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Control of wetting on Ti-based bulk metallic glass surfaces by a hydrothermal method

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Abstract The surfaces of the Ti-based bulk metallic glasses ($Ti_{50}Ni_{20}Cu_{25}Sn_5$) were modified by a hydrothermal method using sodium hydroxide (NaOH) solution, and the surface wettability was investigated. No reflections were observed in the XRD patterns of the NaOH-treated samples even though there was a clear change of the color, indicating formation of amorphous oxide phases. The Raman spectra showed peaks attributed to sodium titanate compounds (Na–O–Ti) and titanium oxide. Some of the samples were observed to have a very rough surface microstructure such as a "house-of-cards" or leaf-like structure. The water contact angle of the treated samples decreased with increasing treatment temperature and time. These results indicate that the wettability of the sample surface was able to be controlled from hydrophobic to hydrophilic by changing the conditions of the hydrothermal treatment.

Introduction

Bulk metallic glasses (BMGs) were discovered in 1988 [1], and soon afterward, many kinds of BMG began to be reported [2–6]. BMGs have been studied extensively because of their excellent physical, mechanical, and chemical properties, which make them attractive for engineering applications [7–11]. Most of the studies were, however, focused on the preparation and characterization of the mechanical and magnetic properties of BMGs, but barely any study has reported on surface properties such as wettability.

Wettability is an important property of a solid surface and plays an important role in daily life, industry, agriculture, biological processes, and so on [12]. Zhao et al. [13] prepared a superamphiphobic CaLi-based BMG surface using a facile water-etching and chemical-coating method. Owing to the combination of the surface roughness and the low surface free energy, the prepared BMG surface exhibited stable superhydrophobic and superoleophobic properties and improved corrosion resistance, which may extend the practical applications of BMG materials [14, 15]. However, little study has reported on the preparation of hydrophilic BMG surfaces, even though this is one of the important factors for the bonding between heterogeneous materials. Since BMG surfaces generally have poor wettability because of their high chemical stability, modification and control of the wettability of BMG surfaces is considered to be important to extend their applications.

In this article, hydrothermal treatment using a NaOH solution was adopted for the preparation of hydrophilic BMG surfaces, because it is important to avoid crystallization of BMGs by heating above the glass transition temperature, degrading the mechanical properties.

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The surfaces of the resulting NaOH-treated BMGs were characterized by XRD, SEM, and Vis-Raman, and the wettabilities were evaluated by the water contact angles.

Experiment

The chemical composition of the BMG samples used was $Ti_{50}Ni_{20}Cu_{25}Sn_5$. They were treated by a hydrothermal method using a Teflon-lined stainless steel autoclave (80 mL). In the treatments, a rectangular plate of BGM with dimensions of 10 × 15 × 0.1 mm was introduced into an autoclave filled with 40 mL of a 1.0 M NaOH solution and treated at 120, 150, and 180 °C for 1, 3, 6, and 12 h. After gradually cooling down the autoclave to room temperature, the samples were washed with ultrapure water to remove residual sodium ions from the surface and dried at 80 °C.

The surface microstructure of the samples was examined by field emission-scanning electron microscopy (FE-SEM, S-4500; Hitachi, Japan) at an acceleration voltage of 15 kV. The crystalline phase was evaluated by a high power X-ray diffractometer (XRD, RINT-TTR3B; Rigaku, Japan) using monochromated Cu Kα radiation. The applied power was 50 kV–200 mA. The chemical composition of the samples was analyzed by an energy dispersive X-ray spectrometer (EDX, SIGMA; Kevex, U.S.A.). The surfaces of the treated samples were analyzed using a Raman spectroscopy (RAMANOR T64000; Jobin–Yvon S.A.S., France) with an Ar laser (514.5 nm) operated at 50 mW. The average surface roughness (R_a) of the samples (area size: $20 \times 20\ \mu m^2$) was evaluated using atomic force microscopy (AFM, JSPM-5200; JEOL, Japan) in the tapping mode using a conventional Si cantilever. The wettability of the sample surfaces was evaluated from the water contact angle (θ) using a commercial automatic contact angle system (Model DM-SA; Kyowa Interfaces Science, Japan). The water droplet volume used for the measurements was 3.0 μL. The values obtained were averages of triplicate measurements.

