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Hematite photoanodes for solar water splitting: Directly sputtered vs. anodically oxidized sputtered Fe

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ABSTRACT

Hematite iron oxide has been extensively studied for photoelectrochemical (PEC) water splitting. Nanostructuring of hematite-based photoanodes represents an effective strategy to supress the negative impact of a short diffusion length of photoexcited holes on the PEC performance. Here we present a comparative structural and photoelectrochemical study of hematite photoanodes fabricated in the forms of two-dimensional (2D) very thin (~25 nm) nanocrystaline films and one-dimensional (1D) nanostructures including nanotubes and nanorods. Hematite films on fluorine-doped tin oxide (FTO) coated glass were prepared by two methods (i) by reactive high-power impulse magnetron sputtering (HiPIMS) and (ii) by anodic oxidation of Fe films deposited on FTO by HiPIMS. While in the first case very thin, dense, compact hematite films were deposited, the second approach yielded transparent nanotubular or nanorod hematite nanostructures. In both cases, the photoelectrochemical response was crucially influenced by the post thermal treatment at 750 °C resulting in the Sn^{4+} diffusion from the FTO substrate and the improvement of conductivity across the FTO/Fe_2O_3 interface. Fe_2O_3 films exhibit a photocurrent onset at potential 1.1 V (RHE) with almost linear increase of photocurrent with applied potential. The highest photocurrents were obtained for planar thin hematite electrodes prepared directly by HIPIMS technique (0.55 mA cm^{-2} at 0.5 V vs. Ag/AgCl). The observed minimal bias for photoelectrochemical water splitting with hematite photoanode was 1.25 V. For applied potential 0.25 V (vs. Ag/AgCl) and bias 1.3 V, the observed photocurrent density and hydrogen production rate was 0.305 mA/cm^2 and 5.8 μmol/h/cm^2, respectively.

1. Introduction

Iron oxide (α-Fe_2O_3) hematite films have the potential application as photoanodes in photoelectrochemical cell for sustainable hydrogen production via water splitting. This is due to its favourable properties such as a band gap between 2.0–2.2 eV, which allows absorbing a substantial fraction of solar spectrum, chemical stability in aqueous environment, nontoxicity, abundance, and low cost. For such band gaps and assuming standard solar illumination conditions (AM 1.5 G, 100 mW cm^{-2}) the theoretical maximal solar-to-hydrogen (STH) conversion efficiency can be calculated as 15% [1]. However, hematite also has certain disadvantages. Among the most cited are the low absorptivity (especially for longer wavelengths) and very short diffusion length of photogenerated holes. This creates a disaccord between the depth where charge carriers are photogenerated (in the bulk) and the distance they diffuse before recombining. The negative effect of the short diffusion length of holes can be suppressed by using very thin films of hematite or their nanostructuring. In the first approach the strategy consists in the deposition of very thin films of hematite by High Power Impulse Magnetron Sputtering (HiPIMS) [2–4]. The second approach consists in the fabrication of well-aligned, one-dimensional (1D) nano-structures such as self-organized anodic nanotubular/nanoporous films [5–8]. Nevertheless, anodically prepared oxide films need to be annealed to convert the amorphous oxide to crystalline hematite. If the layers are formed on metallic iron substrates, thermal annealing leads to oxide layers that consist of a gradient of wustite (FeO), magnetite (Fe_3O), and α-Fe_2O_3. The first two (FeO and Fe_3O_4) are particularly detrimental for the photoresponse because these phases represent a barrier for charge transfer to the back contact [8–10]. In order to avoid this effect, the

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nanostructured hematite film can be fabricated in two steps. In the first step thin iron metal layers is deposited on FTO support and in the second step iron metal layer is completely electrochemically anodized (oxidized) [11]. Both approaches result in the formation of photoanodes on transparent substrate which enables the application of back side illumination, e. g. irradiation from the direction of the substrate/semiconductor interface.

The aim of this work is the comparison of the functional properties of α-Fe_2O_3 films prepared by both methods, e.g. directly prepared by HiPIMS and prepared by Fe film deposition by HIPIMS followed by anodic oxidation. Special attention is given to the influence of calcination temperature as thermal treatment has been found crucial for an improvement of hematite photoresponse [11,12]. The fabricated hematite photoanode films are characterized by XRD, SEM, UV–vis spectroscopy, XPS spectroscopy and by the measurement of chopped light polarization curves. The most promising photoanodes are applied in single band gap photoelectrochemical cell for water splitting and hydrogen evolution rate is evaluated.

2. Experimental

2.1. Preparation of α-Fe_2O_3 films

All layers were prepared on conductive fluorine doped tin oxide (FTO) glass (TCO22-15, Solaronix, Switzerland).

