Applied Surface Science 256 (2010) 4720–4723

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Reversible wettability of nanostructured ZnO thin films by sol–gel method

Jianguo Lü[a,b], Kai Huang[c], Xuemei Chen[b], Jianbo Zhu[b], Fanming Meng[a], Xueping Song[a], Zhaoqi Sun[a,*]

[a] School of Physics and Material Science, Anhui University, Hefei 230039, China
[b] Department of Physics and Electronic Engineering, Hefei Normal University, Hefei 230061, China
[c] Department of Mathematics & Physics, Anhui University of Architecture, Hefei 230601, China

ARTICLE INFO

Article history:
Received 22 January 2010
Received in revised form 24 February 2010
Accepted 24 February 2010
Available online 3 March 2010

Keywords:
ZnO
Sol–gel
Surface topography
Reversible wettability
Hydrophobicity

ABSTRACT

Nanostructured ZnO thin films were deposited on Si(1 1 1) and quartz substrate by sol–gel method. The thin films were annealed at 673 K, 873 K, and 1073 K for 60 min. Microstructure, surface topography, and water contact angle of the thin films have been measured by X-ray diffractometer, atomic force microscopy, and water contact angle apparatus. XRD results showed that the ZnO thin films are polycrystalline with hexagonal wurtzite structure. AFM studies revealed that rms roughness changes from 2.3 nm to 7.4 nm and the grain size grow up continuously with increasing annealing temperature. Wettability results indicated that hydrophobicity of the un-irradiated ZnO thin films enhances with annealing temperature increase. The hydrophobic ZnO surfaces could be reversibly switched to hydrophilic by alternation of UV illumination and dark storage (thermal treatment). By studying the magnitude and the contact angle reduction rate of the light-induced process, the contribution of surface roughness is discussed.

1. Introduction

During the past decade there has been an increasing interest in controlling the wettability of solids, which depends on both the surface energy and roughness. For many applications [1–3], it would be highly advantageous to be able to dynamically manipulate the behavior of liquids on surfaces.

Among other materials, the wetting properties of metal oxides, mainly of TiO_2 and ZnO, have been widely studied, since irradiation with UV light and dark storage (or thermal treatment) may significantly modify their wettability [4,5]. So far, previous works have been focused mainly on ZnO nanorods, nanowires, and nanobelts [6,7]. Wettability of ZnO thin films prepared by various methods, such as two-step method [8], aqueous chemical growth technique [4], pulsed laser deposition [9], spray pyrolysis method [10], rf-magnetron sputtering [11], and sol–gel method [12], was investigated. It is, however, difficult to develop simple and reliable synthetic methods for ZnO hierarchical architectures with controlled morphology, which are important for exploring in detail the effect of surface energy and roughness on wetting response. Due to simplicity, safety and low cost, wettability of ZnO thin films prepared by sol–gel method should be studied intensively and extensively.

In the present study, nanostructured ZnO thin films were deposited on silicon and quartz substrates by sol–gel method. The ZnO thin films were annealed at 673 K, 873 K, and 1073 K for 60 min. These samples were in hydrophobic state. Their contact angle was connected with annealing temperature. The samples could be switched to a hydrophilic state by exposing them to UV irradiation. This transition was found to be reversed upon dark storage (thermal treatment). The effect of annealing temperature, UV irradiation and dark storage (thermal treatment) in wettability of the thin films was studied in detail.

2. Experimental details

2.1. Preparation of samples

Ethylene glycol monomethyl ether and mono-ethanol amine were used as the solvent and stabilizing agent, respectively. Zinc acetate dihydrate was first dissolved in a mixture of ethylene glycol monomethyl ether and monoethanol amine (MEA) at room temperature. The concentration of zinc acetate was 0.5 mol/L. The molar ratio of monoethanol amine 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 one day. ZnO thin films were deposited on Si(1 1 1) and quartz substrate 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

* Corresponding author.
E-mail address: szq@ahu.edu.cn (Z. Q. Sun).