Titania nanosheets were coated on the BMG surfaces with and without the hydrothermal treatment as one of the experiments to validate the bonding with ceramics. Colloidal titania nanosheets of $Ti_{0.91}O_2$ were synthesized by exfoliating layered titanate of $Cs_{0.7}Ti_{1.825}O_4$ through a soft-chemical process [16]. The colloidal solution was then coated on the BMG surfaces with and without the hydrothermal treatment by dip coating. After coating, both samples were heated at 400 °C for 1 h.

Results and discussion

Figure 1 shows SEM images of the prepared sample surfaces. When the hydrothermal treatment time was 1 h, the surfaces were covered with many tiny nanorods intertwined

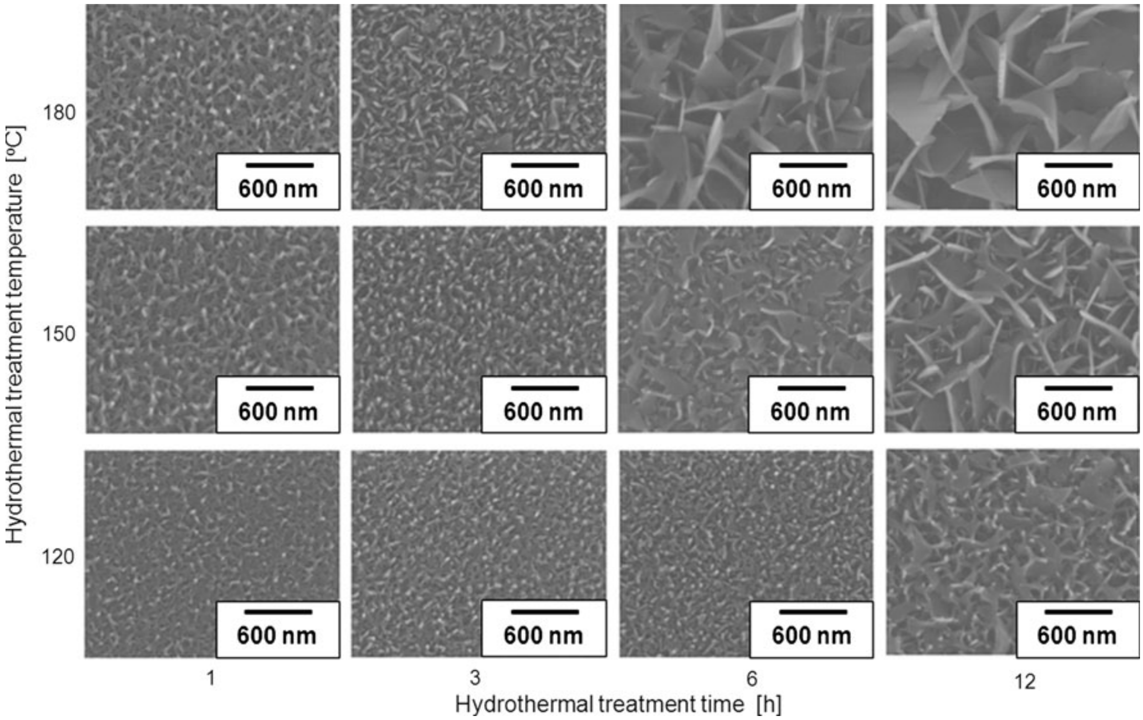


Fig. 1 SEM images of the sample surfaces treated under various hydrothermal conditions

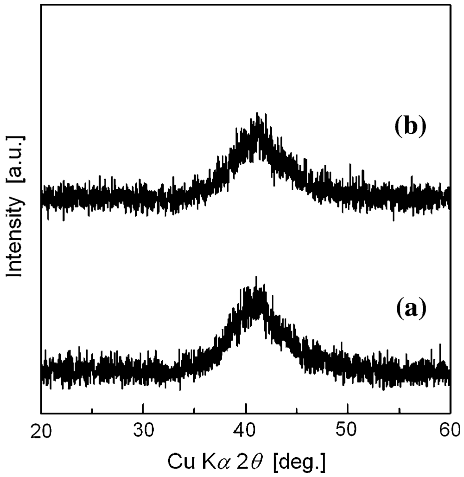


Fig. 2 XRD patterns of the samples; **a** non-treated BMG ($Ti_{50}Ni_{20}Cu_{25}Sn_5$) and **b** hydrothermally treated at 180 °C for 12 h

