Vol 18 No 5, May 2009
1674-1056/2009/18(05)/1942-05
Chinese Physics B
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ZnO micro–nano composite hydrophobic film prepared by the three-step method*

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(Received 27 July 2008; revised manuscript received 26 November 2008)

The hydrophobicity of the lotus leaf is mainly due to its surface micro–nano composite structure. In order to mimic the lotus structure, ZnO micro–nano composite hydrophobic films were prepared via the three-step method. On thin buffer films of SiO_2, which were first fabricated on glass substrates by the sol–gel dip-coating method, a ZnO seed layer was deposited via RF magnetron sputtering. Then two different ZnO films, micro–nano and micro-only flower-like structures, were grown by the hydrothermal method. The prepared films have different hydrophobic properties after surface modification. The structures of the obtained ZnO films were characterized using x-ray diffraction and field-emission scanning electron microscopy. A conclusion that a micro–nano composite structure is more beneficial to hydrophobicity than a micro-only structure was obtained through research into the effect of structure on hydrophobic properties.

Keywords: three-step method, ZnO, micro–nano structure, hydrophobic film
PACC: 6770, 6855, 8116D

1. Introduction

Wettability, which plays a significant role both in natural phenomena and human activities, is not only an important property, but also a kind of normal interphase phenomenon of solid surfaces. It can be measured by contact angle and depends both on the structure configuration and chemical component of the surface. Surfaces with contact angles lower than 90° are called hydrophilic surfaces, otherwise they are hydrophobic. It is an ultrahydrophobic surface when the contact angle is higher than 150°, and this has recently attracted significant attention due to its potential application in self-cleaning materials and micro fluidic apparatus.[1−10]

Both porous aligned-carbon-nanotube (ACNT) films prepared by pyrolysis of metal phthalocyanines[11] and silicon wafers with microscaled pillars prepared by plasma etching[12] have shown ultrahydrophobic properties. However, the complicated and costly process limits their application. On the other hand, ZnO nanorod array films obtained through a simple and low cost process[13,14] have also shown hydrophobic properties, but the dense distribution of ZnO rods limits further improvement of the hydrophobicity due to the Cassie model.[15] In addition, as found through bionic research, the lotus effect is essentially due to the micro–nano composite structure of the leaf surface, which is of more benefit to hydrophobicity than a nano-only or micro-only structure.[16] Thus, we hope that bionic hydrophobic films can be obtained through the control of the surface self-assembly structure.

In this paper, in order to mimic the surface structure of a lotus leaf, ZnO micro–nano composite hydrophobic films were prepared via a three-step method. A thin SiO_2 buffer layer, acting as a rough suface beneficial to the later growth of ZnO, was first fabricated on glass substrates by the sol–gel dip-coating method. ZnO seeds were then deposited via RF magnetron sputtering to make the ZnO micro–nano structures disperse more homogeneously. After that, two different ZnO films, micro–nano and micro-only flower-like structures, were grown by the hydrothermal method. The prepared films have different hydrophobic properties after surface modification.

2. Experimental

ZnO micro–nano composite hydrophobic films were prepared via a three-step method including the

*Project supported by the Science Fund of Anhui Province, China (Grant No 070414187) and the National Fund for Fostering Talents in Basic Science of China (Grant No J0630319/J0103).
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preparation of SiO_2 film substrates, a ZnO seed buffer layer and ZnO micro–nano/micro flower-like structure films. Then the obtained films were surface modified. The chemical reagents were all analytic-grade.

The SiO_2 film was fabricated on glass substrate by the sol–gel dip-coating method according to that described in Ref.[17]. The precursor solution was prepared by mixing tetraethyl orthosilicate (ETOS), ethanol, H_2O and HCl in a volume ratio of 3:4:3:0.035, and became homogeneously transparent after stirring by a magnetic starter for 1h at 50°C. The obtained films were annealed at 200°C for 1h to remove inorganic components such as H_2O and HCl, then at 400°C for 1 h to evaporate the organic remnants. The annealing temperature data was gained through thermoanalysis.

A ZnO seed buffer layer was deposited via RF magnetron sputtering on both the glass and the prepared SiO_2 film. For sputtering a pressed ZnO powder target with 4N purity was annealed in a muffle furnace at 1200°C for 5 h in air ambience, and then cooled slowly down to room temperature. The sputtering gas was a mixture of Ar and O_2 with 4N purity in a volume ratio of 1:1 and at a working pressure of 3 Pa. The distance between the target and the substrate was 70 mm and the sputtering power was 100 W. Under this condition the final thickness of the seed layer obtained was 10 nm.

