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Preparation and Physical Properties of CdSe Semiconductor Films by Ultrasonic Chemistry Method

Zhang zhiqian[1.2.a], Wu guangming[1.b], Gao dewen[1], Zhu yanying[1], Cao yang[1.2], Zhou yang[1.2]

[1]Beijing Institute of Petro-chemical Technology, Beijing 102617, China

[2]Beijing University of Chemical Technology, Beijing 100029, China

[a]zlzxqf@sina.com, [b]wuguangming@bipt.edu.cn

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Abstract. CdSe films have been prepared successfully by an ultrasonic chemical bath method, with $CdCl_2 \cdot 2.5H_2O$ and Na_2SeSO_3 as precursors, and trisodium citrate as complexing agent. The films were characterized by XRD, AFM, and UV-Vis. The results showed that the CdSe films were n-type semiconductor and had absorption in the visible region. The CdSe film electrode had higher electron transfer rate, which leads to a substantial improvement on the photocurrent. Optimal condition for preparing the CdSe thin films were as following: the ratio of Cd^{2+} to trisodium citrate was 1:1.5, the ratio of Cd^{2+} to Se^{2-} was 2.5:1, the pH value was 10, the deposition time was 2.5h, and the annealing temperature was 350°C.

1. Introduction

Due to the semiconductor nanoparticles having specific physical and chemical properties, such as quantum size effect and dielectric limit domain effect, therefore it has broad application prospects in photoelectric function and biological medicine etc devices [1]. CdSe nanocrystals, having the solar spectrum in visible light with the appropriate bandwidth, is used to produce efficient light-emitting device (LED), heterojunction solar cells and photoelectrochemical cells; and because it has a high ability to prevent high-energy rays, may impose a high electric field at room temperature, small leakage, high stability, easy to deliquescence, so it an important material for nuclear radiation detectors at room temperature, and it has been widely used in nonlinear optics, gas sensors , film converter, and γ-ray detectors[2-4].

It has a lot of methods to prepare CdSe thin film, such as vacuum evaporation, solvent heat, electrochemical deposition, chemical bath deposition method, of which chemical bath deposition (CBD) with a simple, low cost, the resulting film uniformity, film quality advantages, has broad application prospects[2-8]. The traditional CBD method to prepare CdSe thin film is mixing the source of cadmium, selenium source, ammonia, or hydrazine and then stirring at high temperature. However, the CdSe film prepared by CBD has a low yield. Ammonia used in the reaction process has volatile, toxic and has a great impact on the environment[9]. Temperature, pH, reaction concentration, film deposition and growth time can influent the film quality. In some conditions, there will be a great deal of and larger grains on the surface of films because of small differences in deposition time, thus affecting the optical electrical, properties and limiting the application of CdSe films [10].

In recent years, researchers have optimized the CBD method. Cui et al. [] have prepared CdS films with certain orientation and less large grains by using ultrasonic chemistry method. The ultrasonic cavitation results in local high-temperature and regional high-pressure zone with micron scale generally, which limits the innumerable chemical reactions within the range of microns. Because of the ultrasonic cavitation at the interface is the most strong, the reaction was carried out faster and more completely in the substrate surface than in solution, and the surface of the substrate is conducive to the generation of CdSe film. In addition, the role of ultrasound in the solution has strong mechanical, thermal and chemical effects. The mechanical effect can promote the interaction between ions thus promoting chemical reactions carried out completely, and the cavitation shock waves break a crystal shape structure, thereby inhibiting the formation of large micelles; thermal effects can promote cohesion; chemical effect can promote the oxidation-reduction reaction, so it's a good role in promoting the growth of the CdSe film.

In this paper, ultrasonic-assisted chemical bath method is involved to synthesize CdSe films, with 34.4 KHz, 50 W ultrasonic instead of high temperature stirring, and sodium citrate as complexing agent instead of ammonia. The effects of experimental parameters on the quality of CdSe film were investigated, such as concentration of reactants, pH value and so on. The films are characterized by XRD, AFM, and UV-Vis.