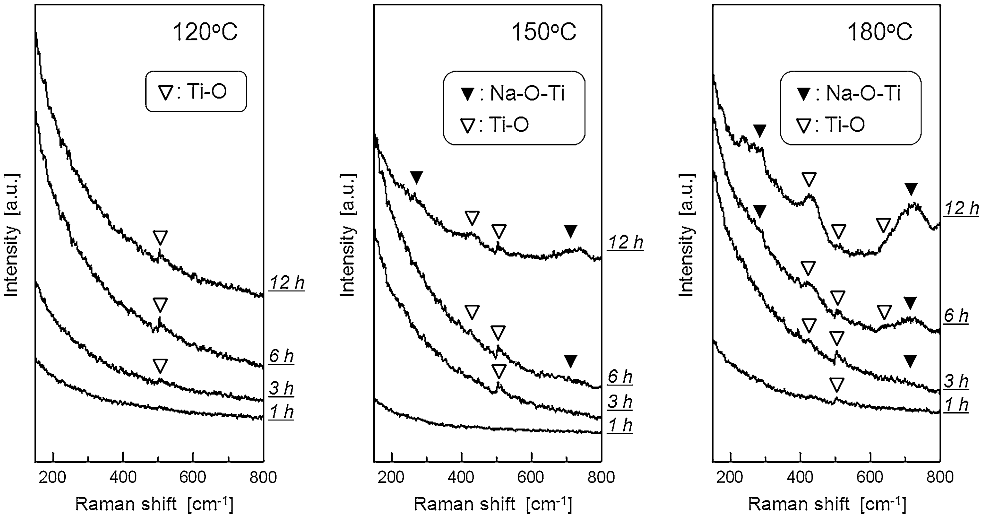
intricately, the so-called wire and/or net-like structure. With increasing hydrothermal treatment temperatures and times, the contacted nanorods coalesced with each other and got converted to thin nanosheets with growing sizes. It is thought that some components in the BMG are dissolved in the solution and some compounds are precipitated on the surface. The surface roughness increased with increasing temperature and longer time of treatment, and the surface texture changed from wire and net-like structure to those of house-of-card-like.

Figure 2 shows the XRD patterns of untreated BMGs and those treated at 180 °C for 12 h. Both samples had no clear reflections but a halo at $2\theta \cong 40°$. All of the other hydrothermally treated samples showed similar results. Thus, no crystallization of BMG occurred because of the present hydrothermal treatments.

The Raman spectra of the treated samples are shown in Fig. 3. When the treatment temperature was 120 °C and the treatment time greater than 3 h, a weak peak was observed at 504 cm^{-1}, which is assigned to the surface-oxidized layer of Ti. In the samples treated at 150 °C and 180 °C, peaks assigned, respectively, to Ti–O and Ti–O–Ti in the anatase structure were observed and became clearer with increasing treatment time. The peaks at 290 cm^{-1} and 660–770 cm^{-1} are suggested to be assigned to Na–O–Ti bonds, as reported for Na_2O–TiO_2 glass [17]. Kasuga et al. [18] suggested that NaOH treatment tended to break a portion of the Ti–O–Ti bonds in TiO_2 and form Ti–O–Na and Ti–OH bonds. Peaks assigned to Ti–O–Na bonds were detected in the samples treated for longer time at 180 °C. The surface texture of the samples showing formation of Ti–O–Na bonds was found to have a house-of-card-like structure. Therefore, it is considered that the resulting nanosheets can be attributed to a sodium titanate compound with a layered structure because no other elements in the BMG (Ni, Cu, and Sn) except for Ti were detected.

Figure 4a shows the changes of the contents of all elements detected in the samples as a function of treatment time at 180 °C. With increasing treatment time, Ti, Cu, and Sn decreased while O and Na increased. The treated BMG is, thus, considered to be oxidized and to have reacted with Na ions. From the composition analysis of the sample treated for 12 h, the chemical formula of the formed sodium titanate is determined to be $Na_2Ti_6O_{13}$. Meng et al. [19] reported that $Na_2Ti_6O_{13}$ crystals tend to grow along the [010] direction to develop nanowires and subsequently to grow into plate-like particles, because its structure is characterized by layers with rectangular tunnels. This morphological change was compatible with the present samples, as shown in Fig. 1. Figure 4b shows the changes of the contents of Ti, Ni, Cu, and Sn, which are the main constituents of the BMG, as a function of hydrothermal time at 180 °C. In the initial stage, after a 1-h treatment, only the Ti content decreased, while those of other

