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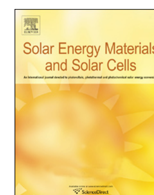

Growth and characterization of thin manganese oxide corrosion barrier layers for silicon photoanode protection during water oxidation

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A B S T R A C T

In this work the potential of thin manganese oxide layers deposited by physical vapor deposition at moderate vacuum pressure to significantly retard the corrosion of silicon photo-anodes during the oxidation of water is reported.

Results show that manganese oxide layers up to 10 nm thick display sufficient transmission of solar frequency radiation and electrical conductivity to facilitate efficient oxidation of water by the underlying silicon while offering complete protection from oxidation of the silicon substrate for more than 14 h. Data from x-ray photoelectron spectroscopy confirms that the increased lifetime observed when using manganese oxide as a protective layer is a result of the inhibition of the growth of silicon oxide during the reaction.

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1. Introduction

Silicon's status as the material of choice for semiconductor applications over the past four decades is well documented. In the renewable energy space, silicon has is used to generate power in conventional solar cells both in its amorphous and crystalline phases and the vast majority of commercially purchased solar cells are silicon based. Another area where semiconductors are useful in the generation of renewable fuels is the photo-electrochemical cell (PEC) [1]. Photo-electrochemical cells use sunlight to generate electron–hole pairs in semiconductors that are in direct contact with water. The electron–hole pairs serve to oxidize the water via the reaction:

$$H_2O \rightarrow 4H^+ + 4e^- + O_2$$

The generated electrons are carried away via a backside contact where they may either reduce the water at a counter electrode to generate hydrogen, or flow in an external circuit to generate energy by some other means. For water splitting, the difference between the oxidation and reduction half cell potentials must be 1.23 V, meaning the silicon with its band gap of 1.1 eV is not suitable for use in a single-material water splitting cell. It can however be used in conjunction with a counter electrode made from another material where it serves as the oxidizing part of the cell.

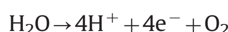
Silicon has to date had limited success when used to oxidize water. The reason for this is that the oxidation half-reaction takes place directly at the interface between the silicon and the water. Due to the presence of dangling bonds and the reactivity of oxygen, silicon readily oxidizes when there is a source of oxygen available. As soon as the reaction begins, the substrate starts to oxidize and the water gradually goes from being in contact with a semiconductor whose bandgap is 1.1 eV to an insulator (SiO_2) with a bandgap of 9 eV. This effect simultaneously reduces the incident photon flux reaching the silicon, and inhibits the flow of holes from the silicon to the water and ends the reaction.

In order to prevent the oxidation of the silicon anode, thin protective overlayers can be used [2–4]. Ideally, these overlayers should act as an oxygen diffusion barrier while being transparent to solar radiation and having sufficient conductivity to maintain the desired current density in the cell.

Several works exist in the literature that employ protective layers on top of the silicon in order to curb it's oxidation, such as nickel [5] which showed 80 h of stability in in 0.65 M K-borate and 0.35 M Li-borate (pH=9.5) and TiO_2 [6], an insulating oxide which remains stable for more than 8 h in acidic and basic electrolytes.

Thicker layers where uniformity is less of an issue are desirable. Stranwitz et al. [7] have reported on the stability of manganese oxide protective layers deposited by atomic layer deposition (ALD) while Kainthla [2] studied Mn-oxide prepared in a chemical bath.

In this work, we examine the properties of manganese oxide deposited by physical vapor deposition in vacuum, and use x-ray photoelectron spectroscopy measurements made on samples before



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and after taking part in water oxidation in order to correlate the observed electrical results with physical changes at the silicon–native oxide and native oxide–manganese oxide interfaces. Section 2 outlines the experimental details including film growth, electrochemical setup, and XPS parameters. In Section 3 we present optical transmission data for the deposited Mn-oxide films, and electrochemical data which shows that the these films provide long term stability to the underlying silicon photo-anode during oxidation, while also catalyzing the reaction. Section 4 presents an XPS study of the samples that took part in water oxidation and shows that the manganese oxide protects the silicon by inhibiting the formation of an SiO_2 like layer on top of the native-oxide which grows readily in the absence of the Mn-oxide.

2. Experimental details

All experiments were performed on silicon (1 0 0) wafers with the n-type samples being phosphorous doped with 100 Ω-cm resistivity while p-type samples were boron doped with a resistivity of.001 Ω-cm. Unless otherwise stated, all samples in this work had a native silicon oxide layer of approximately 1 nm thickness. Some samples had the native oxide stripped by a dip in hydrofluoric acid prior to manganese oxide deposition to evaluate the effect of a pristine silicon surface on the electrochemical performance.

