V at 2°C. The second anodization time was dependent on the pore depth of the AAO template needed.

PMMA (350 kg/mol, Alfa Aesar) was firstly dissolved in chlorobenzene and then the obtained solution was carefully poured onto the surface above-obtained AAO template. Secondly, the sample was immediately put in a vacuum oven and heated at a temperature of 200°C for 4 h. Thirdly, a thick

layer of PDMS (Dowcorning Sylgard 184) was casted onto the surface of the obtained AAO/PMMA sample and cured at 90°C for 50 min. Fourthly, the AAO and the aluminum substrate were completely removed by putting the sample in 10 wt% NaOH aqueous solution, and subsequently washed in a sequence of deionized water, HCl aqueous solution and deionized water, respectively. Finally, the samples were dried at room temperature and thus the PMMA/PDMS hybrid soft template was fabricated.

Sol-gel process was employed to obtain the TiO_2 imprinted material [20-22]. For the nanoimprint, the fabricated PMMA/PDMS soft template was used to imprint the TiO_2 wet gel against a substrate. After the nanoimprinting process, the soft PDMS back layer was firstly peeled off and the PMMA layer was then removed into acetonitrile to dissolve the PMMA pattern layer directly. Thus, the highly ordered TiO_2 nano-pore arrays on a substrate were achieved. Figure 1 shows the schematic diagram of the fabrication process of the PMMA/PDMS soft template. A field emission scanning electron microscopy (JSM-6700F, JEOL Inc., Japan) was used to observe the morphologies of the AAO template, the PMMA/PDMS soft template and the TiO_2 nano-pore arrays. A D/max 2400 X Series X-ray diffractometer was employed to characterize the phase structures of the TiO_2 nano-pore arrays.

Figure 2 shows SEM images of the fabricated AAO templates, which are anodized in 0.3 M oxalic acid at an anodization voltage of 40 V at 5°C and in 10 wt% phosphoric acid at an anodization voltage of 160 V at 2°C, respectively. The diameter and the inter-pore distance of the AAO template
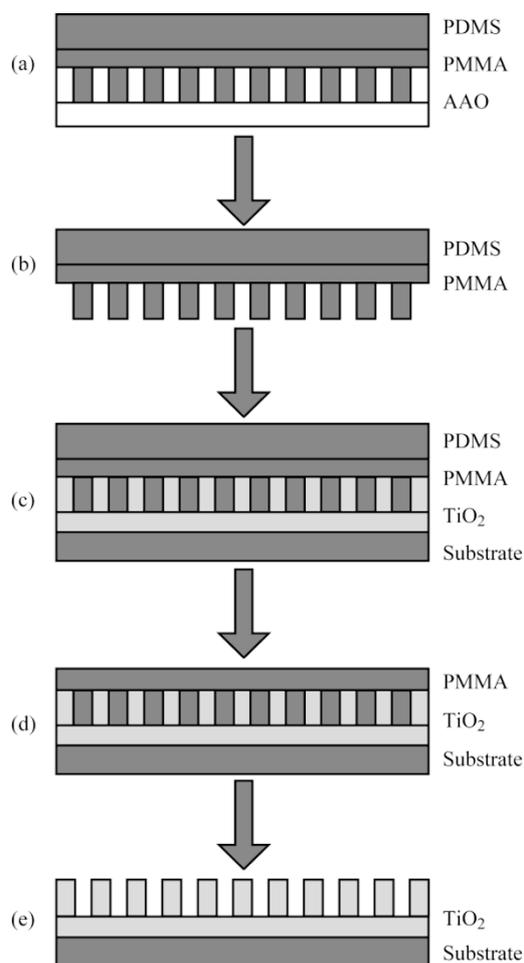