Fig. 3 Raman spectra of the samples treated under various hydrothermal conditions



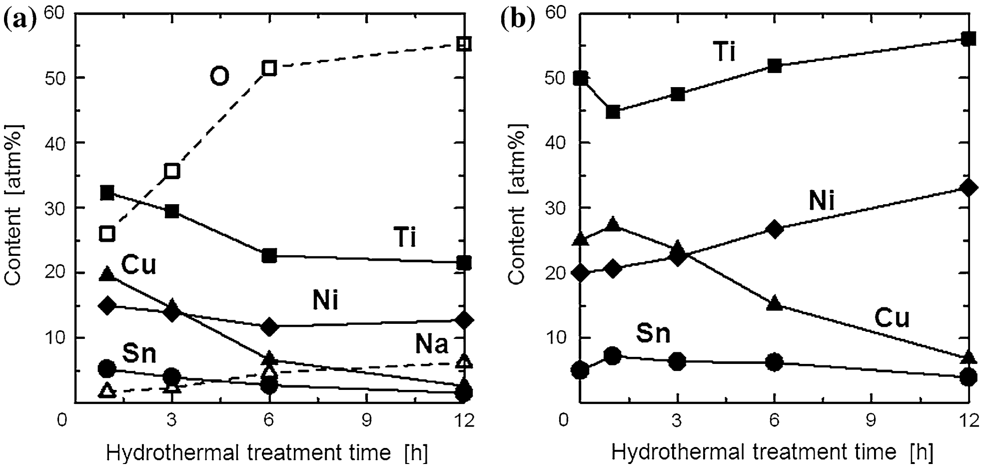


Fig. 4 Changes of elemental contents of the sample surfaces treated at 180 °C as a function of treatment time; **a** all elements detected in the sample and **b** constituent elements of the BMG

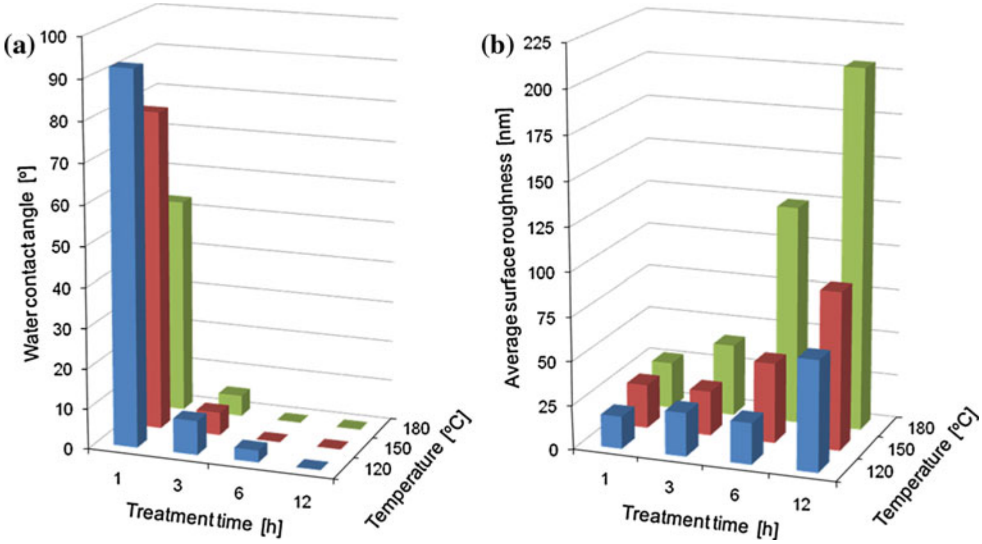


Fig. 5 Water contact angles (**a**) and the average surface roughness values (**b**) of the samples treated at various hydrothermal temperatures for various times

elements, i.e., Cu, Sn and Ni, increased. With increasing time, however, these trends reversed, and the Ti and Ni contents increased monotonically, while the Cu content decreased. Therefore, the surfaces of the BMG became enriched with Ti and Ni after the hydrothermal treatment. Such tendencies are compatible with the published data [10].

