第 38 卷第 10 期
2010 年 10 月

硅 酸 盐 学 报
JOURNAL OF THE CHINESE CERAMIC SOCIETY

Vol. 38，No. 10
October，2010

# Na 掺杂 ZnO 薄膜光诱导亲水性的转化

吕建国[1,2]，黄 凯[3]，陈学梅[2]，朱剑博[2]，孟凡明[1,4]，宋学萍[1]，孙兆奇[1]
(1. 安徽大学物理与材料科学学院，合肥 230039；2. 合肥师范学院物理与电子工程系，合肥 230601；3. 安徽建筑工业学院数理系，合肥 230601；4. 大连理工大学，三束材料改性国家重点实验室，辽宁 大连 116024)

**摘 要**：采用溶胶–凝胶技术在 Si(111)和石英基片上制备 8%(摩尔分数)Na 掺杂 ZnO 薄膜。用 X 射线衍射仪、原子力显微镜、扫描电镜和接触角测试仪测试薄膜的微结构、表面形貌和表面接触角。结果表明：所有薄膜均具有较好的 *c* 轴择优取向，表面由近六边形棒状颗粒构成。随着退火温度升高，薄膜表面接触角由 95°增大到 106°。通过对薄膜交替进行紫外光照和黑暗放置(或热处理)，可以实现其表面疏水与超亲水性之间的可逆转化，光诱导可逆转化效率随退火温度升高而增大。

**关键词**：氧化锌薄膜；溶胶–凝胶；表面与界面；亲水性
**中图分类号**：O472+.1；O484　　**文献标志码**：A　　**文章编号**：0454–5648(2010)10–2010–04

## PHOTO-INDUCED HYDROPHILICITY CONVERSION OF Na-DOPED ZnO THIN FILMS

*LÜ Jianguo*[1,2]，*HUANG Kai*[3]，*CHEN Xuemei*[2]，*ZHU Jianbo*[2]，*MENG Fanming*[1,4]，*SONG Xueping*[1]，*SUN Zhaoqi*[1]
(1. School of Physics and Material Science, Anhui University, Hefei 230039; 2. Department of Physics and Electronic Engineering, Hefei Normal University, Hefei 230601; 3. Department of Mathematics & Physics; Anhui University of Architecture, Hefei 230601; 4. State Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Dalian 116024, Liaoning, China)

**Abstract:** Na-doped 8% (mole fraction) ZnO thin films were deposited on Si(111) or quartz substrate by sol–gel method. The microstructure, surface topography and water contact angle of the thin films have been measured by X-ray diffractometer (XRD), atomic force microscopy, scanning electron microscopy (SEM), and water contact angle apparatus. XRD results show that the thin films have a higher preferential *c*-axis orientation. SEM results reveal that the films consist of nearly hexagonal rod-like grains. With the increase of annealing temperature, the contact angle of the un-irradiated thin films increases from 95° to 106°. The hydrophobic thin films could be reversibly switched to super-hydrophilic by alternation of ultraviolet irradiation and dark storage (or thermal treatment). The photo-induced efficiency of the thin films increases with the increase of annealing temperature.

**Key words:** zinc oxide thin films; sol–gel; surfaces and interfaces; hydrophilicity

Wettability of thin films with water is a very important phenomenon in many industrial and agricultural fields.[1–3] The wettability is controlled by various factors or treatment methods, such as temperature gradient,[4] application of an electric field,[5] and chemical surface modification.[6] In addition to these methods, photo-induction has also been proposed, and has attracted much attention, owing to its high wettability conversion rate.[7] For various applications, both highly hydrophobic[8] (water contact angle larger than 150°) and highly hydrophilic[7] (water contact angle smaller than 10°) thin films are desirable.