2. Experimental

2.1 Experimental reagents and instruments

Ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Ltd.); sodium hydroxide, sodium citrate, anhydrous sodium sulfite (North of Beijing Fine Chemicals Co., Ltd.); cadmium, selenium powder (Tianjin Chemical Reagent Factory Fu Chen). The water used in the experiments was doubly distilled water. Reagents used in the experiment were analytically pure, no further purification. The substrate of glass is degreased, rinsed in deionized water and ultrasonic cleaned.

2.2 Preparation of Na_2SeSO_3 solution

0.02mol selenium powder and excess of anhydrous sodium sulfite were added to flask, then 100ml water added and heated under continued stirring, after most of the selenium powder dissolved, the solution was filtered and the transparent filtrate obtained.

2.3 Orthogonal table

There are many factors influencing in CdSe thin films prepared by ultrasonic-assisted chemistry bath method. We choose four factors to analysis: the proportion of complexing agent (1:1.5, 1:2, 1:2.5, and 1:3), ratio of cadmium to selenium (1:1, 1: 2, 1:3, and 1:4), pH value (7, 9, 10, and 12), and deposition time (1h, 2h, 2.5h, and 3h).

Table 1 Orthogonal experiment table of CdSe films

Sample	Factors				Absorbance
	Proportion of complexing agent	Ratio of cadmium to selenium	pH value	Deposition time (h)	(%)
1	1.5	1	7	1	0.35
2	1.5	2	9	2	0.5
3	1.5	2.5	10	2.5	0.75
4	1.5	3	12	3	0.2
5	2	1	9	2.5	0.5
6	2	2	7	3	0.3
7	2	2.5	12	1	0.25
8	2	3	10	2	0.65
9	2.5	1	10	3	0.7
10	2.5	2	12	2.5	0.35
11	2.5	2.5	7	2	0.4
12	2.5	3	9	1	0.5
13	3	1	12	2	0.2
14	3	2	10	1	0.6
15	3	2.5	9	3	0.55
16	3	3	7	2.5	0.4
K_1	0.45	0.43	0.36	0.43	
K_2	0.31	0.44	0.50	0.45	
K_3	0.49	0.49	0.68	0..36	
K_4	0.44	0.44	0.25	0.44	
S	0.18	0.05	0.43	0.07	

2.4 Preparation of CdSe film

According to the orthogonal table 1, the cadmium chloride and sodium citrate solution were mixed in a certain percentage, and a certain amount of clarified Na_2SeSO_3 solution was added. The clean glass substrate was putted into the as-formed solution, and then the beaker was sealed and placed in the ultrasonic cleaner. The deposition time was 1h-3h. The substrate was took out and rinsed with hot deionized water to remove residue CdSe particles on the surface of the film, then the substrate was putted into the drying oven with 70 °C. Finally, the dry substrate was putted into the furnace; the annealing temperature is about 350 °C.

2.5 Characterizations

The crystal structure of the film was determined by XRD (SHIMAZU XRD-7000, Cu target, Kα radiation). Photoelectric properties of the films were measured by Ultraviolet-Visible Spectrophotometer (SPECTROPKIOTOMETER UV-2100S). The surface morphology was observed by atomic force microscopy (CSPM/BY CSPM5500). Electrochemical workstation (Corrtest) was used to test electrical properties.

3. Results and discussion

3.1 Optical properties of the CdSe thin films

It can be seen from Table 1 that the sample 3 has best absorbance. The optimal experimental conditions were as following: pH value of 10, the proportion of complexing agent 1: 1.5, deposition time 2.5h, ratio of cadmium to selenium 2.5. By analysis of the test results (Table 1) and calculating the absorbance and the very poor S of the various factors, pH value has been the biggest factors in poor, thus the main factors which affecting the CdSe film absorbance is the pH value. The order was as following: pH value, the proportion of complexing agent, the deposition time, and the ratio of cadmium to selenium.