Figure 5 shows the water contact angles (Fig. 5a) and average surface roughness (R_a) values (Fig. 5b) of the BMG samples treated under various hydrothermal conditions. The water contact angle of the BMG before hydrothermal treatment was 93.5°, which is regarded as poor wettability. When the treatment time was 1 h, the contact angle values were still large. However, the contact angles drastically decreased after a hydrothermal treatment of 3 h and further gradually decreased with higher hydrothermal temperatures and longer times. As a result, they decreased to less than 5° (superhydrophilicity) after treatments longer than 6 h at 120 °C or longer than 3 h at 150° and 180 °C. The samples that showed superhydrophilicity corresponded well with the formation of the house-of-cards nanotexture, as shown in Fig. 1. These results indicate that the wettability of the BMG surface is able to be greatly improved by hydrothermal treatment, which forms the house-of-card-like nanotexture.

The R_a values of the samples treated under various hydrothermal conditions are shown in Fig. 5b. They show only a gradual increase under mild hydrothermal conditions but showed drastic increases with further treatment. Such changes show different tendencies compared with those of the water contact angles shown in Fig. 5a. The improvement of wettability can be explained not only by the surface nanotexture change but also by other factors.

A possible model to explain the surface modification and microstructure development by the present hydrothermal treatments is schematically shown in Fig. 6. As-prepared BMG has a flat, chemically stable hydrophobic surface, and a water droplet cannot spread out on the surface. After hydrothermal treatment for 1 h, Ti dissolves more selectively than the other elements in the BMG. Although the surface becomes porous, the wettability is not

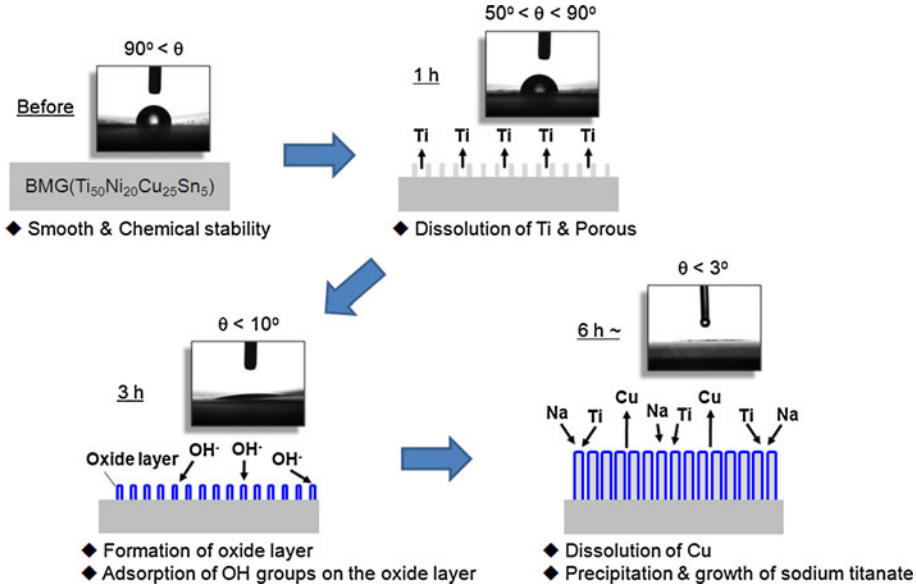


Fig. 6 Schematic illustrations of the surface modification and microstructure generation model by hydrothermal treatment

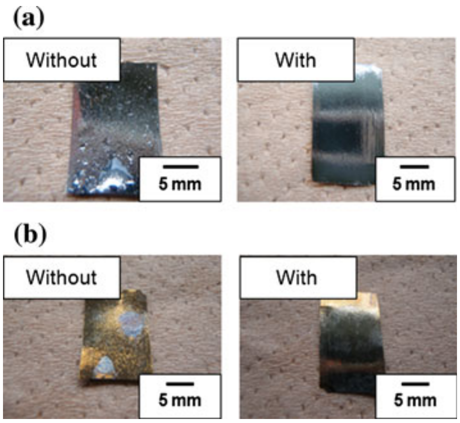


Fig. 7 Photographs showing the appearances of the nanosheet-coated BMGs on the surfaces with and without hydrothermal treatment; **a** nanosheet coating and **b** heating at 400 °C for 1 h after nanosheet coating

greatly improved at this stage. After 3 h, the BMG surface is oxidized, and OH groups are adsorbed on the oxidized surface, which thus becomes hydrophilic. Therefore, a water droplet spreads out on the surface. After time longer than 6 h, the dissolved Ti precipitates with Na components to form sodium titanate (Ti–O–Na) and grows to a layered structure with a house-of-card-like texture. This rough surface enhances the wettability and shows a highly hydrophilic state.

