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Chemical Physics Letters 413 (2005) 450–453
CHEMICAL PHYSICS LETTERS
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Wettability conversion on ZnO nanowire arrays surface modified by oxygen plasma treatment and annealing

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Received 1 July 2005; in final form 9 August 2005
Available online 30 August 2005

Abstract

The ZnO nanowire arrays were synthesized by a simple vapor–solid process. Wettability of nanowire arrays was studied by measuring contact angle. Under both oxygen plasma treatment and annealing at O_2 atmosphere, the wettability of nanowire arrays changed from hydrophobic to super-hydrophilic. By measuring the photoluminescence spectra of modified samples, we affirm that the wettability conversion is not due to oxygen vacancies. It is thought that the oxygen related surface defect is the main reason to make this kind of change.

1. Introduction

Modifying the surface wettability of semiconductor is important in many situations. Wettability is one of the most important properties, which is governed by both the chemical composition and the geometrical structure of solid surface [1,2]. Among the various semiconductors, wettability property of TiO_2 has been considerably studied [3–7] and has already been successfully applied as a transparent super-hydrophilic coating with antifogging and self-coating properties [8].

As a wide band-gap semiconductor, hydrophobic ZnO one-dimensional (1D) nanostructures have drawn great attention in ultra-violet lasers, nanosensors and field emission devices [9–12]. Single ZnO nanowire has also been used to construct gas sensors [13]. In order to extend the application of ZnO nanowires to chemical sensors or even biosensors, one important point is to change the wettability of ZnO from hydrophobic to super-hydrophilic by surface modification because all the biopolymers can be dissolved in water. By now, only a few papers were concerned with wettability conversion of ZnO nanostructures, in which they used ultraviolet (UV) illumination to vary surface from hydrophobic to hydrophilic [7,14]. In this report, we treated the as-synthesized ZnO nanowire arrays by oxygen plasma or annealing at O_2 atmosphere. In both cases, the wettability of samples changed from hydrophobic to super-hydrophilic.

2. Experimental

Vertically aligned ZnO nanowire arrays were synthesized in a traditional horizontal furnace by a simple vapor phase transport process. Zinc powder (99.99%) was loaded into a quartz boat in the center of the furnace as

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doi:10.1016/j.cplett.2005.08.039

the source. Si(1 0 0) substrate was laid above the zinc source with a distance of about 4 mm. The furnace was then ramped to 430 °C under a constant flow (150 sccm) of pure Ar gas. After the desired temperature was reached, pure Ar gas was switched to normal nitrogen gas to start the ZnO growth. The oxygen source was unintentionally introduced by the residual O_2 components in the nitrogen gas. The surface of the sample presented a gray white colored layer after it was cooled down and taken out of the furnace. The as-synthesized sample was characterized by the field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX) attached to SEM, X-ray diffraction (XRD), Photoluminescence (PL) measurement and contact angle (CA) characterization.

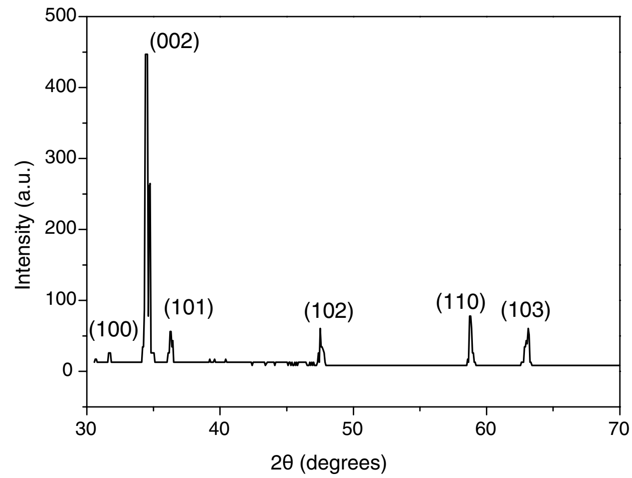

Fig. 2. XRD analysis of the ZnO nanowire arrays.

3. Results and discussion

Fig. 1 shows the FESEM image of the ZnO nanowire arrays grown at 430 °C. The length of the nanowires ranged from 1 to 1.5 μm, with diameters between 70 and 100 nm. Most of the nanowires grow vertically on the substrate surface. The EDX analysis proved that the nanowires contain only zinc and oxygen elements (figure is not given).

The XRD analysis pattern shown in Fig. 2 indicates that the nanowires are ZnO wurtzite structure with lattice parameters of $a = 0.325$ nm, $c = 0.521$ nm. The strong (0 0 2) diffractive peak illustrates that the sample is *c*-axis preferred orientation, which is in consistence with the FESEM result.

The wettability was analyzed by the water contact angle measurement. Fig. 3a shows the hydrophobic properties of the as-synthesized sample with a contact angle of 140°. The hydrophobic is believed to be related with the microstructure of the sample. Because the sample surface is built by nanowires tips, the surface roughness is high. The high surface roughness contributes to the hydrophobic of ZnO nanowire arrays. And because there is much room between the two nanowires, the water will enter and fill the grooves of the films, leaving only the upper part of the nanowires that is not in contact with the liquid, which is the three-dimensional capillary effect of a rough surface [14–16]. According to the above effects, the surface of ZnO nanowire arrays is super-hydrophobic.

