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Photoelectrochemical properties of hematite thin films grown via a two-step electrochemical deposition method

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ABSTRACT

In this study, Fe_2O_3 thin films were deposited via one-step and two-step electrochemical deposition methods. The one-step method used a constant growth potential, and the two-step method used two continuous growth potentials during the deposition. The morphological, electrical, and structural properties of the thin films and the relationships of each property with the photoelectrochemical properties of the thin films from the two methods were analyzed and compared. We determined that the samples grown by the two-step method have better photoelectrochemical properties than those grown by the one-step method. In this study, we attempted to determine the optimum growth potentials for the one-step and two-step methods and the growth durations of the first and second stages in the two-step method in terms of the photoelectrochemical properties. The sample formed at −0.05 V for 30 s in the first step and −0.25 V for 2 min 30 s in the second step in the two-step method has the highest photocurrent density value of 0.28 mA/cm^2 (at 0.5 V vs. SCE), which is higher than that of the samples grown by the one-step method.

1. Introduction

Clean hydrogen energy is currently attracting attention, and many methods to produce hydrogen energy have been studied because of the advantages, including ease of use, theoretical infinite supply and lack of byproducts generated during burning [1,2]. Photoelectrochemical (PEC) cells are an environmentally friendly method to directly produce hydrogen from solar energy via water splitting. Since photoelectrochemical cells produce hydrogen using sunlight and water, they are an ideal environmentally friendly energy production system and a promising method to address the current, serious environmental problems and fossil fuel depletion issues. A photoelectrochemical cell is composed of an electrolyte, a counter electrode, and a semiconductor photoelectrode. The semiconductor photoelectrode is important and influences the photoelectrochemical properties, such as the photocurrent density value and hydrogen-generation efficiency. A photoelectrode requires abundant reserves and should be nontoxic with a theoretical minimum energy bandgap of 1.23 eV, which is required for water splitting [3]. Various materials, such as titanium dioxide (TiO_2), zinc oxide (ZnO), iron (III) oxide (Fe_2O_3), tungsten trioxide (WO_3) and copper (I) oxide (Cu_2O), have been studied as photoelectrode candidates. Among these, Fe_2O_3 has many advantages, such environmental friendliness and abundant reserves, high photocorrosion resistance, and stability in aqueous and alkaline solutions [4–11]. However, due to its high electron-hole recombination rate and short hole diffusion distance, Fe_2O_3 has a low photocurrent density value and low hydrogen conversion efficiency [12]. Therefore, the photocurrent density of the Fe_2O_3 photoelectrode must be further studied and improved.

There are various methods to grow Fe_2O_3, including vacuum and solution processes [13–15]. Vacuum deposition processes can create a photoelectrode with a high photocurrent density and high hydrogen conversion efficiency. However, vacuum deposition processes have many drawbacks, such as high cost and complicated processing steps. In addition, vacuum deposition processes primarily use precursors composed of toxic and ignitable metal-organic sources [16,17]. Compared with the vacuum process, the solution process is simple, inexpensive and enables large-area deposition. In addition, the process is relatively free from environmental pollution and safety problems. Thus, growing Fe_2O_3 using solution processes has recently attracted attention. However, insufficient photoelectrochemical properties and hydrogen conversion efficiencies remain problematic using the solution process; therefore, an in-depth study is needed to improve these processes. Solution processes that can be used to fabricate Fe_2O_3 photoelectrodes include hydrothermal methods [18], electrochemical deposition [19], chemical bath deposition [20], dip coating [21] and spray pyrolysis [22]. Among these processes, electrochemical deposition is a widely

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used method due to its ease, low cost and low process temperature. Additionally, electrochemical deposition is capable of large-area deposition and can result in excellent adhesion between a substrate and a growing thin film [23–25].

When nanostructures are deposited by an electrochemical deposition method, there are four stages: ion transport, discharge, nucleation, and growth. These stages are stepwise and interact with each other. Among these steps, nucleation is considered the most important because it can greatly affect the properties of the final film. As the dimensions of oxide semiconductors continue to scale down into the nanometer range, the importance of the early initial stage in thin film deposition, i.e., the nucleation step, increases [26]. In the electrochemical deposition nucleation stage, the applied growth potential and growth duration are important since they can affect the density of the nuclei, the type of nucleation and the morphological, structural and optical properties of the films grown on the nuclei [27,28]. Therefore, precise control of the nucleation step prior to the following main growth step can be important in the electrochemical deposition process. Generally, nanostructure growth by an electrochemical method is a one-step process in which a constant potential is continuously applied to the sample [29–32]. In a one-step process, the nucleation and growth occur at the same growth potential. However, we considered that a suitable growth potential for the nucleation stage and that for the main growth after the nucleation could be different. Thus, we attempted to determine the optimum growth potential and optimum growth duration for nucleation using a two-step electrochemical deposition method. First, various first-step growth potentials and first-step growth durations were tested to optimize the first-step growth in the two-step electrochemical deposition. Although some studies have been performed on the two-step electrochemical deposition method using zinc oxide nanorods and Cu/In bilayer films [33–35], the growth of Fe_2O_3 thin film oxide semiconductors using this method has not been studied. Therefore, studying the two-step electrochemical deposition of Fe_2O_3 thin film photoelectrodes is important. Thus, in this study, we grew Fe_2O_3 thin films using a two-step electrochemical deposition method and attempted to determine the optimum process conditions in terms of the photoelectrochemical properties. We analyzed the morphological, electrical, structural and photoelectrochemical properties of Fe_2O_3 thin films and discussed the relationships among these properties. Field emission gun scanning electron microscopy (FE-SEM), a standard four-point probe technique, electrochemical impedance spectroscopy (EIS), and X-ray diffraction (XRD) were used to determine the morphological, electrical and structural properties, respectively. A three-electrode potentiostat/galvanostat was used for photoelectrochemical characterizations.

