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All earth abundant materials for low cost solar-driven hydrogen production

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ABSTRACT

Earth abundant materials based photoelectrochemical cells (PECs) are designed using aluminium alloyed iron silicide (FeSi(Al)) as auxiliary electrode, tungsten oxide (WO_3) and iron-oxide (Fe_2O_3) as working electrodes for solar driven hydrogen (SH) production. Low temperature grown metallic α-phase and semiconducting β-phase FeSi(Al) are introduced as auxiliary electrode and hydrogen evolution performance is compared with commercially available platinum electrode. The β-phase FeSi(Al) electrode yields similar hydrogen evolution compared with platinum electrode and are highly stable in electrolyte solution. This study shows that the earth-abundant iron-silicide and cheap metal oxides based PEC cells provide great potential toward Pt-free devices for the development of sustainable and low cost PECs for large scale solar hydrogen production.

1. Introduction

The production of renewable energy from solar light harvesting has been heralded as one of the most important technological solutions to combat climate change in the 21st century [1,2]. Hydrogen, the fuel with the highest energy capacity per unit mass, has the potential to supplement and possibly replace fossil fuels in the next decades. The photo assisted production of hydrogen and oxygen from water offers an extremely promising way for clean, low-cost and environmental friendly conversion of solar energy into chemical energy [3,4]. Many efforts have been directed in recent years towards development and characterization of new types of photocatalysts for water splitting, possibly capable of absorbing a large fraction of the visible solar spectrum [5,6]. Noble metal free co-catalysts have been developed for efficient hydrogen evolution [7,8]. Hydrogen gas evolution using photoelectrochemical water splitting is an attractive process [9]. A photoelectrochemical cell (PEC) consists of working electrode (photo anode or photocathode), reference electrode, and auxiliary (counter) electrode. There is tremendous effort going on to develop photoanode and photocathode for photoelectrochemical water splitting [10–13].

In PECs, the counter electrode is usually platinum; due to its stability and high catalytic activity. Even though platinum is a most effective counter electrode material, its cost and abundance is a concern for the large scale photoelectrochemical hydrogen evolution. Antoniadou et al., demonstrated platinum (Pt) free devices for photoelectrochemical water splitting by employing a Cu_2S/brass cathode [14]. Fan et al., also reported molecular PECs for light driven total water splitting with Pt-free electrodes towards the development of low cost cell [15].

It has been suggested that the surface area of counter electrode should be twice that of the working electrode [16]. The area of counter electrode controls overall water splitting performance depending upon availability of reaction sites for effective charge transfer. Therefore, an alternative of Pt electrode is much sought-after to realize PEC hydrogen evolution in large scale with low cost. In the present work, sputtered grown aluminium alloyed iron silicide films have been used as auxiliary electrode. Semiconducting iron silicide (β-phase) has band gap of ~0.9 eV, it is suitable for light emitting diode and photovoltaic applications [17,18]. The Metallic iron silicide (α-phase) is a potential candidate for microelectronic and photovoltaic applications [18–20].

Sputter deposition method provides high quality thin film over large area. It has great potential for solar energy harvesting applications [20–22]. Furthermore; sputter deposition technique provides precise control of thickness and chemical composition of the thin film [23–26]. The work function of sputter grown α-phase and β-phase aluminium alloyed iron silicide (FeSi(Al)) is ~5.3 eV [18,20], which is very similar to platinum. The silicide materials

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are earth-abundant and environmentally and chemically stable, thus, it is a potential material for low cost PECs for solar hydrogen production. In the present work, we have employed Al-alloyed iron silicide as a counter electrode and developed all earth abundant based PECs for solar hydrogen production.

2. Experimental

Aluminium alloyed amorphous FeSi was co-sputtered on Al-passivated n-Si substrate by using stoichiometry $FeSi_2$ target at 100 W and Al target at ~2 W in an Ar environment. The Al alloyed iron silicide coated Si samples were then subjected to rapid-thermal-annealing (RTA) in nitrogen environment at temperatures of 700 °C for 60 s to form α-phase and β-phase FeSi(Al) ternary alloy. Silicide thickness and Al content are crucial to form the different phases of the silicide layer [19,20,22]. The Al content in α-phase FeSi(Al) ternary alloy is 1.5 times higher compared with that of the β-phase silicide [27]. In this work, Al content in β-phase silicide is ~4–6% [19] and for α-phase, Al content is ~10% [21]. After thermal treatment, native oxide from the surface of FeSi(Al) was removed by using diluted hydrofluoric acid solution. For the photoelectrochemical hydrogen evolution studies, tungsten oxide (WO_3) was used as a working electrode. Thick WO_3 (~1300 nm) was spin-coated on FTO substrate. The WO_3 coated FTO substrates were annealed at 500 °C for 1 h to improve the crystal quality of the WO_3 film. Details of WO_3 preparation can be found in reference [28]. Performance of the PEC water splitting using commercially available Pt auxiliary electrode and iron-silicide auxiliary electrode with WO_3 photoanode has been compared. Then, using iron-silicide as an auxiliary electrode, hydrogen evolution was tested. The hydrogen evolution performance was also tested with ferric oxide (Fe_2O_3) photoanode. The details of Fe_2O_3 photoanode formation can be found in reference [29]. PEC hydrogen gas evolution analysis was carried out in a closed recirculating glass reactor filled with Ar gas. A 3-electrode configuration was used for the water splitting process with the sputtered FeSi(Al) as the auxiliary electrode and Ag/AgCl as the reference electrode. The electrodes were immersed in 0.1 M Na_2SO_4 aqueous electrolyte solution. A DY2100 series potentiostat (Digi-Ivy, Inc.) was used to supply a constant voltage across the reference and working electrode. The WO_3 and Fe_2O_3 electrodes were illuminated with a 150 W Xenon arc lamp fitted with AM 1.5 filter with an intensity of 50 mW cm^{-2}. The amount of evolved hydrogen gas was analyzed with Shimadzu GC-2014 gas chromatography (fitted with TCD detector and MS-5A column and using Ar as carrier gas).

