# On the improvement of PEC activity of hematite thin films deposited by high-power pulsed magnetron sputtering method

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## ARTICLE INFO

## ABSTRACT

The work deals with fabrication of iron oxide ($\alpha$-Fe$_2$O$_3$) hematite films by a novel high-power impulse magnetron sputtering method (HiPIMS). Hematite is regarded as a highly promising material for sustainable production of hydrogen via photoelectrochemical (PEC) water splitting. Some of the crucial issues of hematite are a large overpotential needed to develop the water oxidation photocurrent onset, high extent of surface defects acting as traps, and a short diffusion length (2–4 nm) of photogenerated holes. We report on minimizing these limits by deposition of highly photoactive nanocrystalline very thin ($\sim$30 nm) absorbing hematite films by HiPIMS and their passivation by ultra-thin ($\sim$2 nm) atomic layer deposited (ALD) isocrystalline alumina oxide ($\alpha$-Al$_2$O$_3$) films. A new approach of one-step annealing of this bilayer system is introduced. The films were judged on the basis of physical properties such as crystalline structure, optical absorption, surface topography, and electronic properties. The functional properties were investigated under simulated photoelectrochemical (PEC) water-splitting conditions. The shift by 1 V vs. RHE and the maximal photocurrent value of 0.48 mA cm$^{-2}$ at 1.23 V vs. RHE were achieved.

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## 1. Introduction

Iron oxide ($\alpha$-Fe$_2$O$_3$) in hematite crystalline structure has recently attracted much attention as possibly convenient material to be used for hydrogen production via photoelectrochemical (PEC) water splitting. It is due to its favorable properties such as a band gap between 2.0 and 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 gap and assuming the standard solar illumination conditions (AM 1.5 G, 100 mW cm$^{-2}$) theoretical maximal solar-to-hydrogen (STH) conversion efficiency has been calculated at 15% [1].

On the other hand, hematite also possesses certain handicaps hindering to reach such high efficiency. Among the most cited limitations are [1–3]: (i) the nonideal position of hematite's conduction band, which is too low for spontaneous water reduction; (ii) the low absorptivity (especially for longer wavelengths) near its band-edge due to an indirect nature of the band gap; (iii) poor majority carriers concentration leading a low electrical conductivity and (iv) the penetration depth of photons in hematite is $\alpha^{-1}$ = 118 nm at $\lambda$ = 550, however, due to extremely high bulk recombination rate (time constants in the range of 10 ps), the majority of the photogenerated holes undergo bulk recombination before reaching the semiconductor liquid junction (SCLJ), which causes very short diffusion length of the holes ($L_D$ 2–4 nm) [4].

For each of these drawbacks, several more or less effective solutions have been proposed. The first limitation mentioned can be addressed by applying photovoltaic cell (e.g. dye-sensitized solar cell—DSSC) and/or a p-type semiconductor acting as the photocathode to provide the additional energy needed. In order to optimize solar photon harvesting, the cell can be placed on the top of hematite electrode or vice versa to work in a tandem ensuring that photons not absorbed by the first cell are transmitted to and subsequently absorbed by the second [5,6]. Doping with elements such as Sn, Ti, Si, Pt, etc. [7–10] can significantly increase the electronic conductivity by increasing the number of majority carriers' concentration. The negative effect of the short diffusion length of photogenerated holes can be suppressed by using very

thin films of hematite or their careful nanostructuring in various dimensions and architectures (wormlike structure [11], nanorods [12], nanowires [13], etc.).

A large overpotential with respect to the flat band potential, $V_{fb}$, necessary to promote water oxidation is another key issue. For hematite $Fe_2O_3$, the flat band potential has been found to be around 0.5 V [1,14] versus the reversible hydrogen electrode (RHE). In the ideal case, the photocurrent is observed at all potentials more anodic than $V_{fb}$. The hematite, however, does not usually generate water oxidation photocurrent until the potential of 0.8–1.0 V vs. RHE [15]. Of course a certain external bias is consumed to suppress the energy deficit due to the aforementioned unsuitable energy level of the valance band. The remaining overpotential (0.5–0.6 V) has been attributed to two main reasons. The first one is the slow oxygen evolution reaction kinetics (OER), which has been addressed by anchoring various OER catalyst nanoparticles ($IrO_2$, Co–Pi, etc.) onto the hematite surface [15,16]. The second one suggests the presence of electronic surface states originated from oxygen vacancies and crystalline defects, which serve as traps for photogenerated holes. As a consequence, the so-called Fermi-level pining has been observed. The corundum isocrystalline oxide structures ($Al_2O_3$, $Ga_2O_3$, or $In_2O_3$) have been applied to effectively passivate these surface states and thus reduce the overpotential [17–19].

In this contribution, the attention was paid to the photoelectrochemical (PEC) processes with respect to the photogenerated holes. We clearly demonstrate the synergic effect of very thin nanocrystalline hematite films overlaid by passivating atomic layer deposition (ALD) $Al_2O_3$ ultra-thin (2 nm) coatings. This approach suppresses the negative impact of the short diffusion length of the holes, decrease the required overpotential for the photocurrent onset, and increase the overall current density value due to eliminating the charge backward recombination.