Recently, the reversible wettability of metal oxides by alternation of ultraviolet (UV) irradiation and dark storage, mainly of $TiO_2$ and ZnO, has been widely studied. ZnO thin films with reversible wettability have been fabricated using different techniques including chemical vapor deposition method,[9] radio frequency magnetron sputtering,[10] aqueous chemical growth,[11] pulsed laser deposition,[12] two-step solution approach,[13–14] hydrothermal method.[15] Compared with other deposition methods, sol–gel method is a simple and low cost method

收稿日期：2010–05–08。　修改稿收到日期：2010–06–08。
基金项目：国家自然科学基金(No.50872001)；教育部博士点专项基金(20060357003)；安徽高校省级自然科学研究重点 (KJ2010A-284)资助项目。
第一作者：吕建国(1980—)，男，博士研究生。
通讯作者：孙兆奇(1955—)，男，教授。

**Received date:** 2010–05–08.　**Approved date:** 2010–06–08.
**First author:** LÜ Jianguo (1980–), male, postgraduate student for doctor degree.
**E-mail:** lvjg1@163.com
**Correspondent author:** SUN Zhaoqi (1955–), male, professor.
**E-mail:** szq@ahu.edu.cn

for the fabrication of either small or large-area ZnO thin films, despite the relatively inferior crystal quality. It has been reported that sodium ions doping enhanced the crystalline quality, grain size and optical properties of ZnO thin films.[16] To the best of our knowledge, the effect of annealing temperature on the photo–induced hydrophilicity of the sol–gel-derived ZnO thin films by Na-doping have not been reported yet.

In this work, Na-doped ZnO thin films were prepared on silicon and quartz substrates by sol–gel method. Microstructure, surface topography and wettability of the thin films annealed at different temperatures were investigated. The effect of annealing temperature on photo-induced hydrophilicity of Na-doped ZnO thin films was studied.

## 1 Experimental procedure

8% (mole fraction, the same below) Na-doped ZnO solution was produced using zinc acetate dihydrate, sodium chloride, ethylene glycol monomethyl ether and monoethanolamine (MEA) as raw materials. The concentration of Zn ions in the solution was 0.5 mol/L and the mole ratio of MEA to zinc acetate was kept as 1:1. The solution was stirred at 333 K for 120 min using a magnetic stirrer to get a clear, homogeneous and transparent sol, which served as the coating sol after being kept for 24 h. Na-doped ZnO thin film was deposited on Si(111) or quartz substrates using the spin coating method with 3 000 r/m for 30 s. After spin coating, the substrates were kept at 423 K for 10 min to evaporate the solvent in the film and this procedure was repeated 10 times. These as-deposited films were annealed at 673, 873, and 1 073 K for 60 min in air and then cooled down to room temperature.

The crystallization behavior of Na-doped ZnO thin films was analyzed by a X-ray diffractometer (XRD, Model MACM18XHF) using Cu $K_\alpha$ radiation. Surface morphology of the samples was observed by a scanning electron microscope (SEM, Model S–4800) and an atom force microscope (AFM, Model CSPM4000) operating in contact mode. Contact angle (CA) of water droplet on the surface was measured by a home-made water contact angle apparatus[17] at ambient air (18 ℃, a relative humidity (RH) of 60%). The change of photo-induced wettability was evaluated by irradiating the samples at certain time intervals using an ultraviolet (UV) mercury lamp with an intensity of 2–4 mW/cm$^2$. Following irradiation, the samples were placed in the dark for seven days (or annealed at 473 K for 60 min) in ambient conditions. Subsequently, the respective evolution of the contact angles was determined.

## 2 Results and discussion

Figure 1 depicts the XRD patterns of 8% Na-doped ZnO thin films deposited on silicon substrate and annealed at different temperatures for 60 min. All samples are polycrystalline with hexagonal wurtzite structure. As seen in Fig.1, the intensity of (002) peak of the thin films is much stronger than that of (100), (101), (103) and other diffractive peaks, which indicates that the thin films have a preferential *c*-axis orientation. In addition, the intensity of the (103) peak becomes higher with the increase of annealing temperature.