FIG. 1. Schematic diagram of the preparation procedures of the highly ordered TiO_2 nano-pore arrays.
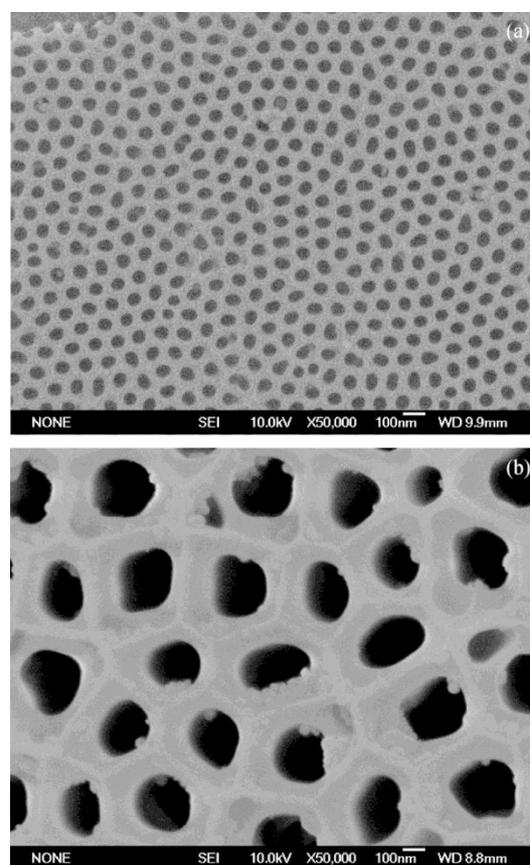

FIG. 2. SEM images of the AAO templates obtained: (a) in oxalic acid at an anodization voltage of 40 V at 5°C; (b) in phosphoric acid at an anodization voltage of 160 V at 2°C.
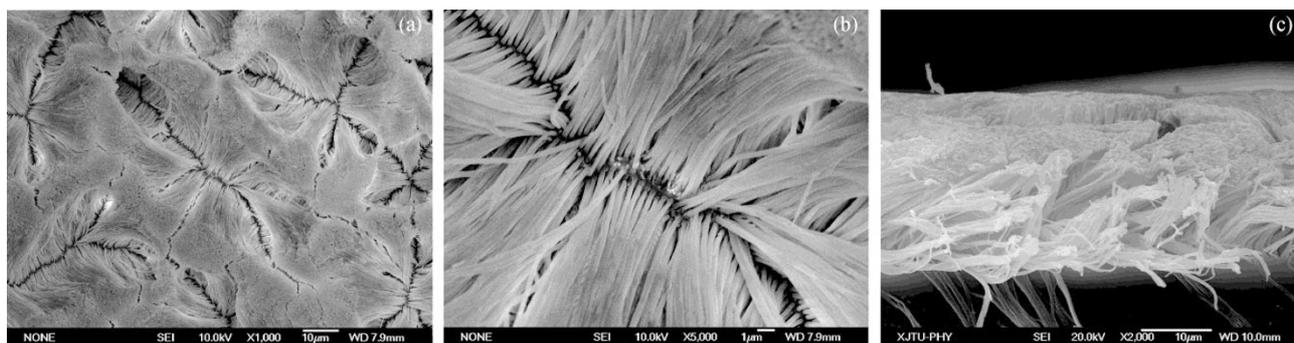
FIG. 3. Top view images of the PMMA nanowires obtained from the AAO template with the second anodization time of 4.5 h with a low magnification (a) and with a high magnification (b); (c) cross-sectional image of the PMMA nanowires.

obtained from the oxalic acid are about 65 nm and 100 nm as shown in Fig. 2(a), and those of the AAO template obtained from phosphoric acid are about 300 nm and 450 nm as shown in Fig. 2(b), respectively. It should be mentioned here that the pore depth of the fabricated AAO templates can be adjusted through varying the second anodization time.