2. Experimental

Fluorine-doped tin oxide (FTO) substrates were sonicated in acetone for 10 min, deionized water for 1 min, and methanol for 10 min, and then they were rinsed in deionized water and dried in filtered air. Then, the substrates were dried at 60 °C for 10 min in an electric oven. The cleaned FTO substrates were UV/ozone pretreated for 10 min using a UV/ozone cleaner.

Goethite (FeOOH) was produced via an electrochemical deposition method, and the hematite (Fe_2O_3) thin film was formed by thermally annealing FeOOH at 600 °C for 2 h. The solutions used to prepare FeOOH for the electrochemical deposition process were 0.025 M $FeCl_3$ (Sigma Aldrich), 1 M H_2O_2 (JUNSEI), and 0.1 M KF (Sigma Aldrich) with 0.1 M KCl as the electrolyte. A glass-jacketed beaker and water circulator were used to maintain a constant growth temperature (65 °C). The reference electrode was Ag/AgCl in a 1 M KCl solution. The FeOOH grown via the electrochemical deposition method was formed through the following reactions.

$$H_2O_2 + 2e^- \rightarrow 2OH^- \quad (1)$$

$$FeF^{2+} + 3OH^- \rightarrow FeOOH + F^- + H_2O \quad (2)$$

$$3H_2O_2 + 2FeF^{2+} + 6e^- \rightarrow 2FeOOH + 2F^- + 2H_2O \quad (3)$$

In this study, four experiments were performed to determine the optimum growth conditions, such as the one-step growth potential in the one-step method, the one-step growth duration in the one-step method, the first-step potential in the two-step method and the first-step growth duration in the two-step method. In the one-step growth experiments to grow the Fe_2O_3 thin film, the applied potential was adjusted from −0.05 V to −0.45 V for 3 min, and the growth duration was adjusted from 1 min to 15 min at −0.25 V. To investigate the effects of the two-step process on the Fe_2O_3 photoelectrode, the second-step potential was fixed at −0.25 V, and the first-step potential and growth duration were adjusted from −0.001 V to −0.35 V and 0–180 s, respectively. For the two-step growth experiments, the total growth duration was fixed at 3 min. FE-SEM (Quanta 200 FEG) was used to characterize the morphology of the Fe_2O_3 thin films, EIS (ZIVE SP1) was used to measure the electrical properties, and XRD (X'Pert PRO MPD) was used to study the structural properties. The sheet resistance was measured using a standard four-point probe technique, and a three-electrode potentiostat was used to measure the photoelectrochemical properties. The grown Fe_2O_3 thin films were used as the working electrode, graphite was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the standard electrode to measure the photoelectrochemical properties. In addition, a 1 M KOH solution was used as the electrolyte. A 300 W Xenon lamp with 1 sun illumination (AM 1.5 filter, 100 mW/cm^2) was employed as the light source, and a voltammetric sweep was performed from −0.4 to 0.6 V. The Xenon lamp beam size on the sample was 0.196 cm^2.

3. Results and discussion

Fig. 1 shows the photocurrent density values for the Fe_2O_3 thin films grown via the one-step and two-step electrochemical deposition methods. The linear sweep voltammetry measurement results for the samples and the maximum photocurrent density values at 0.5 V are shown in Fig. 1. In all the samples, the open-circuit voltage (V_{oc}) appeared at −0.35 V, and a dark current density value close to 0 mA/cm^2 was maintained, despite the increasing growth potential. Fig. 1(a) and (b) show the photocurrent density results for the one-step electrochemical deposition experiments. The photocurrent densities of the Fe_2O_3 thin films grown with different one-step growth potentials (−0.05 V, −0.1 V, −0.15 V, −0.2 V, −0.25 V, −0.35 V and −0.45 V) are shown in Fig. 1(a). The photocurrent density gradually increased as the growth potential increased. The highest value was reached at −0.25 V, and the value decreased over −0.25 V. Fig. 1(b) shows the photocurrent density values for different one-step growth durations of 1 min, 3 min, 5 min, 10 min and 15 min at a growth potential of −0.25 V, which was selected based on the Fig. 1(a) result. The highest photocurrent density was (0.2 mA/cm^2) obtained with a growth duration of 3 min, and this value decreased after 3 min. Jang et al. reported that the photocurrent density of a thin film can deteriorate due to an excessive growth potential or excessive growth duration due to a small grain size or excessive thickness, respectively [36]. Fig. 1(c) and (d) show the photocurrent density results from the two-step electrochemical deposition experiments using different first-step growth potentials and first-step growth durations, respectively. For the two-step growth method, the total growth duration was fixed at 3 min, and the second-step growth potential was set at −0.25 V. These values were chosen based on the one-step experimental results, as shown in Fig. 1(a) and (b). To determine the optimum first-step growth potential, different growth potentials (−0.001 V, −0.005 V, −0.01 V, −0.05 V, −0.1 V, −0.15 V, −0.2 V, −0.25 V and −0.35 V) were used for 30 s, followed by a second-step growth with an applied potential of −0.25 V for 2 min 30 s. The photocurrent density was low at relatively low first-step