The photocatalytic performance of ZnO/Ag multi-layered films: the effect of ZnO-layer thickness

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In this work, the photocatalyst of ZnO/Ag multi-layered film containing a layer of Ag and several layers of ZnO was prepared by multi-spin-coating and magnetron sputtering, and the effect of the thickness of ZnO layers on the photocatalytic performance of the multi-layered films was investigated. The results of X-ray diffraction (XRD) showed that the Ag layer was a face-centered-cubic structure and the ZnO film crystallized into a wurtzite phase. With the rise of ZnO film thickness, the crystalline quality of the ZnO film was improved and the grains also grew up. The photocatalytic tests on methylene blue (MB) showed that the photocatalytic performance of the multi-layered films was largely enhanced in comparison with pure ZnO thin films and the sample containing 6 layers of ZnO exhibited the best photocatalytic activity in all samples. When the thickness of the ZnO film was relatively thin, its crystalline quality was poor and the quantity of photogenerated electron-hole pairs was small. There were many defects including oxygen vacancy in ZnO especially for the region close to the Ag layer, which led to a strong visible emission. When the thickness of the ZnO thin film was more than 6 layers, the photogenerated electrons in ZnO were greatly increased, but most of them were not able to effectively migrate into the Ag layer in a short time, leading to a decrease of the separation efficiency of electron-hole pairs. Therefore, selecting a suitable thickness of the ZnO film is very important for obtaining the best photocatalytic performance for ZnO/Ag multi-layered thin films.

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1. Introduction

Recently, in many developing countries, water pollution is becoming more and more serious. If this situation continues, it will influence human survival security. Photocatalytic degradation is a potential effective technique to handle water pollution problem, because it not only decomposes most of organic pollutants but also reduces the heavy metal ions in water. As an important semiconducting photocatalyst, ZnO has attracted much attention in the world [1-5]. So far, the ZnO photocatalyst in the form of powders has been widely investigated. However, the ZnO powders are not easy to be separated from water after the photocatalytic process is finished and there is the possibility of causing the second pollution [6]. Therefore, substrate-loaded ZnO materials such as thin films will be the main form of ZnO photocatalysts. Compared with ZnO powders, the specific surface area of ZnO thin films decreases, causing the photocatalytic activity to decline. In order to improve the photocatalytic activity of ZnO thin films, some strategies have been adopted, such as making ZnO thin films be porous [5, 7], noble-metal-nanoparticles surface modification [8], forming heterojunction with other materials [9], etc. Many research results show that noble-metal-nanoparticles surface modification can greatly enhance the photocatalytic performance of ZnO thin films. However, these noble-metal nanoparticles will not work after several rounds of photocatalytic process due to being oxidized and these metal particles are also easy to drop from the film surface due to friction or collision. All the above factors will weaken the photocatalytic performance of ZnO thin films.

In this work, we prepared ZnO/Ag multi-layered films which contain a pre-deposited Ag layer on substrate and a post-deposited ZnO thin film on the Ag layer. Due to the large difference of the work function between ZnO and Ag, the photogenerated electrons in ZnO film during the photocatalytic process will migrate into the Ag layer [8]. That is to say, the Ag layer in here plays a role of separating electron-hole pairs. We found that the thickness of the upper ZnO thin film had a great influence on the photocatalytic performance of ZnO/Ag films. As far as we know, the influence of ZnO film thickness on the photocatalytic performance of ZnO/Ag multi-layered films is rarely reported. These multi-layered films are attractive because their photocatalytic performance is more stable compared with that of metal-nanoparticle surface modified ZnO thin films.

2. Experiments

An Ag layer with a thickness of ~ 1μm was pre-deposited on a substrate by magnetron sputtering. Then ZnO thin film was deposited on the Ag layer by multi-spin-coating a ZnO sol. The ZnO sol was prepared using zinc acetate, anhydrous alcohol, monoethanolamine as precursor, solvent and stabilizer, respectively. In order to obtain ZnO thin films with different thicknesses, the spin-coating times adopted were 2, 4, 6, 8 and 10 for five

different samples. The thickness of the ZnO layer by single spin-coating is about 23 nm measured by an ellipsometer. In order to compare the photocatalytic performance, a pure ZnO thin film was prepared under the same conditions. All the samples were annealed at 500 ℃ for one hour.