Figure 3(a) shows top view image of the PMMA nanowires obtained from the AAO template with the second anodization time of 4.5 h. It can be observed that the obtained PMMA nanowires not only do not stand up separately, but also they do an accumulation. It is probably related to that the PMMA nanowires are too long to stand up separately, which leads to an accumulation due to the surface tension of the pillars since the pore depth of the initial AAO template is more than 10 μm. Figure 3(b) is the high magnification SEM photograph of the as-prepared PMMA nanowires, and Fig. 3(c) is the cross-sectional view. In order to achieve an ordered PMMA nanopillar array, the pore depth of the AAO template has to be adjusted to a suitable value by controlling the second anodization conditions, so that the PMMA nanopillars can stand up separately. Figure 4 shows the SEM images of the PMMA nanopillars obtained from the AAO template as shown in Fig. 2(b) for different second anodization time. It can be seen from Fig. 4 that the size of the PMMA nanopillars matches well with that of the initial AAO template as shown in Fig. 2(b). For the sample with the second anodization time of 2 min as shown in Fig. 4(a), the PMMA nanopillars seem all standing up separately and show the ordered PMMA nanopillar arrays. However, with increase the second anodization time to 5 min as shown in Fig. 4(b), the PMMA nanopillars start to appear a bit of aggregation in some spots. With further increase the second

anodization time to 8 min, the aggregation looks more apparent as shown in Fig. 4(c). These results indicate that the longer the second anodization time is, the more obvious the aggregation takes place. For example, Fig. 3 looks like noodles due to too long second anodization time.

Figure 5(a) shows the SEM images of the PMMA nanopillars obtained from the AAO template as shown in Fig. 2(a) for 2-min second anodization time. It can be seen that the ordered PMMA nanopillar arrays look very regular and the size of the PMMA nanopillars matches well with that of the initial AAO template as shown in Fig. 2(a), indicating that the replica process from AAO to PMMA is successful. It can be also found that some contamination can be clearly observed on the surface of the PMMA nanopillar arrays as shown in Fig. 5(b). Presumably, the observed contamination should be related to $Al(OH)_3$ resulted from NaOH solution during removing process of the AAO template and the aluminum substrate. It is also noted that the observed contamination can be easily removed by soaking the contaminated sample into HCl aqueous solution as shown in Fig. 5(a). In addition, some occasional big holes are also observed on the surface of the PMMA nanopillar arrays, which is probably related to the following two reasons. One possible reason is due to the blocking induced by the corresponding AAO surface contamination, and the other possible reason is due to the air bubbles remaining inside the PMMA solution. In order to avoid these problems, besides the careful post-treatment of the AAO templates, putting the PMMA solution in vacuum for some time before being poured onto the AAO surface is very important and necessary, so that the remaining air bubbles inside the PMMA can be removed completely.
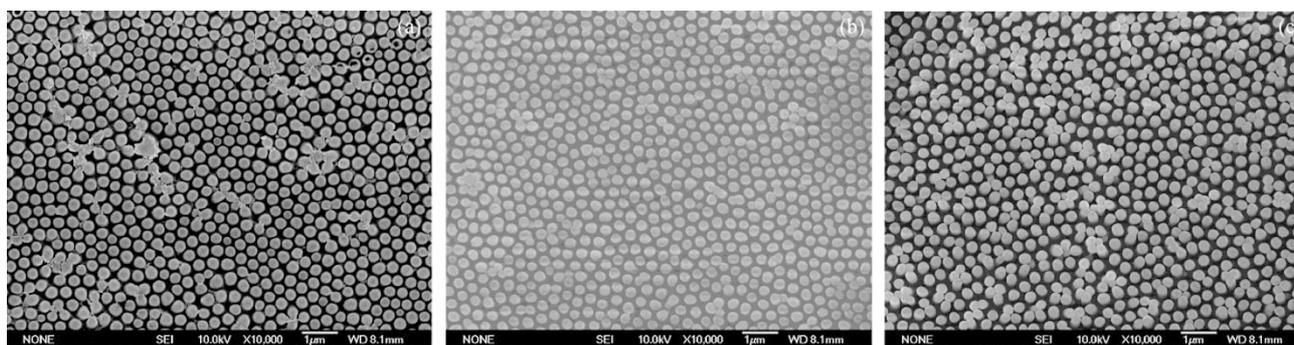

