Effect of magnesium doping on the light-induced hydrophilicity of ZnO thin films*

Huang Kai(黄凯)[1,†], Lü Jianguo(吕建国)[2], Zhang Li(张莉)[1], Tang Zhen(唐震)[1], Yu Jiangying(余江应)[1], Li Ping(李平)[1] , and Liu Feng(刘峰)[3]

[1]Department of Mathematics and Physics, Anhui University of Architecture, Hefei 230601, China
[2]Electronics and Information Engineering, Hefei Normal University, Hefei 230601, China
[3]Schoolof Mathematics and Physics, Anhui Polytechnic University, Wuhu 241000, China

Abstract: Undoped and Mg-doped ZnO thin films were deposited on Si (111) and quartz substrates by using the sol–gel method. Microstructure, surface topography and water contact angle of the thin films have been measured by X-ray diffraction (XRD), an atomic force microscope (AFM) and water contact angle apparatus, respectively. The XRD results show that all the thin films are polycrystalline with a hexagonal structure and have a preferred orientation along the *c*-axis perpendicular to the substrate. With the increase of Mg concentration, the RMS roughness increases from 2.14 to 9.56 nm and the contact angle of the un-irradiated thin films decreases from 89° to 82°. The wetting behavior of the resulting films can be reversibly switched from hydrophobic to hydrophilic, through alternation of UV illumination and dark storage. The light-induced efficiency of the thin films increases with the increase of Mg concentration.

Key words: ZnO; sol–gel; Surface topography; hydrophilicity
DOI: 10.1088/1674-4926/33/5/053003 **PACC:** 8270G; 6855; 6170T

1. Introduction

Wettability is one of the most important properties of a solid surface from both a fundamental research and a practical application points of view[1, 2]. Wetting properties can be tailored by manipulating the chemistry and morphology of any given surface. The control of surface wettability is of great importance since it would be beneficial to be able to switch between hydrophobicity and hydrophilicity for many applications via an external stimulus. Wettability has consequently raised increasing research interest in recent years. It is hoped that this will lead to functional surfaces with applications ranging from self-cleaning surfaces to drug delivery and lab-on-chip devices[3].

In recent years, it is known that many metal oxides can be light-switched between the two wetting states when they are alternatively exposed to ultraviolet (UV) light and stored in the dark, such as TiO_2 and ZnO[4−6]. Among these metal oxides, ZnO has drawn a lot of attention due to its outstanding optical and electrical properties. The light-induced wettability of ZnO has been studied for different nanostructures[7−9]. A variety of fabrication methods for ZnO thin films have been reported in literature, including the chemical vapor deposition method[10, 11], magnetron sputtering[12−14], pulsed laser deposition[15, 16], and thermal evaporation[17]. Compared with other deposition methods, the sol–gel method is one of the simplest methods for growing high quality ZnO thin films as well as nanostructures with reproducible and controlled results. The effect of Mg concentration on the light-induced hydrophilicity of Mg-doped ZnO thin films has not yet been reported.

In this work we described the growth of Mg-doped ZnO thin films by using the sol–gel method. In order to study the wetting properties, microstructure and different surface morphologies were obtained with different Mg concentration annealed at 673 K. The effect of Mg concentration on the light-induced hydrophilicity of Mg-doped ZnO thin films was studied.

2. Experimental

2.1. Experimental procedure

Ethylene glycol monomethyl ether and monoethanol amine were used as the solvent and stabilizing agent, respectively. The source for Mg doping was magnesium chloride ($MgCl_2$). Zinc acetate dihydrate and $MgCl_2$ were first dissolved in a mixture of ethylene glycol monomethyl ether and monoethanol amine at room temperature. The concentration of zinc acetate was 0.5 mol/L. The atomic ratios of Mg/Zn were 0, 0.02, and 0.04 (these films were named ZnO, ZnO:Mg-2%, and ZnO:Mg-4%, respectively). The molar ratio of monoethanol amine to zinc acetate was kept at 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 1 day. Mg-doped ZnO thin film was deposited on Si (111) and quartz substrates using the spin coating method with 3000 rpm 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-coated films were annealed at 673 K for 60 min in air and then cooled down to RT.