The surface morphology of the samples was observed by an atomic force microscope (CSPM4000). The crystal phase was determined by an X-ray diffractometer (Bruker D8 Advance). The composition of the ZnO layers was analyzed by energy dispersive X-Ray spectroscopy (EDX). The photoluminescence spectra were measured by a spectrophotometer (LABRAM800) using a He-Cd laser as the excitation light source. The wavelength of this light source is 325 nm. The absorbance of MB aqueous solution was recorded by a UV-visible spectrophotometer (TU-1901).

3. Results and discussion

Fig. 1 shows the three-dimensional morphology images of the samples. It can be seen that the upper ZnO thin films are composed of many grains which are preferentially oriented along the direction perpendicular to the substrate surface. When the film is thicker, the columnar shape of ZnO grains is more obvious. With the rise of film thickness, the ZnO grains gradually grow up; the average surface roughness of the ZnO films also increases from 1.5 to 2.99 nm.

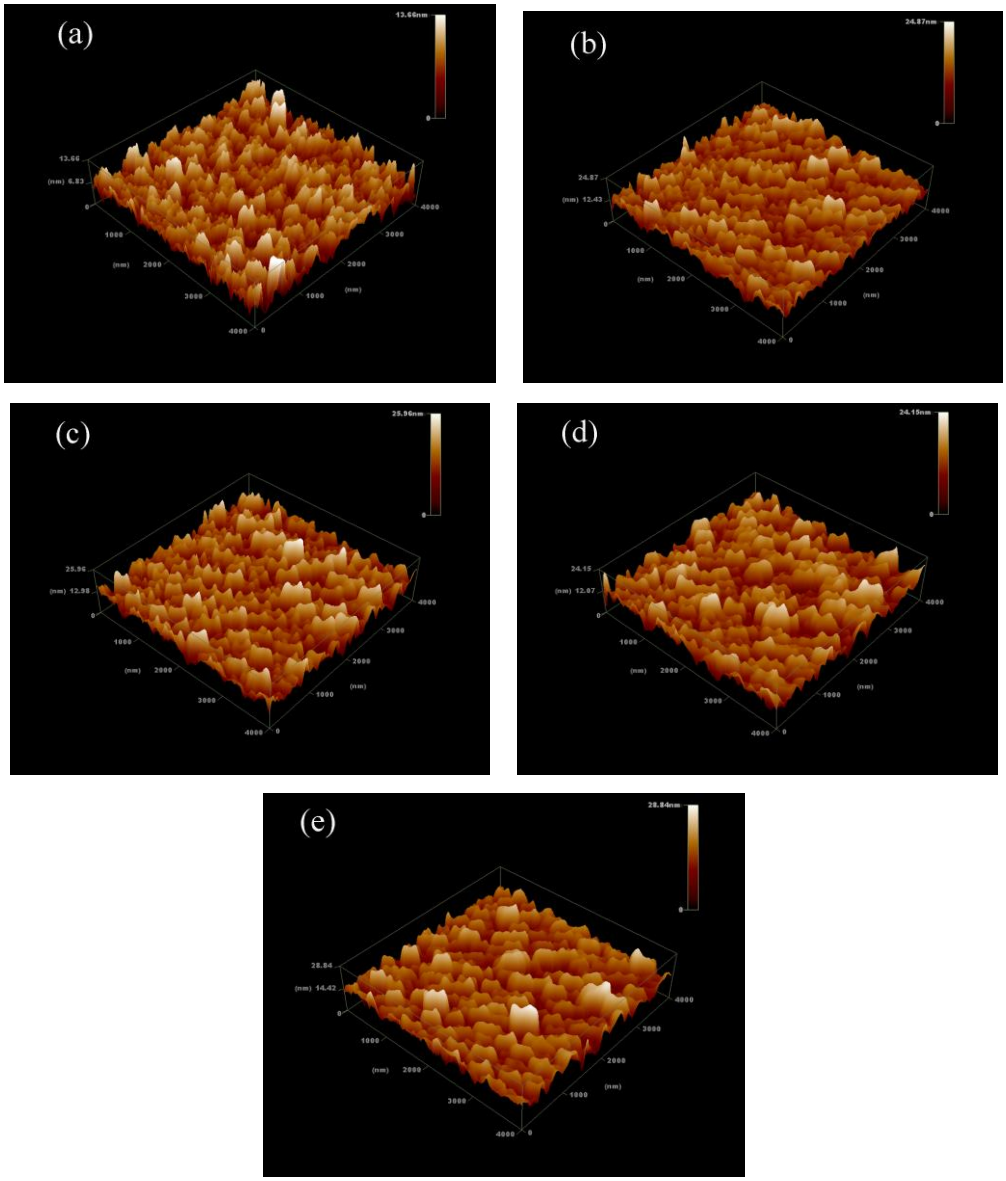

Fig. 1. Surface morphology images of the ZnO/Ag thin films with different layers of ZnO: 2 layers (a), 4 layers (b), 6 layers (c), 8 layers (d) and 10 layers (e)