Because sample 3 has the highest absorbance, so sample 3 was tested as an example. Figure 1 is absorption spectrum of sample 3 without annealing and annealing at 350℃, it shows that anneal shifts the absorption is greatly improved.

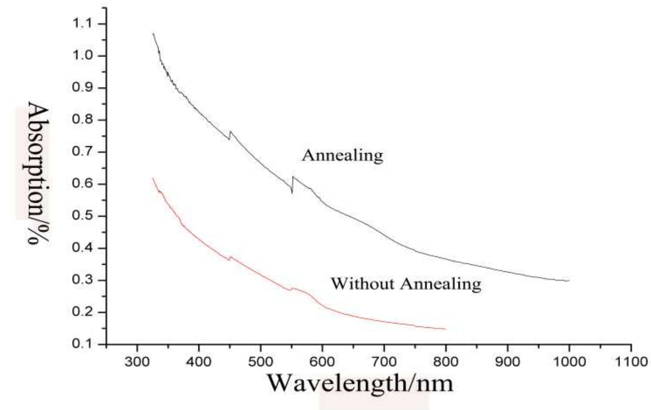

Fig. 1 Ultraviolet-visible absorption spectrum of CdSe films

3.2 Electrical properties of the CdSe thin films

Test system used was the standard three-electrode system, the working electrode used was the CdSe thin-film, working electrode area of illumination is about 0.5 cm^2, platinum as the counter electrode, calomel electrode was used as reference electrode, 0.2 mol/L Na_2SeSO_3 solution as electrolyte.

Figure 2 is the I-V curves of sample 3 under the light of 40 mW/cm^2. Under the dark state, CdSe electrode applied bias only in the cathodic current appeared lost-0.08V; illumination, CdSe electrode produces anode current, indicating that the electrodeisn-type semiconductor. When the anode bias is increased, CdSe electrode photocurrent increases.