0169-4332/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2010.02.080

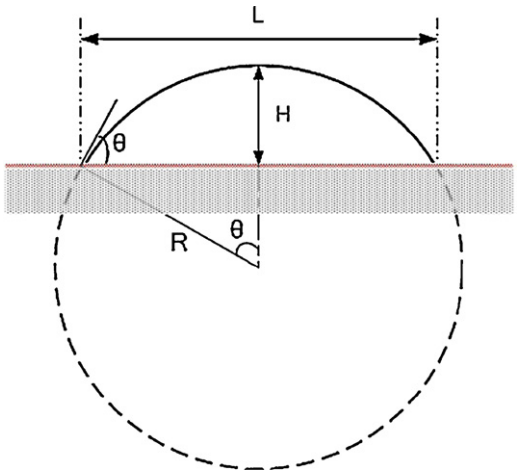

Fig. 1. Geometric pattern for calculation of water contact angle [13].

in the film and this procedure was repeated 10 times. These as-coated films were annealed for 60 min in air and then cooled down to RT.

2.2. Characterization

The crystal structure of these thin films was investigated using X-ray diffractometry (XRD, MACM18XHF). The X-ray source is Cu Kα radiation, accelerating voltage 40 kV, current 100 mA, scanning range 30–80°, scanning step 0.02°, scanning speed 8°/min. Surface topography of the thin films was measured by atomic force microscopy (AFM, CSPM4000) operating in contact mode.

2.3. Contact angle measurements

Contact angle (CA) was measured by a home-made water contact angle apparatus, which was performed at ambient air (18 °C, relative humidity (RH) 60%). Light induced hydrophilicity was studied by irradiating the samples at certain time intervals using a 36 W high pressure mercury lamp, which emits visible light of 404.7 nm, 435.8 nm, 546.1 nm, and 577.0–579.0 nm, and ultraviolet light of 365 nm. The distance between the sample and the high pressure mercury lamp was 8.0 cm. The intensity of light on the films was about 20.2 mW/cm^2 (the intensity is the overall one and not only the UVA part, which is usually given and proposed to be in the range of 2–4 mW/cm^2 for light induced hydrophilicity studies). After each irradiation time interval, a 3 μL distilled, deionised water droplet placed on the irradiated area and the corresponding contact angle was measured. 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.

By measuring the diameter L and height H of the spherical crown of the droplet dropped on the surface of the films from 2 mm height, as shown in Fig. 1. The water contact angle can be calculated from Eq. (1) [13]:

$$\theta = \arctan \frac{4HL}{L^2 - 4H^2} \quad (1)$$

where θ is water contact angle. The experimental error of the measurements was ±1°.

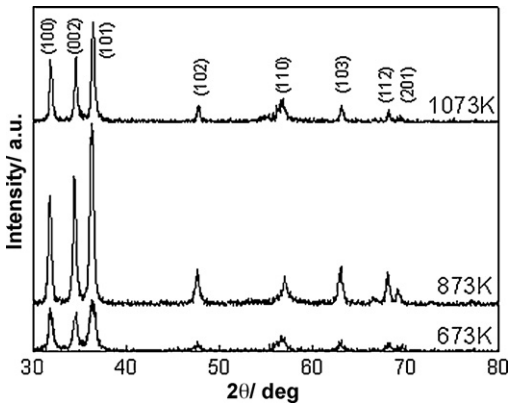

Fig. 2. XRD patterns of ZnO thin films annealed at 673 K, 873 K, and 1073 K for 60 min.

3. Results and discussion

3.1. Microstructure and surface topography

Fig. 2 shows the XRD patterns of ZnO thin films grown on the silicon substrates annealed at 673 K, 873 K, and 1073 K for 60 min, respectively. All the diffractive peaks attributed to the wurtzite ZnO structure. No characteristic diffraction peaks from other phases or impurities are detected. The XRD patterns imply that the samples are polycrystalline with hexagonal wurtzite structure. It also can be observed from the XRD patterns that the maximum value of diffraction intensity of the thin films appears at 873 K.

The diffraction intensity and the full width at half maximum (FWHW) are related to the crystallinity and grain size. The grain size (D) can be computed according to the following Scherrer Eq. (2) [14]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

where λ, β, and θ are X-ray wavelength (0.15406 nm), FWHW of (1 0 1) peak and Bragg diffraction angle, respectively. As shown in Fig. 3, the grain sizes were 11.1 nm, 18.5 nm, and 18.5 nm for the films annealed at 673 K, 873 K, and 1073 K, respectively.