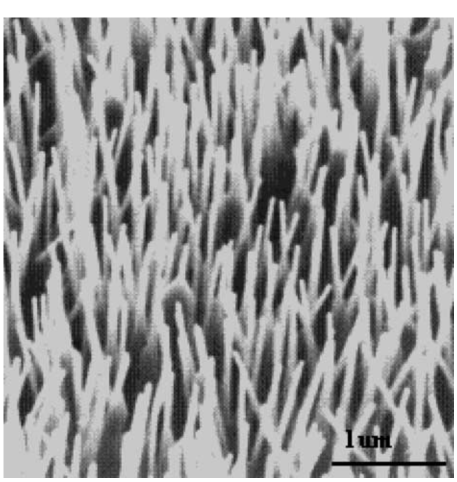

Fig. 1. FESEM image of the ZnO nanowire arrays.

By oxygen plasma treatment for 20 min, which was carried out under a power of 50 W with oxygen gas flow of 6 ml per min at room temperature, the surface turned to super-hydrophilic with a contact angle less than 5°, as shown in Fig. 3b. The contact angle decreases with increasing oxygen plasma treatment times (Fig. 4a). To further our investigation, another ZnO nanowires sample was annealed in O_2 atmosphere for 1 h at 600, 700 and 800 °C, respectively. After annealing, the surface also changed to hydrophilic. But with increasing annealing temperature, the contact angle grows larger. The sample annealed at 600 °C shows a contact angle of less than 10° and the sample annealed at 800 °C shows a contact angle of 40° (Fig. 4b). After being stored in the dark at ambient atmosphere for 108 h, the wettability gradually reconverted to its original hydrophobic properties.

The wettability conversion of ZnO is considered due to some changes of the microstructures on the surface of the nanowires. [17] and Xinjian Fang [8] have used UV light to illuminate the TiO_2 and ZnO samples and they obtained the same wettability conversion. They believed that the surfaces of the TiO_2 and ZnO would generate electron-hole pair under UV illumination, and that some of the holes could react with lattice oxygen to form surface oxygen vacancies. These surface oxygen vacancies provide defect sites for chemisorption, which induces super-hydrophilic of the surfaces.

As photoluminescence (PL) properties of ZnO are very sensitive to oxygen vacancies, we measured the

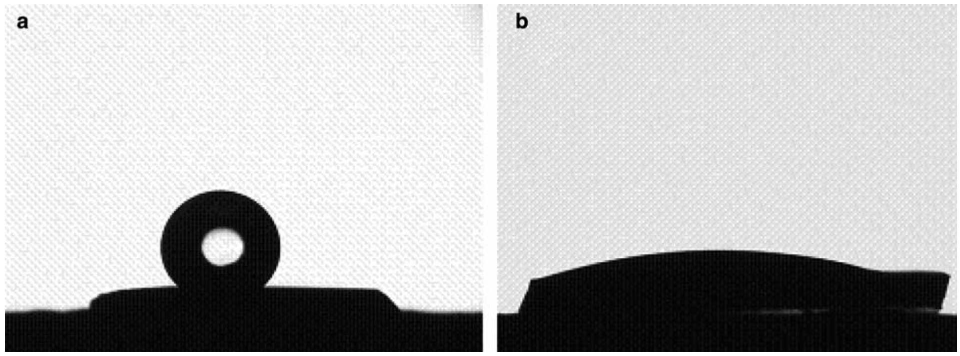

Fig. 3. Contact angle measurement of the ZnO nanowire arrays: (a) as-synthesized and (b) treated under oxygen plasma for 20 min.