The ZnO micro–nano and micro-only flower-like structures were grown by the hydrothermal method given in Refs.[18, 19]. To obtain the micro-only structure, an aqueous precursor solution of the $Zn(en)_2^{2-}$ complex was prepared by mixing zinc acetate, ethylenediamine (en), and methenamine (HMT) in a molar ratio of 1:3:1 while the zinc concentration was 0.001 mol/L. The precursor was poured into a Teflon-lined autoclave and maintained at 96°C for 20 h before being slowly cooled down to room temperature. To obtain the micro–nano structure, an aqueous precursor solution of the $Zn(OH)_4^{2-}$ was prepared by mixing 0.5 mol/L $ZnAc_2$ and 5mol/L NaOH solutions in a volume ratio of 1:1. The prepared precursor was mixed with ethanol in a volume ratio of 1:11 under constant stirring. The mixture was then poured into a Teflon-lined autoclave and maintained at 100°C for 17 h before being slowly cooled down to room temperature. The substrates were erected at the bottom of autoclave to make the micro–nano flower-like ZnO films grow on them.

The prepared samples are presented in Table 1. All the samples were immersed in 0.5 mol/L NaOH solution for 2 h, then in hexane with trimethylchlorosilane (TMCS, 2% volume concentration) for 2 h and after that washed by deionized water and dried in an IR oven.

Table 1. List of samples and their contact angles.

No	film structures of samples	contact angle/(°)
1	glass	98
2	SiO_2 /glass	129
3	ZnO micro–nano flower/glass	122
4	ZnO micro–nano flower /ZnO seeds layer/glass	131
5	ZnO micro flower /ZnO seeds layer/ SiO_2 /glass	114
6	ZnO micro–nano flower /ZnO seeds layer/ SiO_2 /glass	146

The structure of the ZnO films obtained was characterized using field-emission scanning electron microscopy (FESEM) and the crystal quantity was detected using x-ray diffraction (XRD). The three-phase contact angle was measured by an optical contact angle measuring device.

3. Results and discussion

3.1. Film structure

As shown in Fig.1, many micro papillas covered by many serried nano thorns were spread evenly over the lotus surface. It is such a micro–nano composite structure that gives the surface a rough structure and leads to its hydrophobic properties. As presented in Fig.2, the ZnO micro–nano composite flowers, each of which is expected to mimic the papillas of the lotus, are evenly spread over the rough SiO_2 film on which a ZnO seed buffer layer was deposited. Such a stratified film is expected to mimic the lotus surface and possess hydrophobicity.

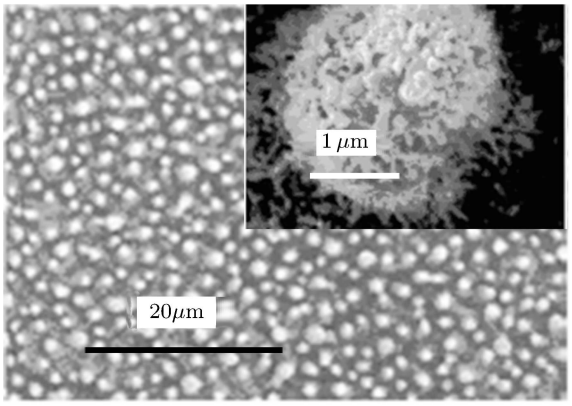


Fig.1. SEM image of lotus.[16]

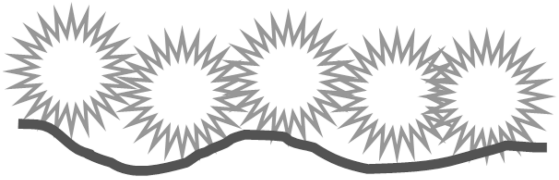


Fig.2. Bionics film structure.

An SEM image of the prepared ZnO micro–nano flower-like film is shown in Fig.3(a). The mean diameter of each micro–nano flower is about 1 μm while the scale of thorns on the flower is about 10 nm. In the preparation of the ZnO micro–nano flower, the reactants disperse more homogeneously and the amalgamation of the nucleus is not intense due to the solvent ethanol with a higher saturated vapour pressure, while the growth rate of the different crystal faces is more homogeneous due to the higher concentration of OH^-. As a result, the micro–nano flower-like morphology is formed.

To compare with the micro–nano composite structure, a micro-only structure of ZnO was prepared. As can be seen from the SEM image in Fig.3(c), the mean diameter of each micro flower is about 15 μm, while the mean diameter of each ZnO rod on the flower is about 100 nm. In the preparation of the ZnO micro-only flower, ZnO nanorods are easier to form in the medium of a lower OH- concentration and self-assemble into micro flower-like structure under the higher pressure caused by the airtight autoclave.