Fig. 2 displays the XRD patterns of the samples. All the samples show four common diffraction peaks. Two of them belong to the (002) and (110) peak of ZnO; other two peaks are the (111) and (200) peak of Ag with a face-centered cubic structure. With the increase of ZnO film thickness, the (002) peak is gradually intensified and

the peaks (100) and (101) of ZnO also appear. In addition, the narrowing of the full width at half maximum of the (002) peak is also observed. According to the Scherer's formula [10], the crystallite size of ZnO has been calculated, which is 12.4, 15.9, 19.9, 20.7 and 20.8 nm, respectively for the samples with 2, 4, 6, 8 and 10 layers of ZnO. The above results indicate that the ZnO thin films deposited on the Ag layer have a wurtzite phase and the increase of thickness improves the crystalline quality of ZnO grains. The similar results (the increase of film thickness improves the crystalline quality of ZnO thin films) have been also reported by others [10, 11].

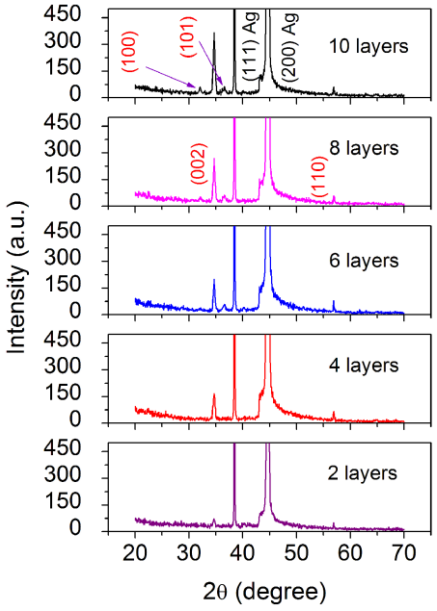

Fig. 2. XRD patterns of the samples

Fig. 3 gives the photoluminescence spectra of the ZnO/Ag multi-layered films. All the samples show a weak UV emission peak and a wide visible emission band. The UV peak is centered at 380 nm which results from recombination of free excitons. The wide visible emission band mainly includes a green emission band centered at 520 nm and a red emission band centered at 650 nm. Lots of researchers deem that the green emission is mainly associated with oxygen vacancy defects [12] and the red emission probably results from oxygen interstitial defects [13]. The compositional analysis based on EDX support the above proposal. The molar ratio of Zn:O is 51:49, 50.8:49.2, 50.1:49.9, 49.8:50.2 and 49.1:50.9, respectively for the samples with 2, 4, 6, 8 and 10 layers of ZnO. It suggests that oxygen is insufficient in those samples with 2-6 layers of ZnO while oxygen is superfluous for other samples. With the increase of ZnO film thickness, the green emission gradually decreases while the UV and red emissions gradually increase. The emission change could be explained as follows. When the thickness of ZnO film is less than 6 layers, there are many defects including oxygen vacancies in ZnO especially for the region close to the Ag layer, which leads to a strong green emission. With the rise of ZnO film thickness, the crystalline quality of ZnO is improved and oxygen vacancies are decreased; accordingly, the UV emission is increased and green emission is decreased. The growth of ZnO thin films in the sol-gel process is in an oxygen-rich environment, so the ZnO thin films probably contain some oxygen interstitial defects. With the increase of ZnO film thickness, the density of oxygen interstitial increases and the red emission gradually dominates the visible emissions. The evolution of the UV emission is consistent with the variation of the (002) peak of XRD, indicating that the increase of ZnO film thickness improved the crystalline quality of ZnO grains.