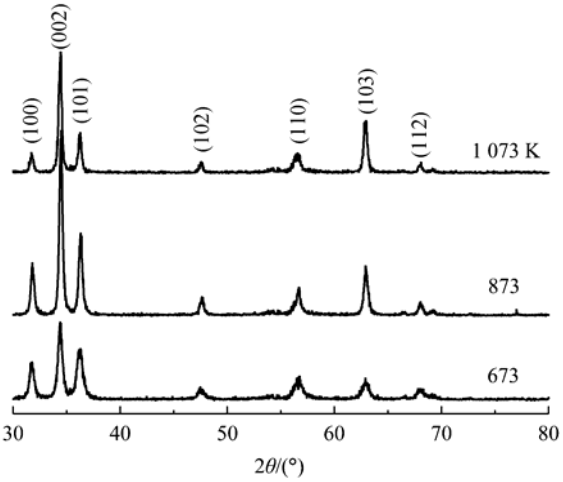
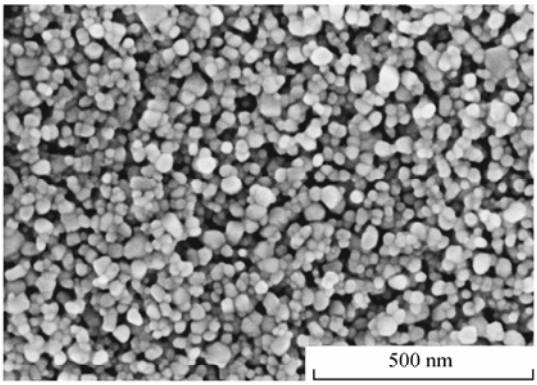


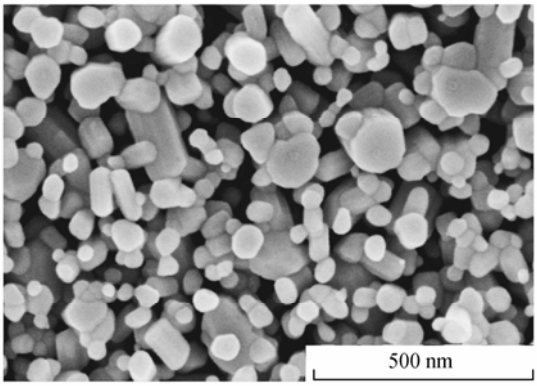

Fig.1　XRD patterns of Na-doped ZnO thin films annealed at different temperatures for 60 min

The surface SEM microstructure images of the Na-doped ZnO thin films formed on silicon substrate annealed at 673, 873, and 1 073 K are shown in Fig.2. It can be seen that the surface of the samples consist of nano-sized and nearly hexagonal rod-like grains. The mean grain size is about 40, 70, and 150 nm for the samples annealed at 673, 873, and 1 073 K, respectively. The AFM images of the samples are shown in Fig.3. The mean root-mean-square (RMS) roughness of the samples, as determined by the corresponding AFM images, increases from 5.7 to 17.9 nm with the increase of annealing temperature.

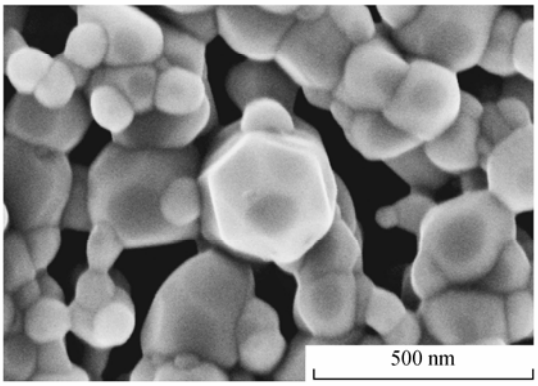
Figure 4(a) shows the contact angle evolution with UV irradiation time for the thin films. It can be seen that the un-irradiated thin films are hydrophobic, and the contact angle increases from 95° to 106° with the increase of annealing temperature. It is well known that surface topography and crystallinity are two main factors governing the surface wettability. The crystallinity does not change appreciably among the thin films annealed at different temperatures. Therefore, the variation of the initial contact angle of the thin films should be primarily attributed to the difference in their surface structures. In this study, with the increase of annealing temperature, the surface roughness, grain size and thus groove size between rod-like particles of the thin films increase. Air can be present in the grooves. The hydrophobicity of a rough surface can be intensified by increasing the proportion of air/water interface.[18] Therefore, the enhancement of hydrophobicity of un-irradiated thin films can be attributed