* Project supported by the National Natural Science Foundation of China (Nos. 51102072, 11104001) and the Natural Science Foundation of Anhui Higher Education Institution of China (Nos. KJ2010A284, KJ2010B172, KJ2010B024).
† Corresponding author. Email: khuang@aiai.edu.cn
Received 27 November 2011, revised manuscript received 17 December 2011

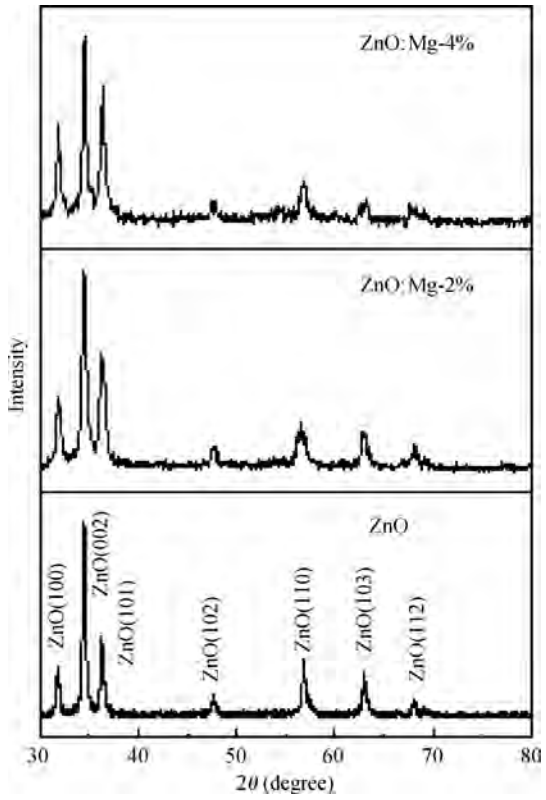

Fig. 1. XRD spectra of Mg-doped ZnO thin films annealed at 673 K for 60 min.

2.2. Characterization

The crystal structure of the thin films was investigated using X-ray diffractometry (XRD, MACM18XHF) with Cu Kα radiation ($\lambda = 0.1540$ nm). The surface morphology of the thin films was measured by using an atomic force microscope (AFM, CSPM4000) operating in contact mode. The contact angle (CA) of water droplet on the surface was measured by using home-made water contact angle apparatus[18] in 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, 365 nm) 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.

3. Results and discussion

3.1. Structural characterization of the ZnO thin films

Figure 1 shows XRD patterns of Mg-doped ZnO thin films prepared on Si substrate with different Mg concentrations annealed at 673 K for 60 min. All the diffractive peaks are attributed to the wurtzite ZnO structure. There is no second phase in these films from the patterns, possibly because of the low doping content. From the patterns, it can be seen that all the ZnO thin films have a polycrystalline structure with a preferential c-axis perpendicular to the substrate. As shown in Fig. 1, the intensity of the (002) peak of the thin films is much stronger than other diffractive peaks, which indicates that the thin films have a preferential c-axis orientation. When the Mg-doped concentration is 0, 2% and 4%, the diffraction peak lies at 34.35°, 34.50° and 34.51°, respectively. The position of the (002) peak is related with the strain in the film. As for the strain-free ZnO crystal, its (002) peak lies at 34.43[19]. From the above data, it can be known that with the increase of Mg doping concentration, the (002) peak gradually shifts toward bigger angle direction, indicating that the strain in the films increased. Mg doping on the (002) diffraction peak position has little effect, but it almost does not affect the peak intensity.

3.2. Surface morphology characterization of ZnO thin films

Figure 2 shows the two-dimensional (a, b, c) and three dimensional (d, e, f) surface morphology images of the samples. A scanning probe microscope was used to observe the surface morphologies of the films over a 3×3 μm^2 area by contact mode. AFM investigations of the surface morphology indicate the surface is smooth, homogeneous and the roughness is of nanometer order for all samples. The RMS roughness is 2.14, 4.70 and 6.56 nm for samples a, b and c, respectively. Similar results of surface morphologies of Mg-doped ZnO thin films were presented by Kumar *et al.*[20]. From the three-dimensional surface morphology images, it can be seen that ZnO thin films comprise columnar grains which grow along the c-axis direction perpendicular to the substrate surface. This is in agreement with the results of XRD.