Surface topography of the thin films was measured by AFM. Fig. 4 shows the AFM images of the ZnO thin films grown on the silicon substrates with different annealing temperatures. It can be seen that the grain size increase with the increase of the annealing temperature. This phenomenon can be explained that as annealing temperature increases, the crystal grain grow up continuously. This result is in agreement with the analysis of X-ray diffraction pat-

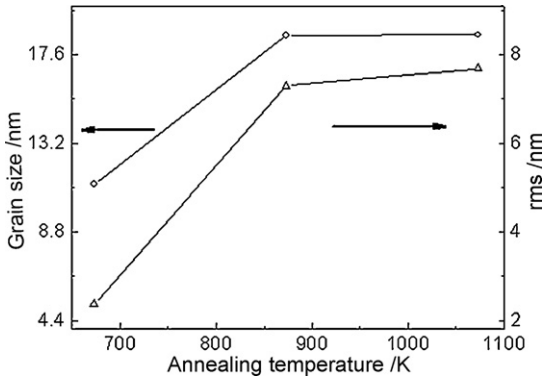

Fig. 3. Variations of the grain size and rms of ZnO thin films with the annealing temperature.

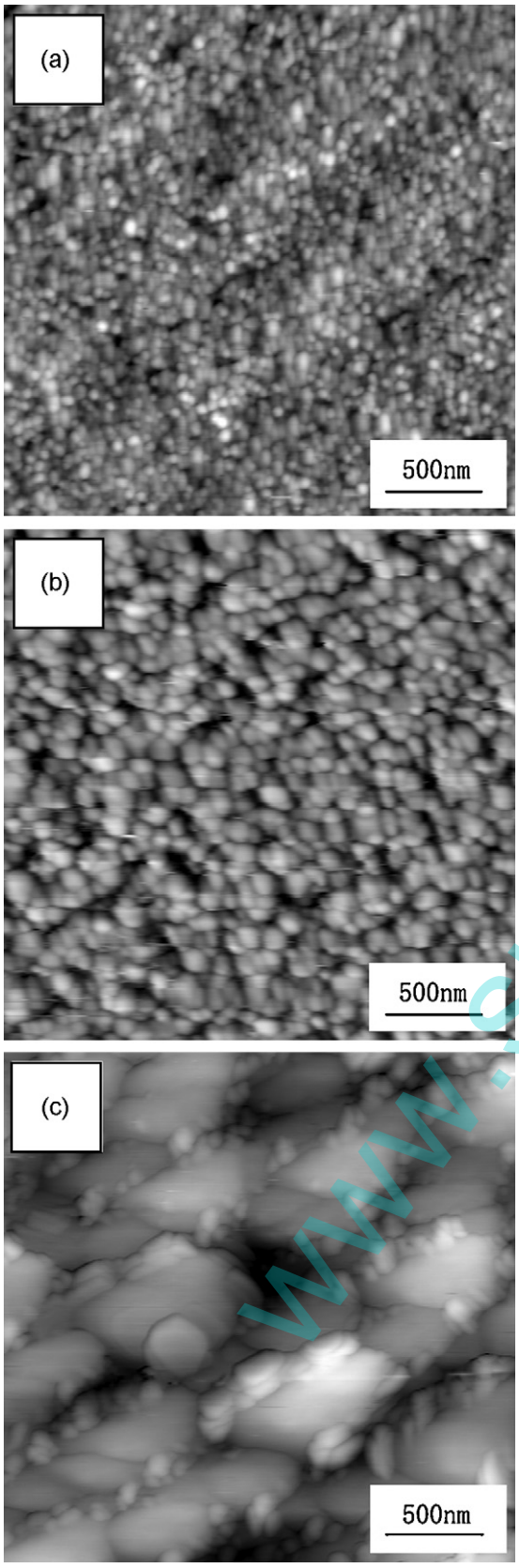

Fig. 4. Surface topography of ZnO thin films annealed at (a) 673 K, (b) 873 K, and (c) 1073 K for 60 min.