(a) 673 K




(b) 873 K




(c) 1 073 K

Fig.2 SEM microstructure images of the surfaces of Na-doped ZnO thin films annealed at different temperatures for 60 min

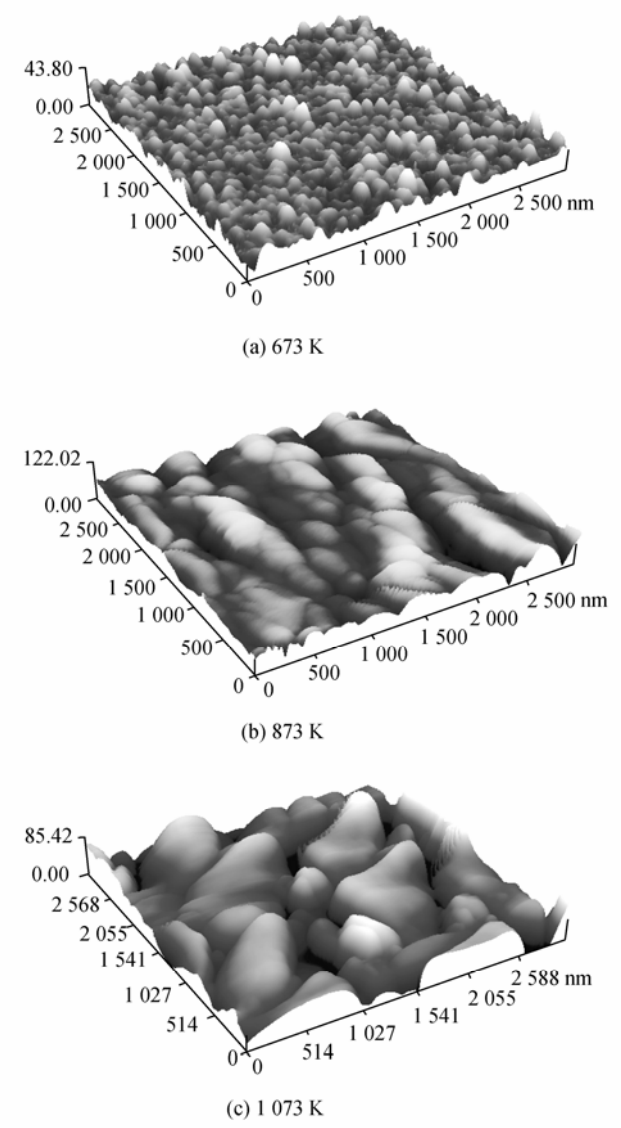
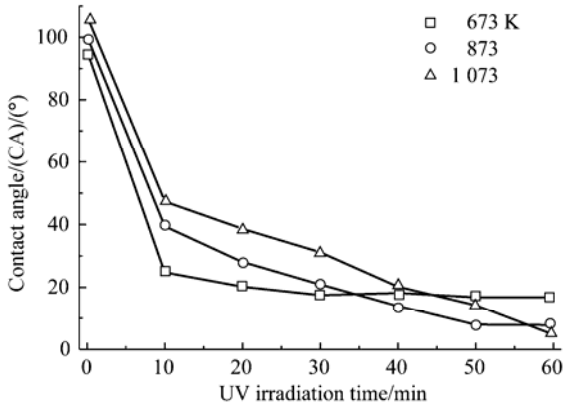



Fig.3 AFM images of the surfaces of Na-doped ZnO thin films annealed at different temperatures for 60 min