3.3. UV-vis transmission spectra of ZnO thin films

Figure 3 shows the UV-vis transmission spectra of the Mg-doped ZnO thin films on quartz substrates. It can be seen that all the thin films have an average optical transparency over 85% in the visible range and a sharp ultraviolet absorption edges. The band gap is preferred to be evaluated from the optical transmission spectra. The optical absorption coefficient α of the direct band gap semiconductor ZnO can be derived as the following equation:

$$\alpha h\nu = A(h\nu - E_g)^{1/2},$$

where A the constant, $h\nu$ is the photon energy, and E_g the optical band gap. Since $E_g = h\nu$ when $(\alpha h\nu)^2 = 0$, an extrapolation of the linear region of the plot of $(\alpha h\nu)^2$ versus photo energy ($h\nu$) on the x-axis gives the value of the optical band gap E_g. The optical band gap calculated from transmission spectra of ZnO, ZnO:Mg-2% and ZnO:Mg-4% thin films are about 3.26, 3.30 and 3.32 eV, respectively. It clearly demonstrates the band gap broadening with increase of Mg incorporation in ZnO thin films. This may be attributed to the fact that new defects are introduced after Mg atoms substitute for Zn atoms due to the electronegativity and ionic radius difference. The new defects are associated with the hydrophilic properties.

3.4. Hydrophilicity analysis of ZnO thin films

Figure 4(a) depicts the contact angle evolution with UV illumination time for the three samples. The relative changes in wettability are better understood in Fig. 4(b), where the normalised contact angle evolution is shown, obtained by dividing