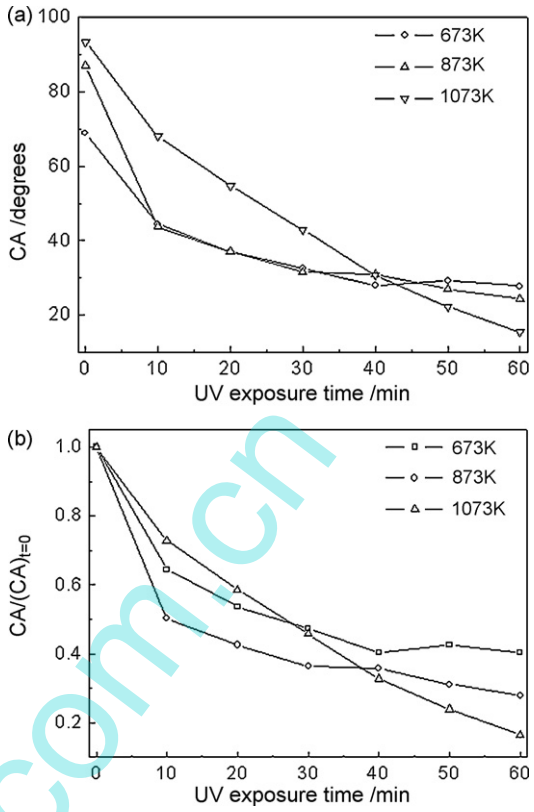

Fig. 5. (a) Dependence of the water contact angle on the UV illumination time for nanostructured ZnO samples. (b) The corresponding evolution of the ratio of the respective contact angles to their initial values is also plotted for comparison.

terns. As shown in Fig. 3, rms roughness of ZnO thin films changes from 2.3 nm to 7.4 nm with increasing annealing temperature. The change law of rms roughness may be attributed to the increase of the grain size.

3.2. Reversible wettability of ZnO thin films

Fig. 5 shows the contact angle evolution with UV irradiation time for ZnO thin films with different annealing temperature. It can be seen that the contact angle of un-irradiated thin films increases from 69° to 93° with increasing annealing temperature. Under UV irradiation all samples exhibit a light induced transition. The sample annealed at 673 K displays a rather weak response, reaching a contact angle of ~27° after 60 min, i.e. a decrease of ~61%. The corresponding difference is greater for the sample annealed at 1073 K and equal to ~84%. The relative changes in wettability are better understood by means of contact angle reduction rate, as shown in Fig. 5, which is a measure of the efficiency of the light induced process. The results show that the contact angle reduction rate increase as annealing temperature increases. More importantly, the contact angle reduction rate is higher than that observed in other ZnO structures [4,9].

It must be pointed out that the changes in wettability of the thin films are reversible. After the UV irradiated films were placed in dark for seven days (or annealed at 473 K for 60 min) in ambient conditions, a new water droplet was used to measure the surface wettability, and the initial wetting state was obtained again, as shown in Fig. 6. This process has been repeated several times, and good reversibility of the surface wettability was observed.

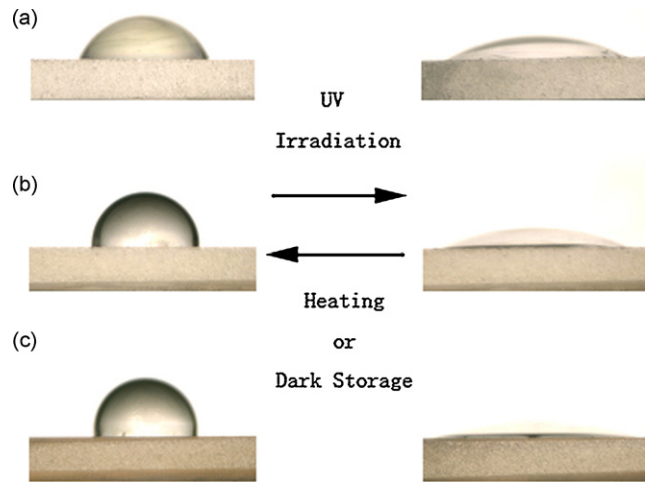

Fig. 6. Photographs of water droplet shape on the ZnO thin films annealed at (a) 673 K, (b) 873 K, and (c) 1073 K before (left) and after (right) UV illumination.

3.3. The mechanism of reversible wettability

It is well known that surface roughness [4,15,16] and crystallinity are two main factors governing the surface wettability. XRD patterns show that the crystallinity does not change appreciably among the thin films with different annealing temperature. Therefore, variation of the initial contact angle of the thin films should be primarily attributed to the difference in their surface roughness. Following the results presented in Figs. 3–5, one can see that surface roughness and hydrophobicity of the un-irradiated ZnO thin films increase as annealing temperature increases. Accordingly, the enhancement of hydrophobicity may be ascribed to increase of the proportion of air/water interface in solid and air composite rough surface structure [17], which is positively correlated with surface roughness of the thin films.

