Research Article

Controllable Growth of the ZnO Nanorod Arrays on the Al Substrate and Their Reversible Wettability Transition

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High-quality ZnO nanorod arrays are formed using the ZnO nanoflakes on the Al substrate as seed layer. A reversible wettability transition can be easily achieved via alternation of UV irradiation and dark storage. The physical adsorption of the water molecules on the surface of ZnO nanorod arrays is considered to be responsible for this transition, which is confirmed by X-ray photoelectron spectroscopy.

1. Introduction

Wettability design and manipulation have received particular attention in modern society because of its potential applications [1–3]. Wettability results from low surface free energy and surface morphology with special micro- and nanorough structures [4, 5]. Recently, with the rapid development of the smart devices, such as intelligent small droplet manipulation, reversible wettability switch has become a research focus and been realized by modification of responsive materials [6]. Such responsive materials present intrinsic reaction when they face the different environmental stimuli such as light illumination [7], pH [8], electric field [9], and temperature [10]. Being a photoresponsive semiconductor, the ZnO has aroused great attention because of its special electronic, optical, and acoustic properties [11]. Reversible wettability switch on the solid surface modified by ZnO nanostructure has been reported [12]. Reversible superhydrophobicity to superhydrophilicity switch was observed on the glass wafer coated by ZnO nanorods [13].

In this paper, high-quality ZnO nanorod arrays are achieved by hydrothermal and chemical vapor deposition route on the Al substrate. The wettability transition between the superhydrophobicity and superhydrophilicity is observed via alternation of UV irradiation and dark storage. The

nanostructure and special photoelectric properties of the ZnO are two important factors for the wettability transition.

2. Methods

The procedure to growing high-quality vertical ZnO nanorod arrays consists of two steps: (1) growing two-dimensional ZnO nanoflakes on the Al substrates using low-temperature hydrothermal route and (2) the formation of high-quality vertical ZnO nanorod arrays on the surface of two-dimensional ZnO nanoflakes through chemical vapor deposition route.

In the first step, Al substrate was cleaned thoroughly in acetone for about 30 min by ultrasonic waves and cleaned with deionized water in sequence. The Al substrate was suspended in the beaker filled with aqueous solution of zinc nitrate hydrate (8 mM) and hexamethylenetetramine (8 mM) at 95°C for 2 h. The Al substrate was then taken out from the solution, rinsed with deionized water, and dried by a nitrogen stream. Last, the sample was annealed at 450°C in air for 30 min.

In the second step, the alumina boat with Zn powder (purity: 99.999%) was placed into the horizontal tube furnace. The sample which was prepared in the first step was put horizontally on the downstream side of the alumina boat at a distance of 8 cm. Before the growth, argon was introduced

FIGURE 1: SEM images of the as-grown ZnO samples on the Al substrate. (a) Large-area view of the ZnO nanoflakes on the Al substrate, (b) top images of the ZnO nanorod arrays and (c) high magnification ZnO nanorod arrays, and (d) side views of the ZnO nanorod arrays.

into the system through a mass-flow controller with a flow 120 sccm and the pressure was maintained at 80 Pa. The temperature of the furnace was changed linearly with time to 600°C at the rate of 20°C/min. Subsequently, oxygen was given to the system at a flow rate of 100 sccm. The reaction was carried out at about 600°C for 40 min. After that, the furnace was cooled to room temperature, while argon and oxygen flow was stopped. The as-grown film was stored in the dark environment for a week before being measured.

The morphologies of sample nanostructure were characterized by scanning electron microscopy (SEM, Philips Sirion 200). The component of the sample was characterized by X-ray diffraction (XRD, D/max-2200/PC). The water contact angles (WCAs) on the surface were measured with deionized water of 5 μ l by using an optical contact angle meter system at ambient temperature (Data Physics Instrument GmbH, Germany). The X-ray photoelectron spectroscopy spectrum (XPS) of the samples was measured by Thermo ESCALAB 250.

3. Results and Discussions

Figure 1(a) shows the typical morphology of ZnO nanoflakes on the Al substrate using low-temperature hydrothermal route. Many sheet-like ZnO nanoflakes were produced and nearly vertical to the Al substrate. Figure 1(b) is image of the ZnO nanorod arrays coated on the ZnO nanoflakes.