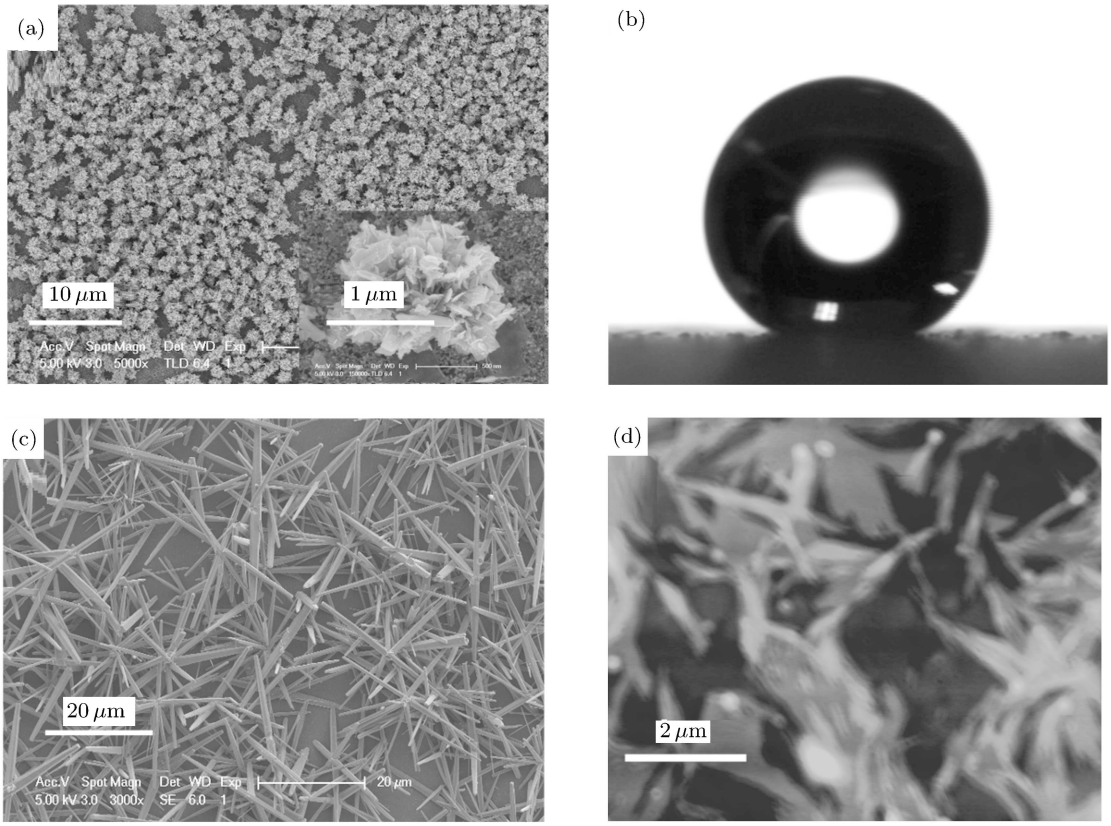


Fig.3. SEM images of the flower-like structure of ZnO, an AFM image of SiO_2 film substrates and an image of contact angle. (a) ZnO micro–nano flower film, (b) contact angle image of sample 6, (c) ZnO micro flower film and (d) SiO_2 film.

In the XRD patterns of ZnO with typical morphologies, shown in Fig.4, all the diffraction peaks are well assigned to hexagonal phase ZnO reported in the JCPDS card (No 36-1451).

Both the XRD patterns of micro–nano and micro flower-like ZnO exhibit similar heteromorphism, but with different configurations. The former is due to the fact that the ZnO micro–nano flower was isotropically grown during the crystallization process. The latter is because the ZnO micro flower was assembled by ZnO rods, each of which was well crystallized, leading to macroscopic isotropy.

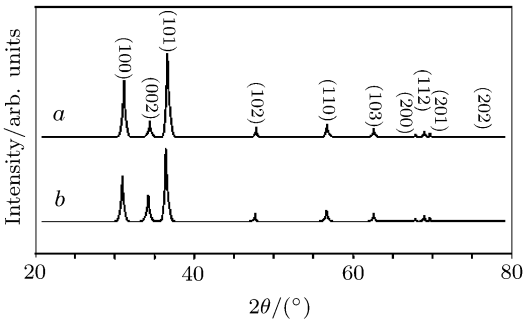


Fig.4. XRD image of the flower-like ZnO structure, where curve a is for micro ZnO and curve b is for micro–nano ZnO.