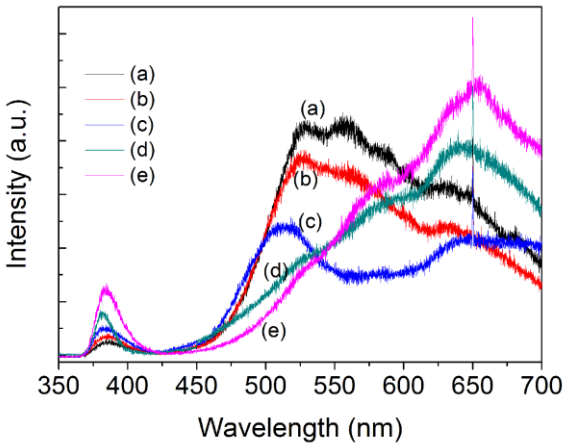

Fig. 3. Photoluminescence spectra of the samples with different layers of ZnO: 2 layers (a), 4 layers (b), 6 layers (c), 8 layers (d) and 10 layers (e)

In order to investigate the photocatalytic performance of ZnO/Ag multi-layered films, the photocatalytic activity was tested using the MB as a simulated pollutant. The concentration of MB in aqueous solution is 5 mg/L; the effective area of the films is 1.5×1.5 cm^2; the light source is an Hg lamp. Fig. 4 (a) shows the change of MB concentration with the increasing reaction time and (b) gives the degradation efficiency of the samples. Obviously, the sample containing 6 layers of ZnO exhibits the highest photodegradation efficiency. As for the samples containing 2 and 4 layers of ZnO, although the photogenerated electrons can rapidly migrate into the Ag layer realizing the separation of electron-hole pairs, the quantity of electron-hole pairs is relatively small in the ZnO films due to the poor crystallization. As a result, the degradation efficiency of these samples is relatively low. As for the samples containing 8 and 10 layers of ZnO, the quantity of electron-hole pairs is largely enhanced due to the improved crystallization of ZnO, but the increase of ZnO film thickness makes most of photogenerated electrons not be able to migrate into Ag layer in a short time. Resultantly, the degradation rate of these two samples decreases compared with that of the sample containing 6 layers of ZnO. From Fig. 4 (b), it can be seen that the degradation efficiency of the pure ZnO thin film is much lower than that of the sample containing 6 layers of ZnO, which directly indicates that the ZnO/Ag multi-layered films are superior to pure ZnO thin films for photocatalytic application.

Some researchers found that the ZnO grain size and

film surface roughness were the decisive factors for photocatalytic application [14]. The smaller the grain size, the rougher the ZnO film surface, the higher the photodegradation efficiency. Here, with the increase of ZnO film thickness, it is found that both the grain size and surface roughness increase. However, the sample containing 6 layers of ZnO which has a medium grain size and surface roughness obtains the best photocatalytic performance. This indicates that the bottom Ag layer plays a greater role than grain size and surface roughness in the photocatalytic process for the ZnO/Ag multi-layered films.

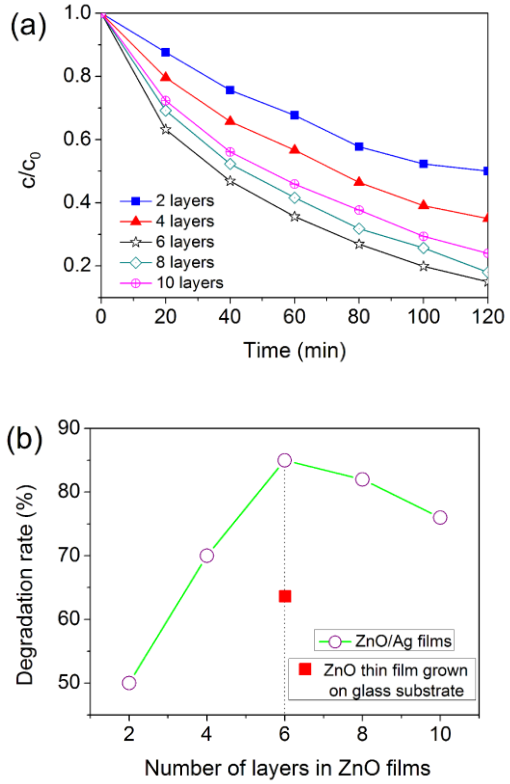

Fig. 4. The c/c_0 at different reaction time (a) and the degradation rates (b) of the samples

4. Conclusion

In this work, the ZnO/Ag multi-layered films with different ZnO-film thicknesses were prepared. The photocatalytic tests on MB solution showed that the sample containing 6 layers of ZnO possessed the highest photocatalytic activity which was far higher than that of pure ZnO thin films with an identical thickness. The improvement of the photocatalytic activity of the ZnO/Ag multi-layered films was mainly attributed to the existence of a bottom Ag layer. As an electron sank, the Ag layer played a role of separating electron-hole pairs. In order to more learn the photocatalytic behavior of the ZnO/Ag multi-layered films, the influence of the thickness of Ag layer on the photocatalytic performance will be investigated in the following studies.

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