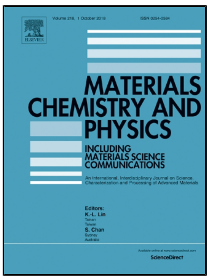
Accepted Manuscript



Sulfurization of Hematite Fe_2O_3 and Anatase TiO_2 by Annealing in H_2S

Woo Jung Shin, Araceli Hernández Granados, Wen-Hsi Huang, Hailin Hu, Meng Tao

PII:	S0254-0584(18)30881-2
DOI:	10.1016/j.matchemphys.2018.10.008
Reference:	MAC 21023
To appear in:	*Materials Chemistry and Physics*
Received Date:	14 November 2017
Accepted Date:	05 October 2018

Please cite this article as: Woo Jung Shin, Araceli Hernández Granados, Wen-Hsi Huang, Hailin Hu, Meng Tao, Sulfurization of Hematite Fe_2O_3 and Anatase TiO_2 by Annealing in H_2S, *Materials Chemistry and Physics* (2018), doi: 10.1016/j.matchemphys.2018.10.008

Sulfurization of Hematite Fe_2O_3 and Anatase TiO_2 by Annealing in H_2S

Woo Jung Shin [a], Araceli Hernández Granados [c,d], Wen-Hsi Huang [a], Hailin Hu [c] and Meng Tao [b]

[a] School for Engineering of Matter, Transport and Energy and [b] School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona 85287, USA

[c] Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Priv. Xochicalco S/N, Temixco, Morelos, 62580, Mexico

[d] Centro de Investigación en Ingeniería y Ciencias Aplicadas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Cuernavaca, Morelos, 62209, Mexico

* Correspondence: Prof. Meng Tao (meng.tao@asu.edu), Woo Jung Shin (wshin4@asu.edu), Tel: +1 480-965-9845

ABSTRACT

Spray-deposited hematite Fe_2O_3 and spin-coated anatase TiO_2 thin films were annealed under H_2S in order to investigate the effect of sulfurization by H_2S. Sulfurized films were characterized using UV–vis spectrophotometry, X-ray diffractometry, Raman spectroscopy, field-emission scanning electron microscopy, and energy-dispersive X-ray spectroscopy. Sulfurized Fe_2O_3 and TiO_2 films are composed of multiple phases. The Fe_2O_3 film undergoes phase transformation from hematite into a mixture of magnetite (Fe_3O_4) and pyrrhotite (FeS) at annealing temperatures above 250˚C. At 450˚C α-Fe_2O_3 is fully transformed into pyrite (FeS_2). The TiO_2 film transforms into a mixture of TiO_2 and TiS_2. TiS_2 formation begins at temperatures above 550˚C. At 700˚C, TiO_2 is completely transformed into TiS_2.

1. INTRODUCTION

Hematite Fe_2O_3 and anatase TiO_2 have received growing interests for solar energy applications such as solar water splitting [1-4] and photovoltaic solar cells [5-8]. They are nontoxic, low-cost, earth-abundant, and environmentally-friendly, which are necessary properties for mass production of their devices for solar energy conversion. However, the realized solar energy conversion efficiencies from devices based on these materials have been insufficient due to a number of issues, such as poor light absorption, short lifetime of photo-excited charge carriers, and large bandgaps [9]. On the other hand, pyrite FeS_2 and titanium disulfide TiS_2 have demonstrated promising properties for applications in photovoltaic solar cells [10] and solar water splitting [11]. FeS_2 has a smaller bandgap (0.95 eV indirect), high absorption coefficient ($\alpha > 10^5$ cm^{-1} for $h\nu > 1.3$ eV), and sufficient minority carrier diffusion length (100–1000 nm) [12]. FeS_2 solar cells have demonstrated a high quantum efficiency of 90% and a high photocurrent of 42 mA-cm^{-2} [10]. In solar water splitting, it possesses excellent stability against photo-corrosion in comparison with other chalcogenide semiconductors (e.g. CdS or CdSe) [11]. For TiS_2, Hall and thermoelectric power measurements suggest that TiS_2 is a semiconductor [13]. TiS_2 has recently been used as the charge transport layer in perovskite solar cells, resulting in a high cell efficiency of 17.37% because of its high carrier mobility and conductivity [14].

It is well known that for a highly-efficient solar cell, a direct bandgap around 1.4 eV is highly desirable. For solar water splitting, the optimum bandgap is about 1.7 eV direct. A major disadvantage of TiO_2 is that it is a semiconductor with a wide bandgap of 3.2 eV and thus can only utilize the ultraviolet (UV) portion of the solar spectrum below 388 nm. That portion of the solar spectrum makes up just 4–5% of the energy from sunlight. α-Fe_2O_3 has a slightly-lower bandgap of 2.1 eV which theoretically allows the utilization of approximately 40% of the solar spectrum [15]. Therefore, narrowing the bandgap of these semiconductors to