Figure 1(c) is the further magnified image. From the SEM image as showed in Figure 1(c), the ZnO nanorod arrays have a flat surface morphology, with almost the same diameters of about 150 nm. Side image of the SEM view of the arrays (Figure 1(d)) suggests that the ZnO nanorod arrays grow completely vertically and the height is about 5 μ m. Figure 2 compared the XRD spectrum of the ZnO nanorod arrays (Figure 2(a)) with the ZnO nanoflakes (Figure 2(b)) on the Al substrate. The XRD spectrum of the ZnO nanorod arrays is almost the same as the ZnO nanoflakes, indicating that the orientation of the ZnO nanoflakes is of great importance to the orientation of the ZnO nanorod arrays. It is well-known that the effect of seeds layer is very important in fabricating high-quality vertical ZnO nanorod arrays. So we can deduce that the role of ZnO nanoflakes on the Al substrate is seeding which directly leads to the formation of ZnO nanorod arrays.

The wettability of the ZnO nanorod arrays is studied by water contact angle (WCA) measurement. The WCA on the surface coated by ZnO nanorod arrays is about 158° as shown in Figure 3(a). After UV illumination, the WCA is about 0°. After depositing the film which was irradiated by the UV in the dark environment for five days, the film is still superhydrophobic again. This process can be repeated many times and the corresponding process is shown in Figure 4.

Surface free energy and surface morphology have important effects on the surface wettability. The high-quality ZnO nanorod arrays on the Al substrate in Figure 1 increase the air

FIGURE 2: XRD patterns of the as-grown ZnO samples. (a) ZnO nanorod arrays. (b) ZnO nanoflakes.

FIGURE 3: The shape of water droplet on the ZnO nanorod arrays (a) before UV irradiation and (b) after UV irradiation.

fraction of the water-air interface. This means that the special nanostructure will increase the WCA. The superhydrophobicity of the ZnO nanorod arrays can be explained by Cassie equation [14]:

$$\cos \theta^* = -1 + f_1 (1 + \cos \theta), \quad (1)$$

where θ^* and θ are CA on the rough and flat surface and f_1 is the solid fraction in contact with water. Because the surface roughness of ZnO nanorod arrays is much higher than ZnO nanoflakes, much air is easy blocked among the ZnO nanorod arrays when the water droplet is placed on it, so the value of f_1 decreases rapidly and the CA increases. This is the reason that the Al substrate coated by ZnO nanorod arrays shows superhydrophobicity.

The wettability of the solid is determined by surface free energy and the geometric structure. The geometric structures of the ZnO nanorod arrays do not change before and after UV irradiation, indicating that the wettability transition is caused by surface free energy. Hole of electron-hole pairs generated in the ZnO by UV irradiation will react with lattice oxygen to form surface oxygen vacancies [15, 16]. Subsequently, water molecules absorbed at the surface oxygen vacancies will produce the hydroxyl groups which lead to the physical adsorption of the water molecules. The hydrophilicity of film

FIGURE 4: Reversible wettability switching by alternating UV irradiation and dark storage.

FIGURE 5: X-ray photoelectron spectroscopy spectra of the O 1s level before and after UV irradiation.

increases. Figure 5 shows the XPS of ZnO nanorod arrays before and after UV irradiation. The shoulder and intensity of the O 1s at the higher binding energy are increased. This confirms the existence of physical adsorption of the water molecules on the surface of ZnO nanorod arrays. From Wenzel equation [17],

$$\cos \theta^* = r \cos \theta, \quad (2)$$

where r is rough factor and the hydrophilicity of film will be enhanced to superhydrophilicity because of the special nanostructure. Oxygen atoms gradually take the place of the hydroxyl groups adsorbed on the ZnO nanorod arrays when the film was placed in the dark. In the end, the surface wettability changes back to the superhydrophobicity.

In order to acquire the detailed information about the effect of UV illumination on the WCA, Figure 6 has given the WCA as the function of UV illumination time. It can be seen

FIGURE 6: Contact angle versus UV irradiation time for the water droplet on the surface of ZnO nanorod arrays.

that the WCA decreases abruptly from 158° to 50° about after 60 min of UV irradiation because of the high speed yielding of electron-hole pairs after UV irradiation. With the increase of illumination time from 60 to 160 min, the change speed of WCA is slow and, at last, the wettability of film changes from superhydrophobicity to superhydrophilicity.

4. Conclusions

Dense and vertically aligned ZnO nanorod arrays with a large area are fabricated by a simple two-step process on the Al substrate. The as-grown film shows good superhydrophobicity and the contact angle is about 158° . The film shows good superhydrophilicity and the contact angle is about 0° after UV irradiation. Reversible wettability transition is achieved via alternation of UV irradiation and dark storage. The nanostructure and special photoelectric properties of the ZnO are two important factors for this behavior.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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