Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Solar Energy Materials & Solar Cells 88 (2005) 131–144
Solar Energy Materials & Solar Cells
www.elsevier.com/locate/solmat

Development of reactively sputtered metal oxide films for hydrogen-producing hybrid multijunction photoelectrodes

Eric L. Miller*, Daniela Paluselli, Bjorn Marsen, Richard E. Rocheleau

Hawaii Natural Energy Institute, School for Ocean, Earth Science, Technology, University of Hawaii, Manoa, HI, USA

Received 1 February 2004; received in revised form 1 April 2004; accepted 1 July 2004

Abstract

The multijunction *hybrid photoelectrode* for hydrogen production developed at UH incorporates a metal-oxide photoelectrochemical top junction which is deposited onto an underlying solid state junction which generates additional voltage bias for efficient water splitting. Initial attempts to fabricate *hybrid photoelectrodes* using nano-structured iron-oxide films deposited by spray pyrolysis were largely unsuccessful because the pyrolysis temperatures of approximately 400 °C were high enough to cause significant damage to the underlying amorphous-silicon-based solid state junctions. This paper describes the development of low temperature (<200 °C) reactively sputtered metal oxide films with properties specifically optimized for use in *hybrid photoelectrode* applications. The primary materials investigated include iron oxide, for use in alkaline photoelectrolysis, and tungsten trioxide, for use in acid photoelectrolysis. To date, the sputtered tungsten trioxide materials have demonstrated higher levels of photo-generated current compared with sputtered iron-oxide films. Initial *hybrid photoelectrode* devices fabricated using tungsten-trioxide films sputter deposited onto tandem amorphous-silicon junctions are described which exhibited stable solar-to-hydrogen conversion in acidic media at efficiencies up to 1% in outdoor tests. Plans to enhance efficiency by

*Corresponding author. Tel.: +1 808 956 5337; fax: +1 808 956 2335.
E-mail address: ericm@hawaii.edu (E.L. Miller).

0927-0248/$ - see front matter
doi:10.1016/j.solmat.2004.07.058

further oxide film optimizations, for example using surface texturing and possible doping, are also discussed.

Keywords: Hydrogen production; Metal oxide films; Photoelectrode; Multijunction

1. Introduction

Under the sponsorship of the US Department of Energy (DOE), the Thin Films Laboratory at the Hawaii Natural Energy Institute of the University of Hawaii (UH) has been developing photoelectrochemical (PEC) systems to produce hydrogen directly from water using sunlight as the energy source. The main thrust of the PEC systems research at UH has been the development of integrated multi-junction photoelectrodes based on low-cost semiconductor, catalytic, and protective thin films [1]. Fig. 1 shows a generic planar photoelectrode structure, where sunlight absorbed in photoactive regions produces electricity to drive the hydrogen and oxygen evolution reactions at opposite surfaces. In order to be commercially viable, the photoelectrode system must be low cost, and must be capable of operating stably in corrosive aqueous electrolyte environments with solar-to-hydrogen (STH) conversion efficiencies approaching 10% by 2015 [2]. In an attempt to meet the cost and performance goals, UH has recently accelerated efforts to develop a "Hybrid Photoelectrode" (HPE) which incorporates low-cost metal-oxide and photovoltaic-grade semiconductor thin films. The basic "Hybrid Photoelectrode" structure developed at UH, shown in Fig. 2, is a multi-junction thin-film device combining PEC with solid-state junctions to meet the voltage, current and stability requirements for hydrogen production. Significant advantages of the HPE design over other structures investigated at UH [3,4] include elimination of lateral current collection, simplification of device geometry for ease of fabrication, and improved stability based on the thick, seamless outer metal-oxide layer.

Current HPE development efforts are focused on integrating amorphous silicon/germanium alloys (a-Si:Ge) as a low cost solid-state junction material with

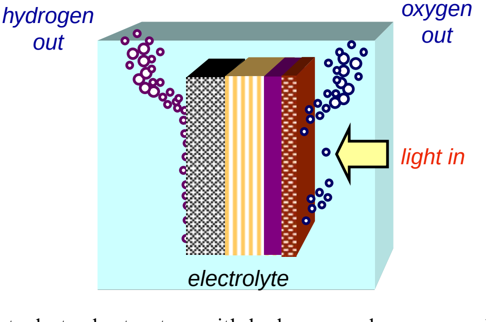

Fig. 1. Generic planar photoelectrode structure with hydrogen and oxygen evolved at opposite surfaces.