3. Results and discussion

The XRD pattern of 40 nm thin Al alloyed FeSi films (rapid thermal annealed at 700 °C for 1 min) shows a sharp distinct diffraction peak at 17°, it confirms the formation of (001) planes of α-phase FeSi(Al) ternary alloy [18]. A low intensity peaks are also observed corresponding to (003) and (111) orientations, respectively [18]. XRD data analysis shows the FWHM value to be 0.44° and crystal size of 17.7 nm for α-phase FeSi(Al) ternary alloy (Fig. 1a). Formation of β-phase FeSi(Al) is achieved when Al content is reduced to ~4–6% in the silicide film [19]. A sharp peak at 28.4° is corresponding to (202/220) planes of β-phase $FeSi_2$[20]. The FWHM and crystal size are 0.39° and 20.4 nm, respectively (Fig. 1b). Both phases have almost similar value of FWHM and crystal size. The surface of iron silicide films is found to be very smooth. Atomic force microscopy study shows that sputter-grown iron-silicide films have a surface roughness of ~0.85 nm (Fig. 2a). Surface morphology of the iron silicide film is also observed in

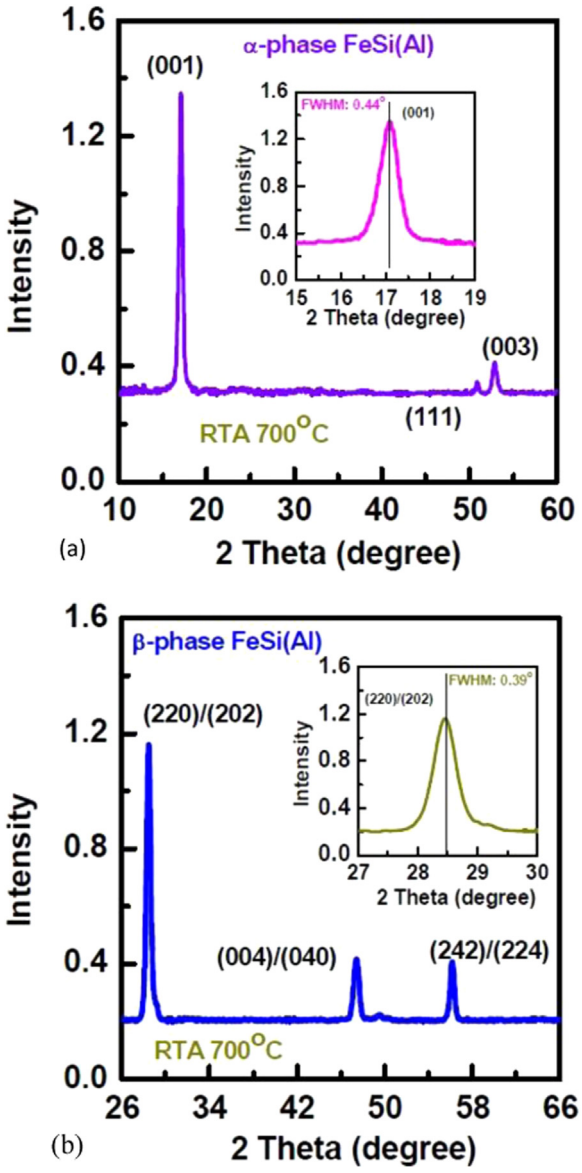

Fig. 1. XRD pattern of FeSi(Al) alloy of (a) α-phase and (b) β-phase after rapid thermal annealing at 700 °C for 1 min in nitrogen environment. Inset images are the zoom-in image of intense peaks.

scanning electron microscopic (SEM) image after rapid thermal treatment at 700 °C, as shown in Fig. 2(b).

The hydrogen evolution test is conducted to prove the potential of FeSi(Al) films to be used as counter electrodes in place of Pt electrode. Fig. 3(a) shows the time dependent hydrogen evolution results for 4 h continuous measurements at a fixed bias of 1 V. The hydrogen evolution rate is measured as 5.1, 3.2 and 4.36 μmol h^{-1} cm^{-2} for Pt, α and β-phase FeSi(Al) electrodes, respectively, with identical WO_3 photoanode. At the beginning (first 30 min), the amount of hydrogen evolution is almost similar for all three auxiliary electrodes. The slope of the hydrogen evolution plot is nearly constant for Pt and β-phase FeSi(Al) electrode. However, hydrogen evolution is reduced in case of α-phase FeSi (Al) auxiliary electrode and shows a non-linear hydrogen evolution behaviour. While, the linear curve in β-phase FeSi(Al) proves the long term durability of the electrode and suggest that it can be a replacement of the Pt electrode in PEC hydrogen evolution reaction.

The hydrogen evolution test was also conducted with iron oxide photoanode (Fe_2O_3) to check the consistency of the β-phase

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