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Fabrication of CdS films with superhydrophobicity by the microwave assisted chemical bath deposition

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Abstract

A simple method of microwave assisted chemical bath deposition (MA-CBD) was adopted to fabricate cadmium sulfide (CdS) thin films. The superhydrophobic surface with a water contact angle (CA) of 151° was obtained. Via a scanning electron microscopy (SEM) observation, the film was proved having a porous micro/nano-binary structure which can change the property of the surface and highly enhance the hydrophobicity of the film. A possible mechanism was suggested to describe the growth of the porous structure, in which the microwave heating takes an important role in the formation of two distinct characteristic dimensions of CdS precipitates, the growth of CdS sheets in micro-scale and sphere particles in nano-scale. The superhydrophobic films may provide novel platforms for photovoltaic, sensor, microfluidic and other device applications.

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Keywords: Wettability; Cadmium sulfide films; Micro-nano-binary structures; Microwave irradiation; Superhydrophobic

1. Introduction

With the rapid development in semiconductor industries and the increasing demand of superior performance for devices, the ability to precisely modulate material interfaces is playing an increasingly dominant part in the development of new technologies relevant to our lives. The wetting ability of liquids on solid surfaces which relies on surface energy and structures has become more and more important in many industrial processes [1–6], because surface energy and geometric structures also have great influence on the performance of many optical, photovoltaic and microfluidic devices [6–9]. For example, semiconductor films with hierarchical pore structures showed improved performance of solar cells [7], the performances of optical band pass filters which depend on relative humidity of surface [8] and sensors which require high sensitivity are determined by the surface characteristics of the materials [9]. Therefore, controlling the structures of material surface and fabricating surfaces with special wettability are extremely important. Superhydrophobic surface has attracted great interests in these years because of its special wettability for promising applications [1,6–9]. In nature, the surfaces of lotus leaf with two-scaled hierarchical structures exhibit fantabulous water repellent properties and self-cleaning performance [1]. Lots of researches have been done to obtain such surface characteristics [1–9]. However, most previous work often uses combination facilities such as depressing surface energy and enhancing surface roughness. The strict preparation conditions (i.e., high temperature, multistep process) and high cost of the previous methods made forming large-scale superhydrophobic surfaces for applications very difficult. Simple, rapid, inexpensive and low temperature processes are highly desired.

Cadmium sulfide (CdS) is a wide band gap semiconductor, which has been widely investigated as photoelectrical materials and nanostructured materials [10–20]. Many researches have been reported on the fabrication of CdS thin films on solid substrates by sputtering [10], thermal evaporation [11], self-assembly growth [12], epitaxial electrodeposition [13], etc. Most previous works aim to obtain a smooth film with better photoelectrical performances. The high surface area CdS film with multi-scale structures is rarely involved. Actually hierar-

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chical structures not only act on the hydrophobicity improvement of surface but also are beneficial to other applications, such as requirement of CdS combinational performances in gas detection sensors. The substantially enlarged film surface area and reduced wettability of CdS films will increase the sensitivity in a great range.

In present study, we introduce a simple fabrication technique based on chemical bath deposition process using microwave heating method to regulate the deposition rate of CdS for large-area superhydrophobic film with micro/nano-binary structures. It is found the hierarchical structure of CdS film can significantly change the property of the film surface, highly enlarge the surface aspect contacting with air and enhance the hydrophobicity. Our method reveals a good example of one-step preparation of superhydrophobic films with intrinsic hydrophilic material. The film deposition with a high degree of crystallinity can proceed on glass substrate and organic substrate that microwave inert. To the best of our knowledge, there has been no report on this kind of surface up to date.

2. Experiment

Cadmium sulfide film has been grown on ($2.5 \times 1 \times 0.2\ cm^3$) commercial glass substrates by MA-CBD method with varying deposition time and microwave powers. The glass substrates were cleaned by degreasing in ethanol in an ultrasonic bath for 30 min, rinsing in distilled water, etching with HCl (6 mol/L), and followed by a further rinse in distilled water. All the reagents used in the experiments were of analytical purity.