Since the wettability of the BMG was successfully improved by modification of the surface phases and nanotexture using hydrothermal treatment, titania nanosheets were coated on the surfaces of BMGs with and without hydrothermal treatment. Figure 7a shows photographs of the BMG-coated nanosheets. Without the hydrothermal treatment, the coated surface was very inhomogeneous because of the poor wettability of the nanosheets. In contrast, the coated surface of the hydrothermally treated BMG was smooth, and nanosheets were found to be uniformly well coated. The photographs of the two coated samples after heating at 400 °C for 1 h are shown in Fig. 7b. The surface of the sample without hydrothermal treatment became more inhomogeneous while that with the treatment maintained a uniformly smooth state. Thus, it is concluded that the BMG can be bonded to the titania nanosheets homogeneously by surface modification using the hydrothermal treatment. This result suggests the possibility that BMGs could be bonded with other materials, and this will extend the applications of BMGs to a variety of fields.

Conclusions

The Ti-based bulk metallic glasses (BMGs) were hydrothermally treated using a NaOH solution to improve the wettability. With increasing hydrothermal treatment temperature and time, the surface nanotextures changed from wire-like and net-like structures to that of a house-of-cards. The surface phases formed were assigned as titanium oxide and/or sodium titanate. The water contact angle of the as-prepared BMG was >90°, i.e., having a hydrophobic character, but this was greatly decreased to <10° (superhydrophilic) with higher temperatures and longer times of hydrothermal treatment. This is considered to be derived from the formation of an oxide layer on the BMG surface and adsorption of OH groups on the oxide layer. The effectiveness of the improvement of the water wettability of the BMG was confirmed by the characteristic ability to coat with titania nanosheets.

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References

1. Inoue A, Ohtera K, Kita K, Masumoto T (1988) Jpn J Appl Phys 27:L2248
2. Inoue A, Kohinata M, Tsai AP, Masumoto T (1989) Mater Trans 30:378
3. Inoue A, Zhang T, Masumoto T (1989) Mater Trans 30:965
4. Inoue A, Zhang T, Masumoto T (1990) Mater Trans 31:177
5. Zhang T, Inoue A, Masumoto T (1993) Mater Lett 15:379
6. Peker AL, Johnson WL (1993) Appl Phys Lett 63:2342
7. Ishida M, Uehara T, Arai T, Takeda H, Yamaguchi Y, Taniguchi T, Kobayashi M, Ofune H (2002) Intermetallics 10:1259
8. Yamaura S, Isogai K, Kimura H, Inoue A (2002) J Mater Res 17:60
9. Hara S, Sakaki K, Ito N, Kimura H-M, Asami K, Inoue A (2000) J Membrane Sci 164:289
10. Sugiyama N, Xu H, Onoki T, Hoshikawa Y, Watanabe T, Matsushita N, Wang X, Qin F, Fukuhara M, Tsukamoto M, Abe N, Komizo Y, Inoue A, Yoshimura M (2009) Acta Biomater 5:1367
11. Onoki T, Wang X, Zhu S, Sugiyama N, Hoshikawa Y, Akao M, Matsushita N, Nakahira A, Yasuda E, Yoshimura M, Inoue A (2009) Mater Sci Eng B 161:27
12. Erbil HY, Demirel AL, Avci Y, Mert O (2003) Science 299:1377
13. Zhao K, Liu KS, Li JF, Wang WH, Jiang L (2009) Scripta Mater 60:225
14. Wang WH (2007) Prog Mater Sci 52:540
15. Wang WH (2006) J Appl Phys 99:093506
16. Sasaki T, Watanabe M (1998) J Am Chem Soc 120:4682
17. Miyaji F, Yoko T, Kozuka H, Sakka S (1991) J Mater Sci 26:248. doi:10.1007/BF00576059
18. Kasuga T, Hiramatsu M, Hoson A, Sekino T, Niihara K (1999) Adv Mater 11:1307
19. Meng X, Wang D, Liu J, Zhang S (2004) Mater Res Bull 39:2163