FIG. 4. SEM images of the PMMA nanopillar arrays obtained from the AAO anodized in phosphoric acid at an anodization voltage of 160 V at 2°C and the second anodization time of: (a) 2 min, (b) 5 min, and (c) 8 min.
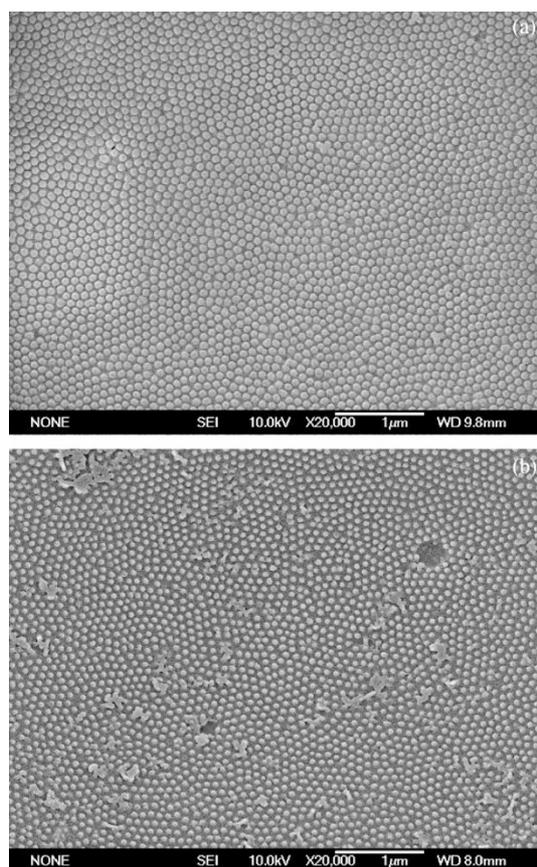
FIG. 5. SEM images of the PMMA nanopillar arrays fabricated (a) from the AAO template obtained in 0.3 M oxalic acid electrolyte at an anodization voltage of 40 V at 5°C; (b) surface morphology of the PMMA nanopillar arrays with some contamination.

It should be mentioned here that PMMA is chosen as the nanopattern layer in this hybrid soft template for nanoimprint due to the following reasons: (1) PMMA can achieve a high resolution since it is stiffer than most polymer materials, as compared the resolution of the common used PDMS (below 100 nm) which makes hard to obtain those complicated patterns other than simple 1-D gratings. Although we only present the PMMA nanopillar arrays with pillar diameter of 65 nm obtained from the oxalic acid electrolyte as shown in Fig. 5, It is also possible that even a higher resolution with a pillar diameter of 20~30 nm could be also achieved if the sulfuric acid electrolyte is used instead of the oxalic acid or phosphoric acid electrolyte. (2) PMMA is highly processible that it can be easily dissolved in some organic solvents like chlorobenzene, and it can be readily filled into the AAO with small pores by using a heat infiltration method under a vacuum condition. (3) PMMA is durable in caustic solutions of NaOH or HCl, which is critical for complete preservation of nanostructure with such a wet chemical method instead of traditional demolding ways. (4) PMMA has a high surface energy that it can stick to the imprinted TiO_2 nano-structures strongly after the imprinting pressure is released and the PDMS layer is easily peeled off, which can protect TiO_2 nano-structures as compared to the conventional demolding process. In addition, the thicker PDMS layer as the back layer is soft enough to ensure a conformal contact between the soft polymer template and the substrate

during the nanoimprint process and can be more easily manipulated.