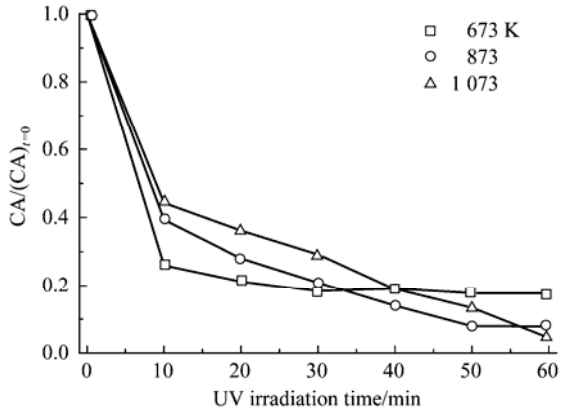
to the increase of the proportion of air/water interface in solid and air composite rough surface structure, which is related to Na doping and annealing temperature.

Under UV irradiation, the contact angle of the thin films decreases rapidly. All the samples exhibit a photo-induced change in their wettability. Particularly the sample annealed at 1 073 K exhibits a remarkable photo-induced transition from hydrophobicity to super-hydrophilicity, reaching a nearly zero contact angle. To better understand the efficiency of the photo-induced process, Fig.4(b) reveals the contact angle reduction rate.[12] The results show that the contact angle reduction rate of Na-doped ZnO thin films after UV irradiation for 60min enhances with the increase of annealing temperature. It must be pointed out that the changes in wettability of the thin films are reversible, either by dark storage for 7 d or heating at 473 K for 1 h. The reversible process in wettability of ZnO nanostructure was studied by many researchers.[11–15] Compared with contact angle reduction rate of other ZnO thin films,[11–12] enhancement of contact angle reduction rate of Na-doped ZnO thin films may be related to the increase of surface roughness and mean particles size, which is attributed to Na doping and annealing temperature.

As reported,[19] UV irradiation will generate electron-hole pairs in the ZnO surface. Some of the holes can react with lattice oxygen, leading to the formation of surface oxygen vacancies; while some of the electrons react with lattice metal ions ($Zn^{2+}$) to form $Zn^{+}$ defective sites (surface trapped electrons). Meanwhile, water and oxygen




(a) Dependence of the water contact angle on the UV irradiation time for the Na-doped ZnO thin films




(b) The corresponding contact angle reduction rate

Fig.4 Dependence of the water contact angle on the UV irradiation time for the Na-doped ZnO thin films and the corresponding contact angle reduction rate $(CA/(CA)_{t=0})$ $(CA)_{t=0}$ is contact angle at start time.

may compete to dissociatively adsorb on these defective sites. The defective sites are kinetically more favorable for hydroxyl adsorption than oxygen adsorption. As a result, the surface hydrophilicity is improved, and the water contact angle is significantly reduced.[19] Since the oxygen adsorption is thermodynamically favored, thus oxygen can create stronger bonds to the defective sites than the hydroxyl. After the hydroxyl adsorption, the surface of thin films becomes energetically unstable. Accordingly, the hydroxyl groups adsorbed on the defective sites can be replaced gradually by oxygen atoms when the UV-irradiated films were placed in the dark. Heat treatment can accelerate the elimination of surface hydroxyl groups.[8] The surface reverts to its original state (before UV irradiation), and the wettability is reconverted from super-hydrophilicity to hydrophobicity. The reversible switching between hydrophobic and super-hydrophilic states of the thin films is a synergy of surface chemical composition and roughness.[12] The surface roughness, mean particles size and photo-induced efficiency of Na-doped ZnO thin films can be increased with the increase of the annealing temperature. So, the surface roughness and mean particles size of thin films plays a key role to improve the efficiency of the photo-induced process. For the rougher surface, the surface to volume ratio is higher, and the total interface area between water and the thin films is larger. This leads to an effective increase of the photo-active defective sites, which are in contact with water molecules. Based on this analysis, it can be concluded that the sol–gel method can yield Na-doped ZnO thin films which exhibit a reversible and efficient change in their wettability.