The SiO_2 films made under acidic conditions have two characteristics. The surface of the SiO_2 film is accidented in a wide dimension, which is beneficial to the protection of the flower-like structure and the enhancement of its adhesive ability. Additionally, a kind of rough surface structure, which is present in the micron dimension, is propitious to form the ZnO crystal. This results from crystal theory. When there is a solid and liquid interphase existing in solution, the process of crystal formation belongs to heterogeneous nucleation. The critical nuclear forming energy is

$$\Delta G_h^* = \frac{16\pi\sigma_{\mathrm{LN}}^3}{3(\Delta G_\nu)^2} f(\theta), \tag{1}$$

where ΔG_ν is the change of free energy per unit volume, σ_{LN} is the surface free energy, $f(\theta)$ is the shape factor and θ is the contact angle in crystal formation,

$$f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}. \tag{2}$$

When $\theta = 0°$, the crystal grows in the solid and liquid interphase, then $f(\theta) = 0$ and $\Delta G_{\mathrm{h}}^* = 0$.

When $\theta = 180°$, the crystal grows in the liquid phase, then $f(\theta) = 1$ and $\Delta G_{\mathrm{h}}^* = \Delta G^* > 0$.

From the above analysis, the lower critical nuclear forming energy in the interface could be obtained. Furthermore, the increase of solid and liquid interphase roughness will lead to the decrease of supercooling and faster crystal formation. Therefore ZnO crystal formation occurs more readily on the rough surface of SiO_2.

3.2. Hydrophobicity comparison of the prepared films

A hydrophobicity comparison of different film samples presented in Table 1 is made in order to analyse the effect of structure on hydrophobic properties. The contact angles can be found in Table 1. A drop image is shown in Fig.3(b).

Influence of SiO_2 film substrates

The contact angle of the SiO_2 film is 31° higher than that of glass from the comparison between samples 1 and 2 in Table 1, demonstrating that the SiO_2 film has a certain hydrophobic ability itself due to the rough surface structure.

The contact angle of the ZnO micro–nano flower film with SiO_2 film substrates is 24° higher than its counterpart without SiO_2 film substrates from the comparison between samples 3 and 6, indicating that SiO_2 film substrates are of benefit to the hydrophobicity of ZnO micro–nano flower film. Here the SiO_2 film has two functions in the formation of ZnO flower-like films: the roughness scale of the SiO_2 film substrates is close to the ZnO micro–nano flower's diameter, which helps the ZnO flowers spread more homogeneously and cohere with the substrates more solidly. Additionally the ZnO flower-like film can inherit the surface roughness of the SiO_2 films, which has a certain hydrophobic ability itself.

Influence of ZnO seed layer

The contact angle of the ZnO micro–nano flower-like film with a ZnO seed layer is 9° higher than its counterpart without a ZnO seed layer from the comparison between samples 3 and 4, demonstrating that the ZnO seed layer is of benefit to the hydrophobicity of ZnO micro–nano flower-like film. As the crystal nucleus of the ZnO flowers, the ZnO seed layer can not only make the ZnO flower spread more homogeneously on the substrate, but also enhance the quantity of the ZnO crystal.

Influence of ZnO flower structure

From the comparison between samples 2 and 5, the contact angle of the ZnO micro flower film with SiO_2 film substrates is 15° lower than that of the SiO_2 film, indicating that the ZnO micro flower film does not have fine hydrophobicity. As analysed in Section 3.1, the ZnO micro flower-like film has a micro-only structure, whose roughness scale is too large to have good hydrophobicity. On the other hand, by comparing samples 2 to 6, the contact angle of the ZnO micro–nano flower film with SiO_2 film substrates is 17° higher than that of the SiO_2 film. Therefore the ZnO micro–nano flower-like film has the best hydrophobicity. As an explanation, the ZnO micro–nano flower possesses a typical micro–nano composite structure which is close to the lotus papilla's structure.

4. Conclusion

In summary, ZnO micro–nano and micro-only flower-like films were successfully prepared via the three-step method. These films gained a certain hydrophobic ability after surface modification. The conclusion that a micro–nano composite structure is more beneficial to hydrophobicity than a micro-only structure was obtained through the study of the effect of structure on hydrophobic properties. The prepared ZnO film does not show a process of superhydrophobicity, due to the surface modified reagent trimethylchlorosilane with higher surface free energy than that of fluoride,, which is much more expensive. However, the intent of this paper was to prepare hydrophobic film through the control of surface structure. Considering the low cost of preparation, our research is of great value in application.

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