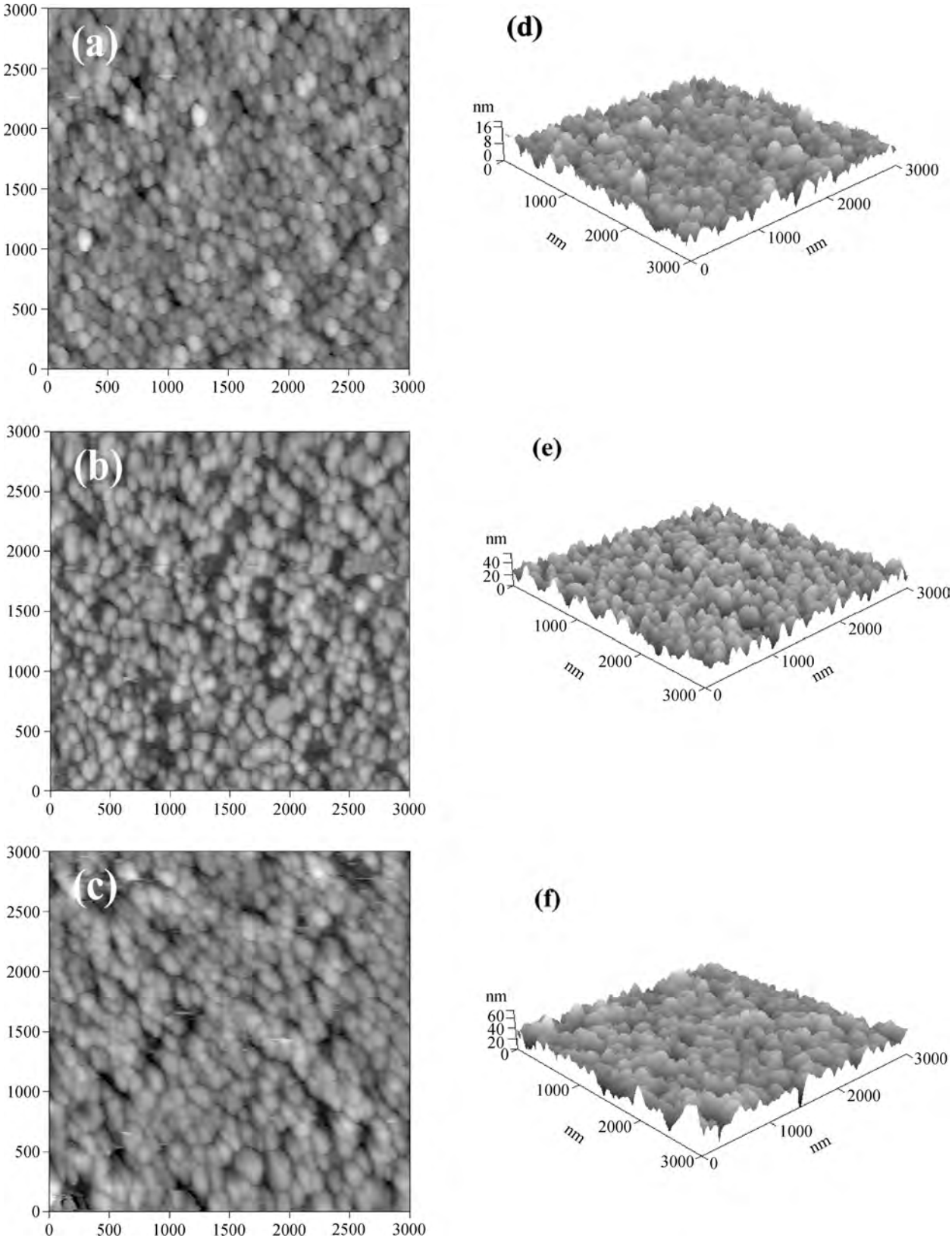

Fig. 2. (a, b, c) Two-dimensional and (d, e, f) three-dimensional surface morphology images of sample (a) ZnO, (b) ZnO: Mg-2%, (c) ZnO: Mg-4% thin films annealed at 673 K for 60 min.

each CA value to that at $t = 0$. Evidently, the contact angle reduction rate, which is a measure of the efficiency of the light induced process, is higher for the roughest samples. It can be seen that the un-irradiated thin films are hydrophobic, and the contact angle decreases from 89° to 82° with increasing Mg concentration. Under UV irradiation, the contact angle of the thin films decreases rapidly. All the samples exhibit a photoinduced change in their wettability.

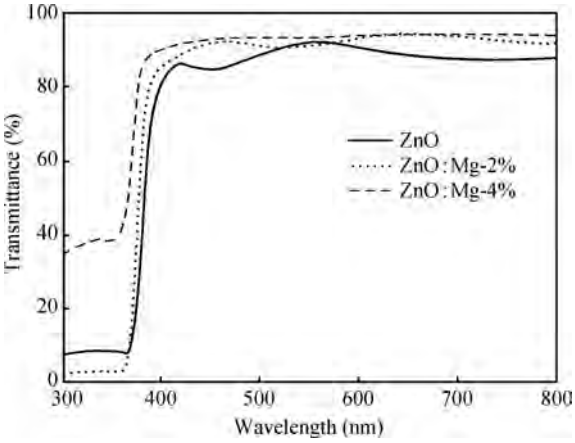

Fig. 3. UV-vis transmission spectra of ZnO thin films annealed at 673 K for 60 min.

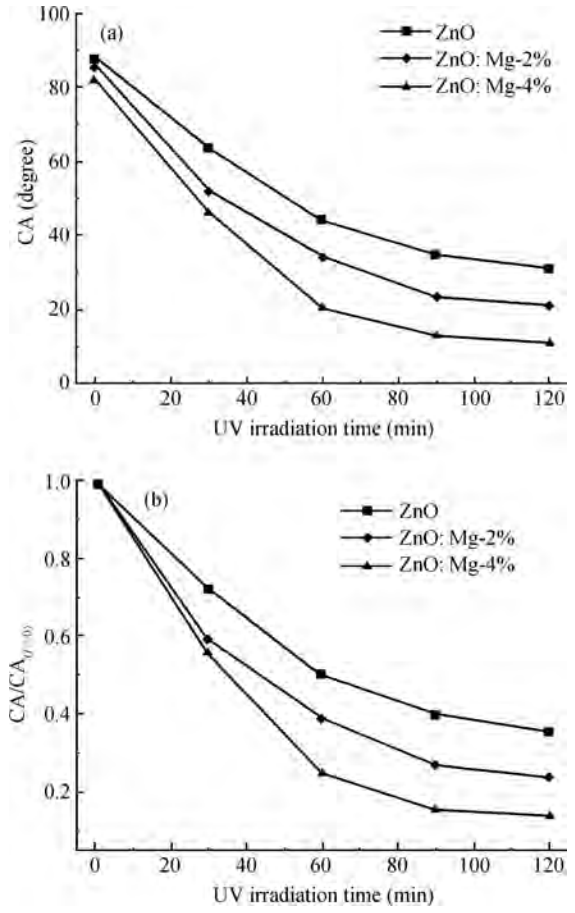

Fig. 4. (a) Dependence of the water contact angle on the UV irradiation time for the Mg-doped ZnO thin films and (b) the corresponding contact angle reduction rate. $(CA/(CA)_{t=0})$ $(CA)_{t=0}$ is the contact angle at start time.