The mechanism of light-induced wettability of ZnO nanostructure has been investigated by many researchers [8–11]. It is well known that UV illumination will generate electron–hole pairs in the ZnO surface. Some of the holes can react with lattice oxygen to form 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 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 [10]. After the hydroxyl adsorption, the surface becomes energetically unstable. Because oxygen adsorption is thermodynamically favored, it is more strongly bonded on the defect sites than on the hydroxyl groups. Consequently, 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 [18]. As a result, the surface reverts back to its original state (before UV irradiation) by means of dark storage (or heat treatment), and the wettability is reconverted from hydrophilicity to hydrophobicity. The reversible change between hydrophobic and hydrophilic states is connected with both surface chemical composition and roughness [5]. In present work, the change of light-induced wettability is more marked for the sample exhibiting higher surface roughness, which annealed at the higher temperature. The explanation of the change in wettability is as follows: for a rougher surface, (1) water can enter and fill the grooves of the thin films more easily [5], (2) the total interface area between water and the ZnO thin films, which leads to an increase of the light-induced defect sites, is higher.

4. Conclusion

Nanostructured ZnO thin films with hexagonal wurtzite structure were prepared by sol–gel method. The rms roughness and the crystal grain increase with annealing temperature increases. Accordingly, the higher surface roughness contributes to the hydrophobicity of the un-irradiated ZnO thin films. Nanostructured ZnO thin film annealed at 1073 K was found to exhibit a significant reversible transition from hydrophobicity to hydrophilicity after exposure to UV light, and the thin film can revert back to its original state (before UV irradiation) by means of dark storage (or heat treatment). As a result, this method can be adopted to control the surface topography of ZnO thin films, resulting in reversible efficient wettability changes. The present study is quite valuable, and can potentially be applied to various industrial areas, such as the production of self-cleaning coatings, antifogging materials or microfluidic devices.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 50872001), Research Fund for the Doctoral Program of Higher Education of China (No. 20060357003), Talent Foundation of Anhui Province (No. 2004Z029) and Natural Science Foundation of Anhui Higher Education Institution of China (No. KJ2010A284).

References

[1] O.D. Velev, B.G. Prevo, K.H. Bhatt, Nature 426 (2003) 515.
[2] N. Verplanck, Y. Coffinier, V. Thomy, R. Boukherroub, Nanoscale Res. Lett. 2 (2007) 577.
[3] V. Zorba, E. Stratakis, M. Barberoglou, E. Spanakis, P. Tzanetakis, S.H. Anastasiadis, C. Fotakis, Adv. Mater. 20 (2008) 4049.
[4] G. Kenanakis, E. Stratakis, K. Vlachou, D. Vernardou, E. Koudoumas, N. Katsarakis, Appl. Surf. Sci. 254 (2008) 5695.
[5] X.J. Feng, L. Feng, M.H. Jin, J. Zhai, L. Jiang, D.B. Zhu, J. Am. Chem. Soc. 126 (2004) 62.
[6] C. Badre, T. Pauporte, M. Turmine, D. Lincot, Nanotechnology 18 (2007) 365705.
[7] C.S. Lao, Y. Li, C.P. Wong, Z.L. Wang, Nano Lett. 7 (2007) 1323.
[8] E.L. Papadopoulou, M. Barberoglou, V. Zorba, A. Manousaki, A. Pagkozidis, E. Stratakis, C. Fotakis, J. Phys. Chem. C 113 (2009) 2891.
[9] E.L. Papadopoulou, V. Zorba, A. Pagkozidis, M. Barberoglou, E. Stratakis, C. Fotakis, Thin Solid Films 518 (2009) 1267.
[10] R.D. Sun, A. Nakajima, A. Fujishima, T. Watanabe, K. Hashimoto, J. Phys. Chem. B 105 (2001) 1984.
[11] M. Miyauchi, A. Shimai, Y. Tsuru, J. Phys. Chem. B 109 (2005) 13307.
[12] L.Y. Lin, D.E. Kim, Thin Solid Films 517 (2009) 1690.
[13] F.M. Meng, L. Xiao, Z.Q. Sun, J. Alloys Compd. 485 (2009) 848.
[14] S. Kuo, W.C. Chen, F. Lai, C.P. Cheng, H.C. Kuo, S.C. Wang, W.F. Hsieh, J. Cryst. Growth 287 (2006) 78.
[15] N.A. Patankar, Langmuir 20 (2004) 7097.
[16] N.A. Patankar, Langmuir 20 (2004) 8209.
[17] A.B.D. Cassie, S. Baxter, Trans. Faraday Soc. 40 (1944) 546.
[18] M. Miyauchi, N. Kieda, S. Hishita, T. Mitsuhashi, A. Nakajima, T. Watanabe, K. Hashimoto, Surf. Sci. 511 (2002) 401.