## 3 Conclusions

8% Na-doped ZnO thin films with a higher preferential *c*-axis orientation were prepared by sol–gel method. As the annealing temperature increases from 673 to 1 073 K, the mean size of nearly hexagonal rod-like grains increases from 40 to 150 nm. Before irradiation, all samples are intrinsically hydrophobic, and the contact angle enhances with the increase of annealing temperature. The Na-doped ZnO thin film annealed at 1 073 K was found to exhibit a remarkable reversible conversion from hydrophobicity to super-hydrophilicity after exposure to UV irradiation. The results presented here can be potentially applied to the production of self-cleaning coatings, antifogging materials.

**References:**

[1] VELEV O D, PREVO B G, BHATT K H. On-chip manipulation of free droplets [J]. Nature, 2003, 426: 515–516.

[2] WULF M, WEHLING A, REIS O. Coatings with self-cleaning properties [J]. Macromol Symp, 2002, 187: 459–467.

[3] ZORBA V, STRATAKIS E, BARBEROGLOU M, et al. Biomimetic artificial surfaces quantitatively reproduce the water repellency of a lotus leaf [J]. Adv Mater, 2008, 20: 4049–4054.

[4] CAZABAT A M, HESLOT F, TROIAN S M, et al. Fingering instability of thin spreading films driven by temperature gradients [J]. Nature, 1990, 346: 824–826.

[5] SCHNEEMILCH M, WELTERS W J J, HAYES R A, et al. Electrically induced changes in dynamic wettability [J]. Langmuir, 2000,16: 2924–2927.

[6] CHAUDHURY M K, WHITESIDES G M. How to make water run uphill [J]. Science, 1992, 256: 1539–1541.

[7] MASAHIRO M, NOBUO K, SHUNICHI H, et al. Reversible wettability control of $TiO_2$ surface by light irradiation [J]. Surf Sci, 2002, 511: 401–407.

[8] SATOSHI S, TOMOHIRO Onda, NAOKI Satoh, et al. Super water-repellent surfaces resulting from fractal structure [J]. J Phys Chem, 1996, 100: 19512–19517.

[9] HUAN L, LIN F, JIN Z, et al. Reversible wettability of a chemical vapor deposition prepared ZnO film between superhydrophobicity and superhydrophilicity [J]. Langmuir, 2004, 20: 5659–5661.

[10] MIYAUCHI M, SHIMAI A, TSURU Y. Photoinduced hydrophilicity of

(continued on p.2020)

[3] FU Qiangan, LI Hejun, SHI Xiaohong, et al. Silicon carbide coating to protect carbon/carbon composites against oxidation [J]. Scr Mater, 2005, 52: 923–928.

[4] HUANG Jianfeng, ZENG Xierong, LI Hejun, et al. Influence of the preparation temperature on the phase, microstructure and anti- oxidation property of a SiC coating for C/C composites [J]. Carbon, 2004, 42: 1517–1521.

[5] ZENG Xierong, YANG Zeng, LI Hejun, et al. Investigation of oxidation protection system of $MoSi_2$/SiC coating for carbon/carbon composites [J]. Aero Astro Sin (in Chinese), 1997, 18: 427–431.

[6] ZENG Xierong, LI Hejun, YANG Zeng. Effect of microstructure and component of $MoSi_2$–SiC multiplayer ceramic coating on oxidation resistance [J]. J Chin Ceram Soc (in Chinese), 1999, 27: 8–10.

[7] ZHANG Yulei, LI Hejun, FU Qiangang, et al. An oxidation protective Si–Mo–Cr coating for C/SiC coated carbon/carbon composites [J]. Carbon 2008, 46: 179–182.

[8] HUANG Jianfeng, LI Hejun, XIONG Xinbo, et al. Progress on the oxidation protective coating of carbon–carbon composites [J]. New Carbon Mater (in Chinese), 2005, 20: 373–378.

[9] JIAO Gengsheng, LI Hejun, LI Kezhi, et al. Multi-composition oxidation resistant coating for SiC-coated carbon/carbon composites at high temperature [J]. Mater Sci Eng A, 2008, 486: 556–561.