It is well known that surface topography and crystallinity are the two main factors governing surface wettability. XRD patterns show that the crystallinity does not change appreciably among the thin films of different Mg concentrations annealed at 673 K. Therefore, variation of the initial contact angle of the thin films should be primarily attributed to the difference in their surface roughness. The mechanism of light-induced wettability of a ZnO nanostructure has been investigated by many researchers[8−10]. The origin of light-induced hydrophilicity has been explained in the frame of creation of oxygen vacancies. It is known that upon UV illumination, electron–hole pairs[21] are formed in the ZnO surface. Some of the holes react with lattice oxygen to form surface oxygen vacancies, while the electrons can react with the metal ions (Zn^{2+}) present in the lattice, forming Zn^{+} defective sites. At the same time, water and oxygen may compete to dissociatively adsorb on these vacancies. The Zn^{+} defective sites are kinetically more favorable for hydroxyl adsorption than oxygen adsorption[15]. Thus the surface hydrophilicity is enhanced and the water contact angle is significantly reduced. It has also been demonstrated that the surface becomes energetically unstable after the hydroxyl adsorption. The oxygen adsorption is thermodynamically favored, thus oxygen can create stronger bonds to the defect sites than the hydroxyl group. Consequently, when a sample is placed in the dark after UV illumination, oxygen atoms gradually replace the hydroxyl groups adsorbed on the defective sites. Subsequently, the surface evolves back to its original state (before any UV illumination), attaining the initial wetting state. Heat treatment accelerates the elimination of surface hydroxyl groups and, as a result, the hydrophilic surface reconverts quickly to a hydrophobic one. As shown in Fig. 5, both processes lead to the restoration of the initial C_{AS}. The reversible switching between hydrophobic and hydrophilic states is a synergistic effect defined by surface chemical composition and roughness[22]. So the surface roughness of thin films plays a key role to improve the efficiency of the photo-induced process, where the light-induced wettability is more pronounced for the samples exhibiting higher roughness.

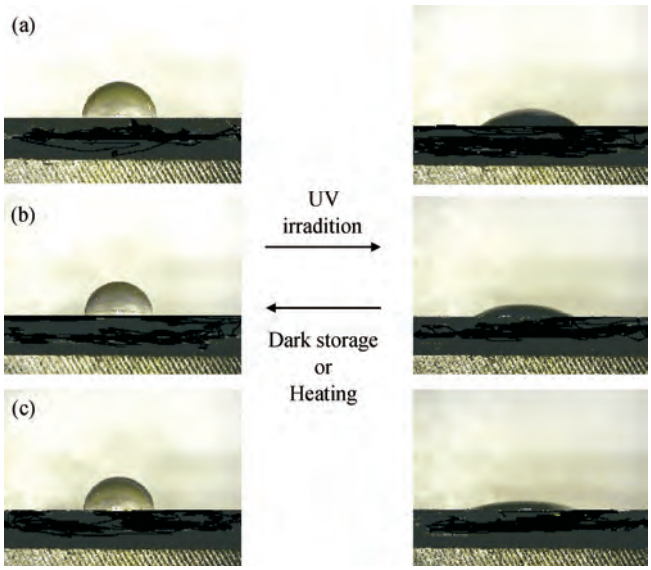

Fig. 5. Photographs of water droplet shape on the ZnO thin films of (a) ZnO, (b) ZnO:Mg-2%, and (c) ZnO:Mg-4% before (left) and after (right) UV illumination.

4. Conclusion

Undoped and Mg-doped ZnO thin films were deposited on Si (111) substrates using the sol–gel process. The XRD

patterns indicate that all thin films possess a polycrystalline ZnO with the hexagonal wurtzite structure. The RMS roughness increases with the increasing of Mg concentration. The light-induced wetting behavior is highly dependent on the film nano-roughness. The wetting transition from a hydrophobic to a hydrophilic state was fully reversible. These findings demonstrate the possibility of using sol–gel as an effective technique for the fabrication of high-quality ZnO functional, photosensitive nanostructures. The potential application of the results presented here are multiple such as the production of antifogging materials or microfluidic devices.