Considering that the T_g of PMMA is about 105°C, the imprinting process should be below such a temperature, otherwise, the PMMA nano-pillar might be softening. In order to make the imprinted TiO_2 nano-structure become solid, a proper imprinting period should be taken corresponding to different temperatures. In addition, the pressure should be below the critical value, which the PMMA nano-pillars can bear, and the concentration of the TiO_2 sol-gel precursor should be in a proper range. After plenty of experiments, a group of optimal variables are carried out in the imprinting process. During the imprinting process, the PMMA/PDMS soft templates are employed to imprint a TiO2 gel against a substrate at 80°C for 3 h under a pressure of 3 bars. Figure 6 shows a SEM image of the imprinted TiO2 nano-pore arrays under present conditions. It can be seen that a few imperfect spots such as not round pores still exist, but the imprinted TiO2 nano-pore arrays seem highly ordered, which resembles the initial AAO pore arrays as shown in Fig. 2(a). It is also noted that the diameter and the inter-pore distance of the imprinted TiO2 nano-pore arrays are almost the same with those of the initial AAO mold, which are about 65 nm and 100 nm, respectively. Our results indicate that the TiO2 nano-pore arrays with an anatase crystalline property can be easily obtained after a heat treatment at 450°C for 30 min as shown in Fig. 7. It should be mentioned here that the
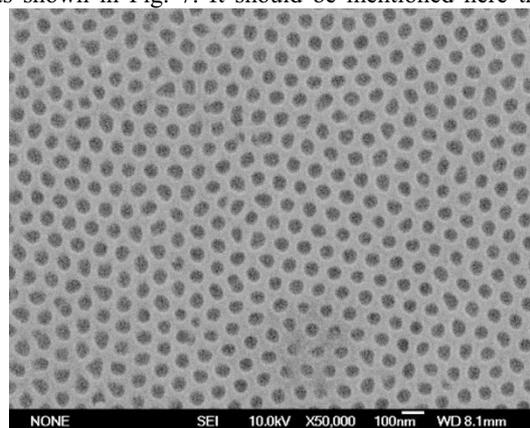

FIG. 6. SEM image of the imprinted regular TiO_2 nano-pore arrays on a substrate by the as-fabricated PMMA/PDMS soft template as shown in Fig. 3(a).
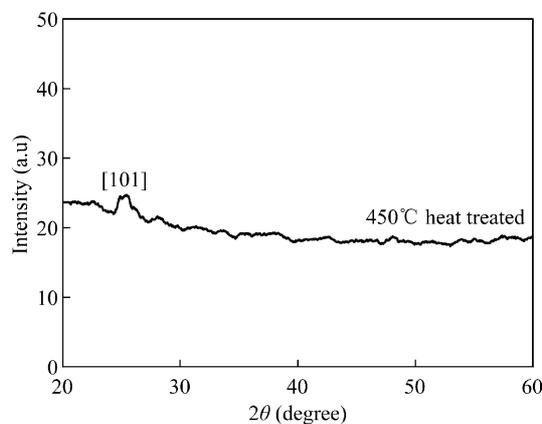

FIG. 7. XRD result of the imprinted TiO_2 nano-pore arrays after 450°C calcination for 30 min.

TiO2 nano-pore arrays appear a little shrinkage after a heat treatment of 450°C, which is probably related to the removal of the solvent and the organic components, as well as the structural change due to the crystallizing process. It can be concluded based on above these results that the as-fabricated PMMA/PDMS soft template has the advantages of cost-effective, high resolution, large-scale, adjustable nano-sizes and short processing time, indicating that this unique way of patterning would be a considerable option for nanoimprint process. For example, the TiO_2 sol-gel precursor can be imprinted against a substrate to form regular TiO_2 nano-pore arrays, which are potential applications for clean energy and environment, as shown in Fig. 6 by using this PMMA/PDMS soft template. In addition, this method reported here might be helpful to obtain other functional polymer nanopillar array applications such as anti-reflection, luminescence and so on [23-26].

The PMMA/PDMS soft templates for nanoimprint TiO_2 nano-pore arrays have been fabricated by the replica molding process from the AAO mold. This soft template contains a double layer structure including the PMMA patterning layer and the PDMS back layer, which takes advantage of the two different polymer materials. Results indicate that the AAO molds with different nano-sizes can be easily fabricated by controlling the anodization conditions and then they can also be easily replicated to achieve the corresponding PMMA/PDMS soft templates with different nano-sizes, which were fabricated by using the thermal infiltration method under a vacuum environment. At the optimal conditions, highly ordered TiO_2 nano-pore arrays have been successfully achieved by combining the fabricated PMMA/PDMS soft template with a nanoimprint process. This way of obtaining highly ordered TiO_2 nano-structured arrays might be universal, helpful, and potential in nanofabrication, nanopatterning and nanostructure applications of other materials.