Dense thin layers of α-Fe_2O_3 were prepared by reactive high-power impulse magnetron sputtering method (HiPIMS) followed by annealing at 750 °C. HiPIMS deposition employed a metallic target of pure iron (99.995%, Plasmaterials) with outer diameter 50 mm and an Ar-O_2 atmosphere as working gases mixture in an ultra-high vacuum (UHV) reactor continuously pumped down by a turbo-molecular pump providing the base pressure of 10^{-5} Pa. Glass substrates were carefully cleaned before deposition. The working gases were fed to the reactor with the flow rates of 30 sccm (standard cubic centimeters per minute) and 12 sccm corresponding to argon and oxygen, respectively. The depositions were carried out at room temperature, operating pressure was 1 Pa. The pulsing frequency of DC HiPIMS discharge was in the range 70–1000 Hz with the "ON" time of 100 μs and the maximal current density achieved in a pulse was $5 \approx \mathrm{Acm}^{-2}$ at 70 Hz [13].

Nanotubular/nanoporous layers of α-Fe_2O_3 were prepared in two steps consisting of sputtering of iron films on FTO glass followed by anodic oxidation.

(i) The sputtering of iron precursive films applied the same HiPIMS conditions as in the previous case except the working gas mixture, which of course contained only argon to avoid any oxidation. Three different sputtering times 9, 26 and 52 min were applied to prepare Fe layers of thickness 100, 300 and 600 nm, respectively.

(ii) Anodization was performed in a solution of ethylene glycol (EG, Sigma Aldrich) containing 0.4 w% of NH_4F (Merck) and 3 w% of H_2O at 50 V at room temperature. Two-electrode system with Pt counter electrode was used. After anodization, the samples were rinsed with water and ethanol, followed by drying in nitrogen. The amorphous iron oxide samples were then annealed in air at 450 °C for 2 h and 750 °C for 20 min in air.

2.2. Film characterisation

The thickness of the deposited films was determined by profilometry measurements (Alpha-Step 500). The structural, morphological and optical properties of the deposited films were determined using X-ray diffraction (an X'pert Philips MPD with a Panalytical X'celerator detector using graphite monochromized Cu Kα radiation (wavelength 1.54056 Å)), a field emission scanning electron microscope (FE-SEM, Hitachi SEM FE 4800), UV–vis absorption spectroscopy and optical microscope Axio Scope A1 (Zeiss).

The X-ray photoelectron spectra were acquired by a PHI 5000 VersaProbe II XPS system (Physical Electronics) using a monochromatic Al-Kα source (15 kV, 50 W) with photon energy of 1486.7 eV. All spectra were measured in a vacuum of 1.4×10^{-7} Pa and at room temperature of 22 °C. For the high-resolution spectra, a pass energy of 23.500 eV and step size of 0.200 eV.

2.3. Photoelectrochemical measurements

Photoelectrochemical properties of films and photoelectrochemical hydrogen production were tested in a three compartment glass cell consisting of anodic, cathodic and reference electrode compartment. Anodic and cathodic compartments were separated by glass frit to prevent mixing of electrolyte and to minimize transport of evolved hydrogen and oxygen. Aqueous solution of NaOH was used as electrolyte. α-Fe_2O_3 on FTO glass was used as photoanode, platinum sheet as cathode and Ag/AgCl as reference electrode (0.196 V vs. SHE). The exposed photoanode area (1 cm^2) was defined by teflon tape. The electric contact was made by pressing stainless steel to upper part of FTO layer, not covered by α-Fe_2O_3. Solar simulator (150 W Xe arc lamp (Newport) with AM1.5G filter) was used as the source of irradiation. An irradiance 1 sun (100 mW/cm^2), entering the cell, was measured by calibrated reference cell (91150 V, Newport) for AM1.5G solar simulator light. Linear voltammetry was measured with sweep rate 5 mV/s while periodically illuminated (5 s light/5 s dark) from the electrolyte/electrode (EE) interface. The photocurrents were measured using Voltalab10 PGZ-100 potentiostat (software VoltaMaster 4). The starting potential was around −0.5 V (Ag/AgCl), sweeping was positive towards the end potential in the range 0.7–1.0 V (Ag/AgCl).

During PEC water splitting experiments anodic and cathodic compartment were bubbled by argon (1 ml/min). Output gas from the cathode chamber (Pt electrode) was analysed by gas chromatograph (Master, Dani) equipped with plot column (Rt®-Msieve 5A, Restek) and μTCD detector (Vici). Two experimental arrangement were used namely (i) at controlled bias (cell voltage) or (ii) at controlled potential of working electrode (photoanode) vs. reference electrode.

3. Results

3.1. HIPIMS hematite films

Based on the previous study devoted to the optimisation of the HIPIMS deposition conditions and calcination temperature of hematite films [12], the 25 nm thin films of hematite were deposited on FTO and calcined at 750 °C. The crystalline hematite structure was confirmed independently by X-ray diffraction and Raman spectroscopy. Chopped light polarization curve is shown in Fig. 1.

The onset of the photocurrent is at 0.05 V (vs. Ag/AgCl), the photocurrent increases almost linearly and at potential 0.5 V the photocurrent density reaches 0.55 mA/cm^2. The onset of the dark current is at potential 0.7 V (Table 1).

3.2. Anodised HIPIMS Fe films on FTO

Fig. 2 shows the 100 nm Fe layer on FTO before and after anodization. It can be seen that deposited Fe film is not transparent and contains very small amount of pinholes. The adhesion of Fe film was very good and the anodization results in the complete oxidation of Fe to transparent nanotubular Fe_2O_3. Due to the geometry

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