Fabrication of Indium-doped n-Fe_2O_3 Thin Films by Spray Pyrolytic Method for Photoelectrochemical Water Splitting

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INTRODUCTION

The field of photoelectrochemical splitting of water using semiconductor electrodes has seen several advances over the past 30 years [1-6], but the greatest need is still the ability to produce a stable and low cost semiconductor with a low bandgap; therefore, being able to absorb a large amount of solar energy photons. Nonetheless, most of today's stable semiconductors absorb almost exclusively in the ultraviolet radiation range. Iron (III) oxide (Fe_2O_3) is a low-cost semiconductor having high stability and can absorb most of the visible light in the solar spectrum. Iron (III) oxide has a bandgap of 2.0 to 2.2 eV; therefore, it can absorb solar radiation from 565 to 295 nm, which comprises 38% of the photons of sunlight at AM 1.5 [7]. Although the Fe_2O_3 can absorb 38% of the sunlight, its photoresponse were found to be quite low [3-6] towards water splitting reaction due to its high resistivity and consequent recombination of photogenerated carriers. To minimize these effects, iron (III) oxide was doped with iodine [4] but no reports on indium doping have been made as of yet. An efficient n-Fe_2O_3 semiconductor can be used as an important front layer to protect a Si or an amorphous Si solar cell to be used in the back to supply the required photovoltage for efficient water-splitting reaction. In this study, we focused on spray pyrolytic (SPD) methods to fabricate In-doped p-Fe_2O_3 thin films with various dopant concentrations and substrate temperatures using different spray times.

EXPERIMENTAL

Thin films n-Fe_2O_3 were deposited by SPD methods on conducting tin-oxide coated glass using the spray solutions of different concentrations of 0.11 M $FeCl_3{\cdot}6H_2O$ having various concentrations (0.0022 M to 0.011 M) of $InCl_3.6H_2O$ in 200 proof ethanol. The substrate (conducting tin oxide coated glass) temperature was varied from 410 ^oC to 425 ^oC. The spray solution was propelled by oxygen gas at a pressure of 20 psi at an interval of five min. after each 10 sec spray period. The electrolyte solution used for photoelectrochemical splitting of water was 1.0 M NaOH in a triply de-ionized water.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of photocurrent density (j_p) as a function of measured electrode potential, E_{meas} vs SCE for the samples prepared at an optimal temperature of 415°C at optimum spray time of 60 seconds for different dopant solution concentrations. A maximum photo current density at an illumination intensity of 40 mW cm^{-2} was observed A maximum quantum efficiency of 26.5% at wavelength of 295 nm. The threshold quantum efficiency at 565 nm corrresponds a bandgap of 2.2 eV for I*n*-doped n-Fe_2O_3.

The presence of indium and iron (III) indium (III) oxides were confirmed from the results of X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements. XPS results showed 1.5 atomic % indium-doping relative to other elements present on the surface. XRD data indicates that alpha (α) Fe_2O_3 is the only form of iron oxide present in the thin films. Indium oxide from the indium-doped tin oxide substrate was identified. The indium doped into the iron (III) oxide formed $FeInO_3$.[9] These peaks indicate that spray pyrolytically synthesized indium-doped n-Fe_2O_3 have mixed structures of α-iron (III) oxide and iron (III) indium (III) oxide ($FeInO_3$).[8]

The addition of optimum amounts of indium improved conductivity and photoresponse of spray-pyrolytically deposited thin films of n-Fe_2O_3 electrodes. The results of this study indicate the possibility of using other dopants or combinations of those dopants to improve the photoresponse of n-Fe_2O_3[10] for use in conjunction with an optimized p-Fe_2O_3 thin film electrode[11] to fabricate a p/n-Fe_2O_3 solar cell and use it for efficient photoelectrochemical water splitting.

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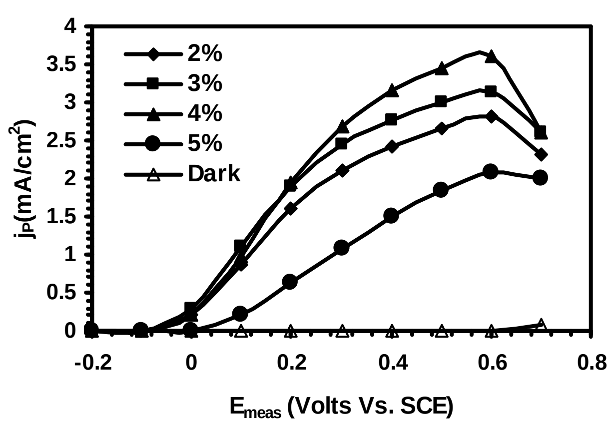

Figure 1. Photocurrent density, j_p (mA/cm^2), at an illumination intensity of 40 mW/cm^2 from a 150 Watt xenon arc lamp versus measured potential (E_{meas}) for n-Fe_2O_3 samples produced at an optimum total spray time of 60 sec having 10 sec spray periods at a substrate temperature of 415°C. Various indium dopant concentrations from 2 atomic % to 5 atomic % were used. The electrode potential at open circuit conditions was found to vary from -0.372 Volts/SCE at 2 atomic % dopant conc. to +0.470 Volts/SCE at 5 atomic % dopant conc. The dark current for all samples started to appear only at +0.7 Volts/SCE to higher potential values, as evidenced by the lowering of photocurrent in the plot.