The hematite films were prepared by a novel low-temperature plasma deposition technique known as high-power impulse magnetron sputtering (HiPIMS). Generally, HiPIMS discharges work under pulse-modulated regime with a low repetition frequencies (typically about 100 Hz) and very short duty cycles (~1%), during which very high peak power powers are applied (~kW/cm²) to the cathode (metal deposition target). A distinguishing feature of HiPIMS is its high degree of ionization of the sputtered metal and a high rate of molecular gas dissociation owing to very high plasma density near the target (order of $10^{13}$ ions cm$^{-3}$) [20,21]. This method is thus particularly convenient to implement the highly active hematite films in more complex and sophisticated 1D nanostructures (i.e. nanotubes) and the so-called host scaffold–guest absorber structures recently applied for PEC water splitting reactions. Such organizations provide a significant enhancement of the absorbed photon to current efficiency (APCE) due to a high surface area [22,23] simultaneously suppressing recombination of the holes in bulk.

Very thin hematite films demonstrating enhanced carrier collection and the APCE have been previously fabricated by spray pyrolysis [24] and ALD method [25]. Hisatomi et al. [24] demonstrated the maximum photocurrent density of 0.7 mA cm$^{-2}$ at around 1.6 V vs. RHE and around 0.25 mA cm$^{-2}$ at 1.23 V vs. RHE obtained by the system consisting of hematite (20 nm) electrode modified by an $Nb_2O_5$ underlayer (2.0 nm) and deposited at 520 °C. To the best of our knowledge, the combination of very thin hematite electrode and passivating overlayer has not been introduced yet.

## 2. Experimental

The preparation of hematite films was carried out in an ultra-high vacuum (UHV) chamber continuously pumped down by a combination of rotary and turbo-molecular pumps providing the base pressure of $10^{-5}$ Pa. The depositions were performed as the low-temperature HiPIMS reactive sputtering of pure iron target (99.995%, 50 mm outer diameter, Plasmaterials). Owing to a ferromagnetic behavior of the iron target, its thickness had to be reduced to 18 mm in order to ensure magnetic field of a sufficient intensity present at the surface of the magnetron target. The Ar–$O_2$ working gas mixture with the flow rates of 30 and 12 sccm (standard cubic centimeters per minute), respectively, was used. The operating pressure was 1 Pa. The average discharge current was always held constant on the value $I_{AV} = 600$ mA for the described experiments with HiPIMS magnetron. The pulsing frequency of HiPIMS discharge was varied in the range $f_P = 70$–1000 Hz and the "ON" time when the discharge was active was held on constant value $T_{ON} = 100$ μs and the maximal current density achieved in a pulse was 5 A cm$^{-2}$ at 70 Hz. The distance between the magnetron target and the substrate was $l_S = 60$ mm. All these deposition conditions were kept constant during each deposition. The same technique has been used for photoactive hematite coating recently [26]. In that previous work, the ratio of ionized to neutral fluxes of depositing particles (parameter $r$) on the surface of substrate during hematite deposition was investigated. It was shown that the HiPIMS provides a high degree of ionization of sputtered particles ($r = 0.44$) for the highest pulse power applied ($3.5 \times 10^4$ W). As the substrates carefully cleaned (combination of acetone, ethanol, and deionized water ultrasonic baths) transparent conductive fluorine-doped tin oxide (FTO, TCO-7, Solaronix) coated glass slides were applied. The HiPIMS deposition was carried at room temperature. However, a slight increase in the temperature of the substrate (~100 °C) can be expected owing to the sputtering process itself. The film thickness was measured by a set of techniques including optical ellipsometry, XPS, and SEM.

The depositions of $Al_2O_3$ overlayers were performed by means of Cambridge Nanotech–Fiji commercial ALD system. As the precursors , trimethylaluminum and water were used. The temperature raised up to 150 °C due to the ALD itself. Coatings consisted of 4 (~4 Å), 6 (~6 Å), 10 (~10 Å), and 20 (~20 Å) ALD cycles were compared. The ALD process was in-situ monitored by optical ellipsometry.

The crystalline phase of the $Fe_2O_3$ films was determined by Raman spectroscopy using Renishaw Raman Microscope RM 1000 (unpolarized beam in back scattering mode of a 514.5 nm Ar$^+$ laser). Optical properties were investigated by means of photothermal deflection spectroscopy (PDS) based on the deviation of the laser beam collinearly propagated with the sample surface [27]. The surface topography images were obtained with help of SEM (Hitachi S-520) and AFM (Thericroscopes). The 3D AFM scans served to estimate the surface RMS roughness.

The photoelectrochemical measurements were carried with help of a standard three-electrode arrangement, which has been previously applied for testing other photoresponding coatings [28,29]. In this configuration, the hematite-coated FTO substrate served as the working electrode, the Ag/AgCl (3 M KCl) introduced the reference electrode, and platinum plate was employed as the counter electrode. As the electrolyte, 1 M NaOH solution (pH 13.6) was used.

The measured potentials vs Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$ER_{HE} = E_{Ag/AgCl} + 0.059pH + E^{\circ}_{Ag/AgCl}$$

where $E_{RHE}$ is the converted potential vs. RHE, $E^{\circ}_{Ag/AgC} = 0.207$ V at 25 °C, and $E_{Ag/AgCl}$ is the experimentally measured potential against Ag/AgCl reference. The Mott–Schottky characteristics were