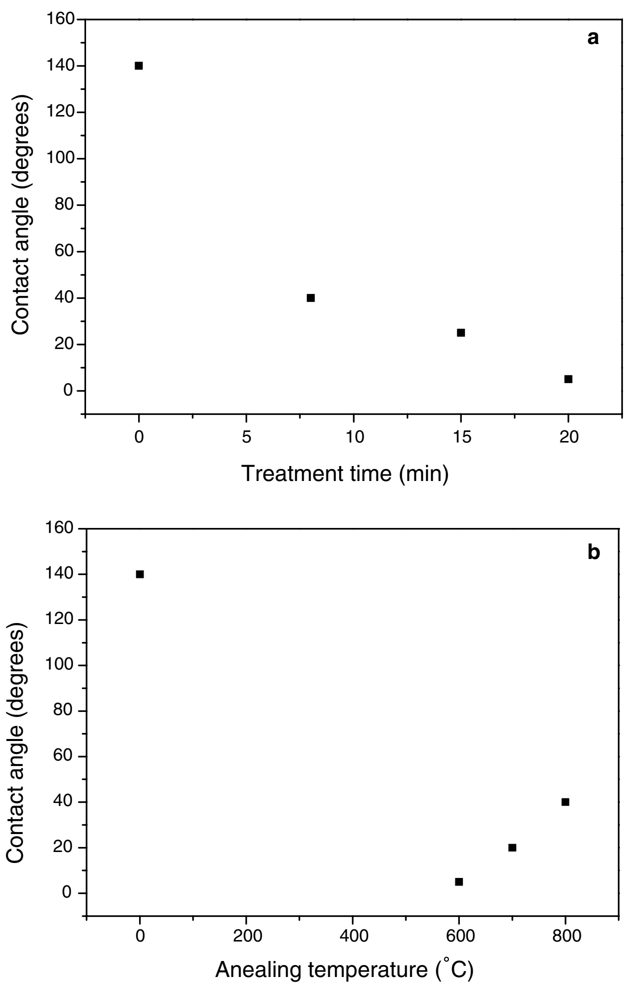

Fig. 4. Contact angle as a function of: (a) oxygen plasma treatments time and (b) annealing temperature at O_2 atmosphere.

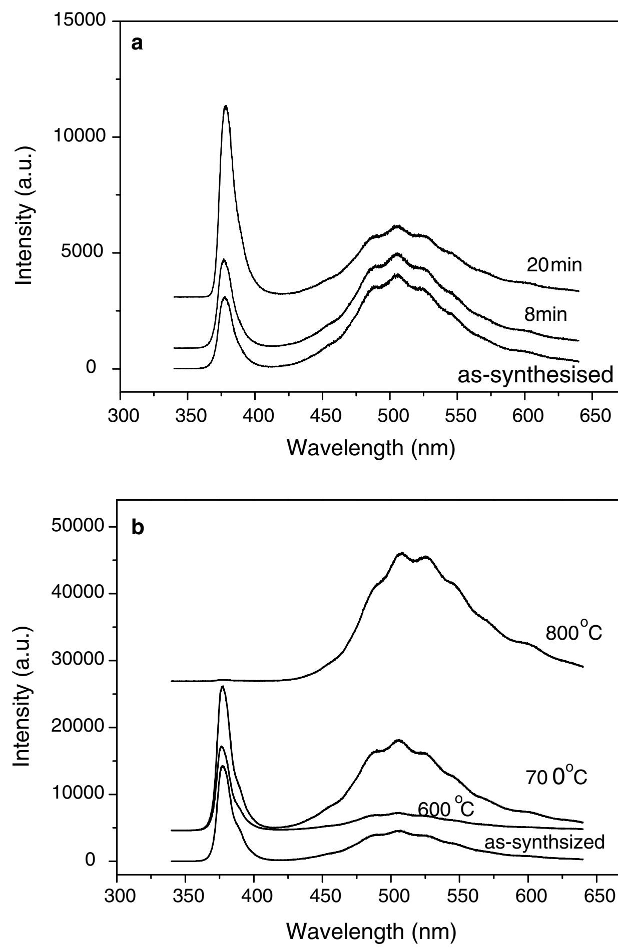

Fig. 5. PL spectra of: (a) the as-synthesized nanowire arrays and oxygen plasma treated samples for 8 and 20 min, respectively and (b) the as-synthesized nanowire arrays and annealed samples at different temperatures.

ZnO nanowires emission spectra using a He–Cd laser of 325 nm as an excitation source. From the PL spectra of the as-synthesized sample and the oxygen plasma treated ones shown in Fig. 5a, we can observe that all the curves contain a strong UV emission and a visible band. The UV emission is considered to have originated from the radiative recombination of exciton, and the visible band is commonly attributed to the singly ionized oxygen vacancies [18–20]. The intensity of the visible emissions decreases with increasing treatment times, which indicates that the oxygen plasma treatment could reduce oxygen vacancies density in nanowires. But the annealing samples show that visible emission first decreases at 600 °C, then increases with the annealing temperature at 700 and 800 °C (Fig. 5b). Comparing this result with that of the contact angle as a function of the annealing temperature, it appears that with increasing the density of oxygen vacancies the contact angle will become larger. Both of the above evidences suggest that wettability conversion of ZnO nanowires array is not originated from oxygen vacancies in our results.

In our experiment, both the treatments with oxygen plasma and the annealing at O_2 atmosphere have excess oxygen. The excess oxygen may create some oxygen related defects on nanowires surface, such as the dangler bonds of O-, which make the surface have high surface free energy. These kinds of defects could connect with water molecular by forming some weak bonds. Due to this reason, the wettability of ZnO nanowire arrays changes from hydrophobic to super-hydrophilic. Because these defects are not stable, when the time is sufficient enough the surface will reconvert to its original wettability.

4. Conclusions

In summary, well aligned ZnO nanowire arrays were synthesized by a simple vapor–solid process. And reversible surface wettability conversion has been accomplished under both oxygen plasma treatment and annealing at oxygen atmosphere. The conversion from hydrophobic to hydrophilic is not caused by oxygen vacancies but due to the surface state variety.

Acknowledgments

This work was supported by the key Project of National Natural Science Foundation of China under Grant Nos. 60336020, 60429403, 6078031, 60376009, and 50402016, and by the Innovation Project of Chinese Academy of Sciences.

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