For the deposition of CdS films, 0.015 mol of $CdCl_2 \cdot 2.5H_2O$ and 0.045 mol of thiourea ($CS(NH_2)_2$) were sequentially put into a 250 ml laboratory beaker. The beaker was filled with 200 ml distilled water with constant stirring, and then ammonia ($NH_3 \cdot H_2O$) was used to adjust the pH value to 12. The beaker was maintained in a microwave oven under power 200 and 300 W and the deposition duration of CdS film is 5 to 30 min. All experiments were carried out initially at room temperature (about 25 °C) without further temperature control. The solution reached its boiling point in 3–5 min. After deposition, the films were washed by distilled water and dried in air for 72 h.

During the deposition process, the substrates were floated on the surface of the precursor solution as referred [14]. This is different from the conventional method in which the substrates were placed vertically in the solution. The floating substrate which favors high quality films would in a certain extent prevent the formed particles in the solution accumulating on the substrate surface.

The morphologies of the microstructures were observed on scanning electron microscope (SEM, Hitachi, S-4300). The contact angle (CA) was measured with a water droplet of 5 µl at ambient temperature (25 °C) with an optical contact angle meter (SurfaceTech Co. Ltd., Goniostar). The crystallization of the samples was characterized by X-ray diffraction (XRD), using a Bruker Advance D8 diffractometer.

3. Results and discussion

3.1. Morphology and contact angles

Fig. 1 shows the morphology and CAs of the CdS films obtained by MA-CBD with microwave irradiation time in the range of 10 min to 27 min. Fig. 1a is a typical SEM image of 10 min, the film surface is almost built by leaf-like structures, an enlarged view clearly shows that the structures with sheet thicknesses of 80–120 nm and pore diameters of 1–1.5 µm. The wall of the sheet is very smooth and the characteristic dimension of the porous structures is in a micro-scale. The CA on such surface is 112°. As the deposition time extends to 15 and 20 min, the surface morphology and the CAs of the resultant film change dramatically. It can be found from Fig. 1b the dimensions of the pore and the sheet reduce but the quantity increases. Moreover, a small quantity of nano-sized particles begins to appear on the surface layer of the film, and the CA on the surface increases to 141°. When the irradiation time gets to 20 min, the surface morphology of the resultant film is similar but more regular in the particle size. It is shown from Fig. 1c that the coating is built by more stacking of particles with diameter of about 80 nm, and forms a two-scaled structure, so called micro/nano-binary structure. The CA on such surface reaches 151°. However, if the deposition duration is too long, such two-scaled structures are not obvious, too many particles infill the hollow structures. Fig. 1d show that the film is almost covered by accumulation of particles, and the CA on the film of 27 min decreases to 128°. The relationship between deposition time and CAs is shown in Fig. 2. It is very obvious that the wettability on the surface changes dramatically with the deposition time.

Fig. 3 is the SEM image of some detailed samples of 5, 6, and 7 min. These specimens were prepared in order to elucidate how the film with porous structure formed. Unexpectedly, in the case of 5 min, the film is very smooth and it is composed of a thin layer of CdS particles with 80–100 nm wide, piled on by one another, shown in Fig. 3a. The CA on the smooth thin film is only 25°, which is very close to the intrinsic contact angle 26.2° reported in previous literature [26]. After little longer observed growth period of 6 min, another layer of larger, leaf-like fragments grow 1–2.5 µm wide and are observed from Fig. 3b, as the duration extends to 7 min, the surface is almost covered by the leaf-like structures. In Fig. 3c, a flat lower layer can also be seen beneath through gaps between the crossed growths, the film is consisted of a smooth layer of particles and a secondary layer of sheets that attached to the first layer.

3.2. Some relevant information of CdS deposition

The morphology of film is often determined by the preparation methodology and the growth process relating to materials. The growth mechanism of CdS films by Chemical bath deposition (CBD) has been discussed by different authors [14–25]. It is reported that the reaction rate often takes an important role on the morphology conversion in sulfide deposition. In the process, $NH_3 \cdot H_2O$ is used as chelating agent to control the hydrolysis