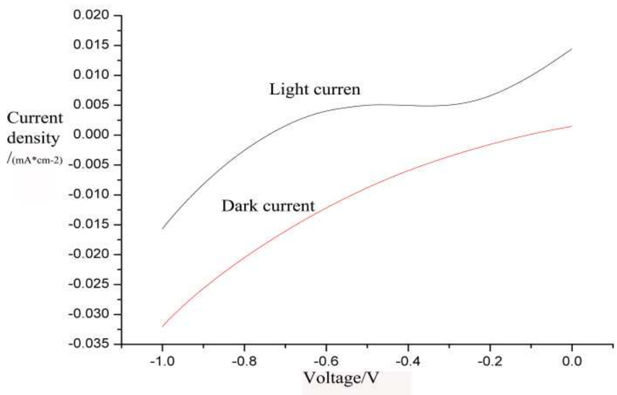

Fig. 2 I-V curves of CdSe films

3.3 Surface morphology of CdSe thin films by AFM

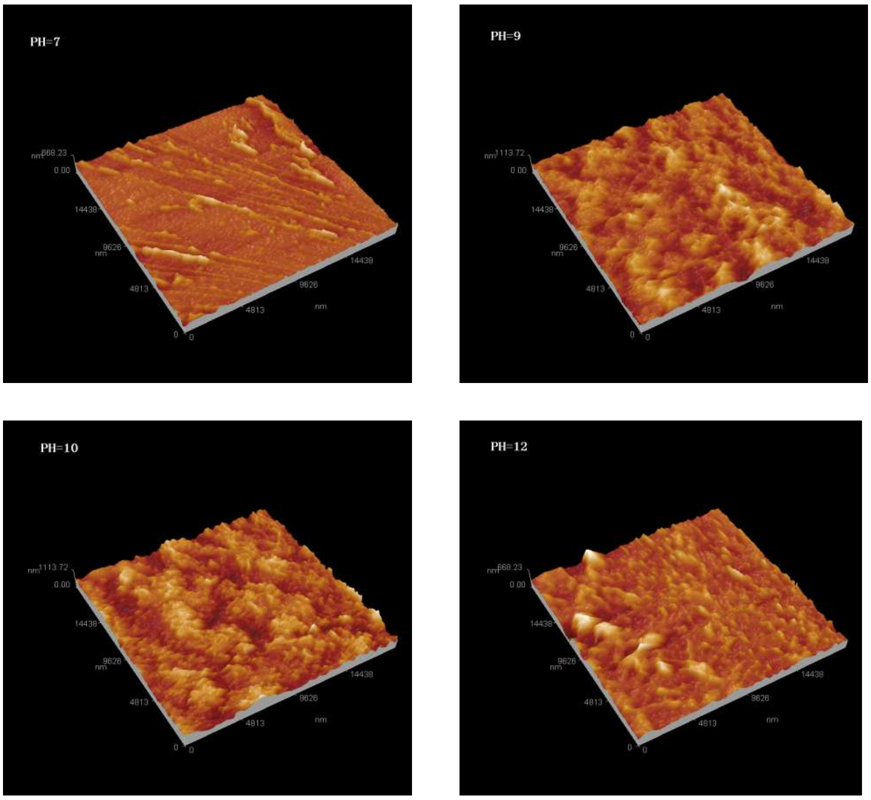

Fig.3 AFM imagine of CdSe films

According to the main factors affecting the absorption is pH value, We changed the preparation of samples 3 PH, and tested their surface morphology. From the figure we can see that the surface of film becomes more dense with the increasing of pH value, But when the PH is too large, the film surface becomes loose. It is because that with the increasing of pH value, the lower the reaction rate in solution, so the more uniform particle size, but when the pH value is too large, Cd^{2+} reacts with OH^{-}, which in turn makes the big particles reunion, affacting the thin film deposited on the substrate surface. We also can see that film showing a wavy linear.

3.4 XRD test

Figure 4 is the XRD test results of sample 3. From Figure 4 we can see that four peak positioned at 25.34°, 35.06°, 41.84°, 49.58°correspond to (002), (102), (110), (112) planes of hexagonal CdSe.

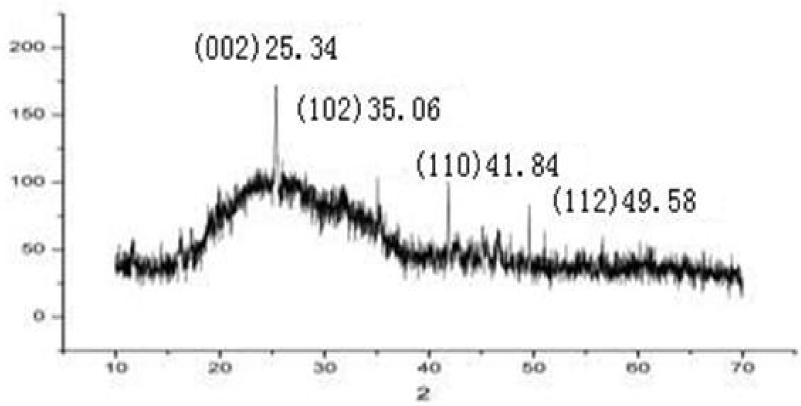

Fig 4 XRD pattern of CdSe film

4. Conclusions

Ultrasonic-assisted chemistry method is involved to synthesize CdSe films. The conditions for preparing the CdSe thin films were that the proportion of the Cd^{2+} and trisodium citrate was 1:1.5, the proportion of the Cd^{2+} and Se^{2-} was 2.5:1, the pH value was 10, the deposition time was 2.5h, the annealing temperature was 350℃. The main factor for preparing CdSe films is the pH value. The CdSe films was n-type semiconductor, absorption in the visible region was 0.75%. The CdSe film electrode had high photoelectron transfer rate, which leads to a substantial improvement on the photocurrent.

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