Hydrochloric acid (HCl) etched Mn chips, with a purity of ~99.9%, were used as a source material for the deposition of Mn by thermal evaporation from a boron–nitride crucible in a Leybold Univex chamber at a vacuum pressure of 5×10^{-6} mbar at a deposition rate of approximately 0.2 nm/min. At this moderate pressure, the resultant film is fully oxidized manganese. All quoted film thicknesses are based on measurements from a quartz crystal resonator in the deposition chamber. A range of thicknesses of deposited Mn from 2 nm to 37 nm were prepared for evaluation. Electrochemical tests were performed by positioning the silicon sample as the working electrode in a 3-electrode photo-electrochemical cell purchased from Zahner Electric GMBH, schematically illustrated in Fig. 1a. The cell consists of a circular quartz window, which allows light to travel through 6.3 cm^3 of electrolyte where it is incident on an area of the sample which is equal to that of the window. The sample is contacted on the backside by an aluminium plate that serves as an Ohmic contact. The counter electrode is a coil of platinum wire placed opposite the sample encircling the quartz window, and the reference electrode is an Ag/AgCl electrode from Basinc which is dipped in the electrolyte but does not obstruct the path of the incident light. The wetted (active) specimen area is ≈3.16 cm^2. The cell manufacturers state that the estimated ratio between incoming light and light intensity on the sample is (in non-absorbing aqueous medium) ≈3.16, so that an effective surface of 1 cm^2 can be assumed for photocurrent density calculations. All quoted potentials in this work are those of the working electrode with respect to the reference electrode. Fig. 1b shows a band diagram of the photo-electrochemical test measurement

The Ag/AgCl electrodes used in this work have a potential of +0.198 V vs. the normal hydrogen electrode (NHE). All experiments used in this work had as the electrolyte a pH 7.5 phosphate buffer solution (Sigma-Aldrich) with a conductivity of 18 mS/cm at room temperature.

Electrochemical tests were performed using a CH Instruments 760B potentiostat. The light source used was a Newport 150 W Xenon Arc lamp with an intensity of 100 mW/cm^2 at the sample.

Optical transmission of the deposited films was evaluated using a standard UV–vis spectrophotometer and IV measurements were performed on the samples using a fixed separation dual probe stage and a Keithley 4200-SCS.

The XPS analysis was carried out using a VG Microtech electron spectrometer at a base pressure of 1×10^{-8} mbar. The photoelectrons were excited with a conventional Mg $K\alpha$ ($h\nu=1253.6$ eV) x-ray source and an electron energy analyser operating at a 50 eV pass energy. Spectra were fitted using Aanalyzer fitting software.

3. Optical and electrical performance of manganese oxide protected photo-anodes

The first requirement of a protective layer is that it be optically transmitting across the range of the solar spectrum. In order to ascertain to what extent manganese oxide is transparent to radiation in the 300–800 nm range, manganese oxide layers of varying thicknesses were deposited as described in the experimental section on glass slides and the transmission characteristics were evaluated in a spectrophotometer. Losses due to the glass slides have been subtracted from the reported figures. Fig. 2 shows the measured transmissivity for 5 nm, 10 nm, 20 nm and 37 nm film thicknesses, indicating that a 5 nm film transmits 75% of the incident light at a wavelength of 550 nm. Interestingly this number only drops to 51% when the film thickness is increased by a factor of 4. For the 37 nm film almost all incident light is absorbed or reflected, with only 4% reaching the detector.

It is clear that it would be desirable to keep the film thickness below 10 nm in order to allow sufficient photons to reach the silicon

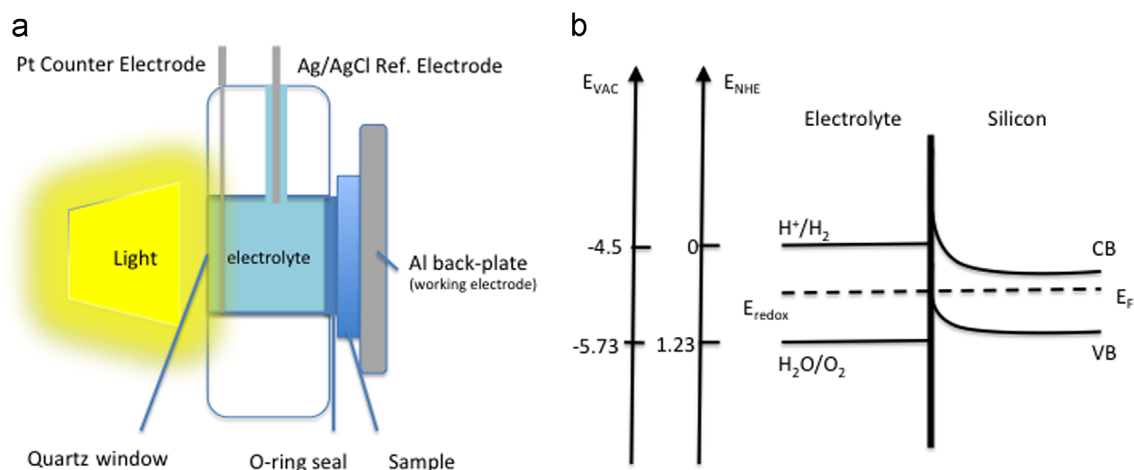

Fig. 1. (a) Schematic diagram (side on) of the test cell setup used for electrochemical measurements and (b) band diagram of the n-Si/electrolyte interface showing the position of the water oxidation and reduction potentials and the band bending in n-Si when it is brought into contact with the electrolyte.

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