[10] ZHANG Yujun, ZHANG Weiru. Structure Ceramic Materials and Its Application [M] (in Chinese). Beijing: Chemical Industry Press, 2005: 36–39.

[11] SEKIGAWA T, TAKEDA F, TAGUCHITAL M. High temperature oxidation protection coating for C/C composites [C]//The 8th Symposium on High Performance Materials for Severe Environments, Tokyo, 1997: 307–315.

[12] LIU Bobo, WANG Fen, ZHU Jianfeng, et al. Synthesis of machinable ternary TiC/$Ti_3AlC_2$ composites by in-situ reactions [J]. Aero Mater Technol, 2009, 3: 74–76.

[13] EROGLU S, GALLOIS B. Design and chemical vapor deposition of graded TiN/TiC coatings [J]. Surf Coat Technol, 1991, 49: 275–278.

[14] GUO Haiming, SHU Wubing, QIAO Shengru, et al. Preparation and properties of the multilayer oxidation protection coating for carbon-carbon composites [J]. Aero Mater Technol, 1998, 28: 37–40.

[15] LI Hejun, JIAO Gengsheng, LI Kezhi, et al. Multilayer oxidation resistant coating for SiC coated carbon/carbon composites at high temperature [J]. Mater Sci Eng A, 2008, 475: 279–284.

[16] JIAO Gengsheng, LI Heiun, LI Kezhi, et al, Mechanism of defect formation and control of silcon carbide coating for carbon/carbon composites made by the pack cementation method [J]. J Chin Ceram Soc (in Chinese ), 2007, 35: 721–724.

[17] ZHAO Baorong, WANG Jianjun, SASIKI M, et al .Research on toughening mechanism of SiC–TiC ceramics [J]. Ordnancde Mater Sci Eng(in Chinese ), 1999, 19: 3–9.

※ ※ ※ ※ ※ ※ ※ ※ ※

(continued from p.2013)

heteroepitaxially grown ZnO thin films [J]. J Phys Chem B, 2005, 109: 13307–13311

[11] KENANAKIS G, STRATAKIS E, VLACHOU K, et al. Light-induced reversible hydrophilicity of ZnO structures grown by aqueous chemical growth [J]. Appl Surf Sci, 2008, 254: 5695–5699.

[12] PAPADOPOULOU E L, ZORBA V, PAGKOZIDIS A, et al. Reversible wettability of ZnO nanostructured thin films prepared by pulsed laser deposition [J]. Thin Solid Films, 2009, 518: 1267–1270.

[13] FENG X J, FENG L, JIN M H, et al. Reversible super-hydrophobicity to super-hydrophilicity transition of aligned ZnO nanorod films [J]. J Am Chem Soc, 2004, 126: 62–63.

[14] PAPADOPOULOU E L, BARBEROGLOU M, ZORBA V. Reversible photoinduced wettability transition of hierarchical ZnO structures [J]. J Phys Chem C, 2009, 113: 2891–2895.

[15] GUO M, DIAO P, CAI S M. Highly hydrophilic and superhydrophobic ZnO nanorod array films[J]. Thin Solid Films, 2007, 515: 7162–7166.

[16] WANG D, GAO S. Influence of annealing condition on the structure and optical properties of Na-doped ZnO thin films prepared by sol–gel method [J]. J Alloys Compd, 2009, 476: 925–928.

[17] MENG F M, XIAO L, SUN Z Q. Thermo-induced hydrophilicity of nano-$TiO_2$ thin films prepared by RF magnetron sputtering [J]. J Alloys Compd, 2009, 485: 848–852.

[18] CASSIE A B D, BAXTER S. Wettability of porous surfaces [J]. Trans Faraday Soc, 1944, 40: 546–551.

[19] SUN R D, NAKAJIMA A, FUJISHIMA A, et al. Photoinduced surface wettability conversion of ZnO and $TiO_2$ thin films [J]. J Phys Chem B, 2001, 105: 1984–1990.