References

[1] Velev O D, Prevo B G, Bhatt K H. On-chip manipulation of free droplets. Nature, 2003, 426: 515

[2] Zorba V, Stratakis E, Barberoglou M, et al. Biomimetic artificial surfaces quantitatively reproduce the water repellency of a lotus leaf. Adv Mater, 2008, 20: 4049

[3] Wulf M, Wehling A, Reis O. Coatings with self-cleaning properties. Macromol Symp, 2002, 187: 459

[4] Watanabe T, Nakajima A, Wang R, et al. Photocatalytic activity and photoinduced hydrophilicity of titanium dioxide coated glass. Thin Solid Films, 1999, 351: 260

[5] Vernardou D, Kalorerakis G, Stratakis E, et al. Photoinduced hydrophilic and photocatalytic response of hydrothermally grown TiO_2 nanostructured thin films. Solid State Sci, 2009, 11: 1499

[6] Asahiro M, Nobuo K, Shunichi H, et al. Reversible wettability control of TiO_2 surface by light irradiation. Surf Sci, 2002, 511: 401

[7] Feng X J, Feng L, Jin M H, et al. Reversible super-hydrophobicity to super-hydrophilicity transition of aligned ZnO nanorod films. J Am Chem Soc, 2004, 126: 62

[8] Chantal B, Chantal B, Mireille T, et al. A ZnO nanowire array film with stable highly water-repellent properties. Nanotechnology, 2007, 18: 365705

[9] Lü J G, Huang K, Chen X M, et al. Reversible wettability of nanostructured ZnO thin films by sol–gel method. Appl Surf Sci, 2010, 256: 4720

[10] Uan L, Lin F, Jin Z, et al. Reversible wettability of a chemical vapor deposition prepared ZnO film between superhydrophobicity and superhydrophilicity. Langmuir, 2004, 20: 5659

[11] Shi H L, Ma X Y, Hu L, et al. Low-temperature growth of ZnO films on GaAs by metal organic chemical vapor deposition. Journal of Semiconductors, 2008, 29(1): 12

[12] Miyauchi M, Shimai A, Tsuru Y. Photoinduced hydrophilicity of heteroepitaxially grown ZnO thin films. J Phys Chem B, 2005, 109(27): 13307

[13] Zhang H F, Yang S G, Liu H F, et al. Preparation and characterization of transparent conducting ZnO:W films by DC magnetron sputtering. Journal of Semiconductors, 2011, 32(4): 043002

[14] Wu X P, Chen X Q, Sun L J, et al. Photoelectric conversion characteristics of ZnO/SiC/Si heterojunctions. Journal of Semiconductors, 2010, 31(10): 103002

[15] Papadopoulou E L, Zorba V, Pagkozidis A, et al. Reversible wettability of ZnO nanostructured thin films prepared by pulsed laser deposition. Thin Solid Films, 2009, 518: 1267

[16] Zhao C Y, Li R P, Sun B, et al. A study of ZnO/Si(111) interface structure by synchrotron radiation X-ray grazing incident diffraction. Journal of Semiconductors, 2007, 28(11): 1156

[17] Huang M H, Mao S, Feick H, et al. Room-temperature ultraviolet nanowire nanolasers. Science, 2001, 292: 1897

[18] Eng F M, Xiao L, Sun Z Q. Thermo-induced hydrophilicity of nano-TiO_2 thin films prepared by RF magnetron sputtering. J Alloys Compd, 2009, 485: 848

[19] Sagar P, Shishodia P K, Mehra R M, et al. Photoluminescence and absorption in sol–gel-derived ZnO films. Journal of Luminescence, 2007, 126: 800

[20] Kumar S, Gupte V, Sreenivas K. Structural and optical properties of magnetron sputtered $Mg_xZn_{1-x}O$ thin films. J Phys Condes Matter, 2006, 18: 3343

[21] Spanakis E, Stratakis E, Tzanetakis P, et al. Light induced stress in a-$Si_{1-x}Ge_x$:H alloys and its correlation with the Staebler–Wronski effect. Journal of Non-Crystalline Solids, 2002, 299–302: 521

[22] Kenanakis G, Stratakis E, Vlachou K, et al. Light-induced reversible hydrophilicity of ZnO structures grown by aqueous chemical growth. Appl Surf Sci, 2008, 254: 5695