References

1. S. Y. Chou, P. R. Krauss and P. J. Renstrom, Appl. Phys. Lett. 67, 3114 (1995). doi:10.1063/1.114851
2. H. Schulz, D. Lyebyedyev and H. C. Scheer, J. Vac. Sci. Technol. B 18, 3582 (2000). doi:10.1116/1.1319821
3. M. Tormen, L. Businaro and M. Altissimo, Microelectron. Eng. 73-74, 535 (2004). doi:10.1016/S0167-9317(04)00134-0
4. S. Park, S. Saxer, C. Padeste, H. H. Solak, J. Gobrecht and H. Schift, Microelectron. Eng. 78-79, 682 (2005). doi:10.1016/j.mee.2004.12.085
5. H. Schift and J. Vac, Sci. Technol. B 26, 458 (2008). doi:10.1116/1.2890972
6. A. Bietscha and B. Michel, J. Appl. Phys. 88, 4310 (2000). doi:10.1063/1.1289816
7. K. Liu, S. Fournier Bidoz, G. A. Ozin and I. Manners, Chem. Mater. 21, 1781 (2009). doi:10.1021/cm900164b
8. Cao. Y and T. E. Mallouk, Chem. Mater. 20, 5260 (2008). doi:10.1021/cm801028a
9. A. Johansson, E. Widenkvist, J. Lu, M. Boman and U. Jansson, Nano. Lett. 5, 1603 (2005). doi:10.1021/nl050964u
10. D. Guo, L. Fan, J. Sang. Y. Liu, S. Huang and X. Zou, Nanotechnology 18, 405304 (2007). doi:10.1088/0957-4484/18/40/405304
11. A. P. Li, F. Muller, A. Birner, K. Nielsch and U. Gosele, J. Appl. Phys. 84, 6023 (1998). doi:10.1063/1.368911
12. H. Masuda and K. Fukuda, Science 268, 1466 (1995). doi:10.1126/science.268.5216.1466
13. O. Jessensky, F. Muller and U. Gosele, Appl. Phys. Lett. 72, 1173 (1998). doi:10.1063/1.121004
14. H. Masuda, K. Yada and A. Osaka, Jpn. J. Appl. Phys. 37, 1340 (1998). doi:10.1143/JJAP.37.L1340
15. C. Goh, K. M. Coakley and M. D. McGehee, Nano Lett. 5, 1545 (2005). doi:10.1021/nl050704c
16. S. S. Williams, M. J. Hampton, V. Gowrishankar and I. Ding. Chem. Mater. 20, 5229 (2008). doi:10.1021/cm800729q
17. S. Banerjee, S. K. Mohapatra, M. Misra and I. B. Mishra. Nanotech. 20, 075502 (2009). doi:10.1088/0957-4484/20/7/075502
18. D. Wang, Y. Liu, B. Yu, F. Zhou and W. Liu. Chem. Mater. 21, 1198 (2009). doi:10.1021/cm802384y
19. A. Schroeder, G. Francz and A. Bruinink, Biomaterials 21, 449 (2000). doi:10.1016/S0142-9612(99)00135-0
20. W. X. Que, A. Uddin and X. Hu, J. Power Sources 159, 353 (2006). doi:10.1016/j.jpowsour.2006.04.009
21. M. J. Alam and D. C. Cameron, J. Sol-Gel Sci. Tech. 25, 137 (2002).
22. K. Pomoni, A. Vomvas and C. Trapalis, Thin Solid Films 479, 160 (2005). doi:10.1016/j.tsf.2004.12.005
23. T. Yanagishita, T. Kondo, K. Nishio and H. Masuda, J. Vac. Sci. Tech. B 26, 1856 (2008). doi:10.1116/1.2998731
24. M. Aryal, F. Buyukserin, K. Mielczarek, X. M. Zhao and J. M. Gao, J. Vac. Sci. Tech. B 26, 2562 (2008). doi:10.1116/1.2981076
25. D. Cheyns, K. Vasseur, C. Rolin, J. Genoe, A. Poortmans and J. P. Heremans, Nanotechnology 19, 424016 (2008). doi:10.1088/0957-4484/19/42/424016
26. E. Mele and A. Camposeo, Small 4, 1894 (2008). doi:10.1002/smll.200800210