THE STABILIZATION OF Si PHOTOELECTRODES BY A BORON PHOSPHIDE (BP) PROTECTIVE OPTICAL WINDOW

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Abstract

Boron phosphide can be grown epitaxially on Si substrates with CVD using a cold wall reactor. The Si/BP heterostructure is employed as photoelectrode in PEC solar cells. Here we report on the band structure of such laminate composites. The flatband potential of BP is determined to be –0.32 V vs SCE at pH 0. If p–type Si is overcoated with n–type BP, holes cannot reach the semiconductor / electrolyte interface while photoelectrons can easily pass. Efficient and stable solar energy conversion is feasible with p–Si/n–BP photoelectrodes.

Introduction

The application of photo–electrochemical (PEC) cells in the conversion of solar energy into electrical energy or fuel has attracted widespread attention recently. Since Fujishima et al. [1] reported on the successful utilization of TiO_2 semiconductor electrodes, much effort has been directed towards improvement of the PEC solar cell materials. Many different semiconductor electrodes have been investigated thoroughly and detailed information about the physics and chemistry of semiconductor / electrolyte (sc/el) interfaces has become available.

In general there are three major drawbacks for the successful conversion of solar energy with PEC cell configurations. Firstly, the semiconductors that are known to be photochemically stable all have a bandgap of 3 eV or larger. However, as the maximum of the solar spectrum lies at about 1.4 eV, these semiconductors are not sensitive for a substantial part of the solar spectrum. Consequently PEC cells based on the photosensitivity of these materials can only operate with very low efficiencies. Secondly, semiconductors that exhibit a suitable bandgap, i.e. of about 1.4 eV, are all known to be (photo)–chemically unstable. This instability is caused predominantly by the presence of holes at the sc/el interface. Holes represent electron vacancies in bonding valence band orbitals. Their presence at the sc/el interface weakens the surface atom bondings which leads to solvation of the semiconductor. In case of Si a passivating SiO_2 layer is formed within 30 seconds after exposing to an aqueous electrolyte. This layer inhibits any further charge flow through the cell. In p–type materials an appreciable amount of holes is present at the sc/el interface if the electrode is either in the dark or illuminated. In n–type materials holes are absent in the dark, but are generated upon irradiation ,and subsequently flow towards the surface when depletion exists. Thirdly, many electrolytes with fast electron kinetics are known to be photochemically active. In addition to absorption of solar radiation a concomitant photochemical dissociation reaction may occur if the electrolyte is irradiated strongly.

In order to overcome the first and second drawbacks, the utilization of heterojunction electrodes have been proposed [2]. If a wide bandgap semiconductor is deposited onto a small bandgap substrate it may serve as a protective optical window. Both the efficiency as well as the stability can be optimized in such composites.

Here we report on the utilization of boron phosphide (BP) as a protective optical window material for silicon electrodes. Butler and Ginley [3] recorded the first promising features of Si/BP heterojunction composites. The photoelectrochemical properties of polycrystalline BP were elucidated in our previous study [4]. Lee at al. employed crystalline p–BP as photocathode [5]. BP is a semiconductor with a 2 eV indirect bandgap and possesses an extreme resistance against aggressive chemical environments. Si is chosen for its nearly ideal bandgap of 1.1 eV and its wide availability. Both n–Si/n–BP and p–Si/n–BP heterojunction configurations have been investigated. With Scanning Electron Microscopy (SEM), X–Ray Diffraction (XRD), and Auger depth profiling the crystal structure and the stoichiometry of the laminate composite is studied. The spectral photocurrent response of both configurations n–Si/n–BP, and p–Si/n–BP is recorded. Impedance spectroscopy is used to determine the flatband potential of BP and the donor density. The photocurrent quantum yield spectra and the Mott–Schottky behavior provides coherent information about the band structure of this heterojunction. BP is observed to stabilize Si photoelectrodes successfully. Only when the p–Si/n–BP configuration is used energy can be converted at current densities of 15 mA cm^{-2} without deterioration of the cell characteristics for more than 1000 hours of continuous operation.

Experimental Aspects and Results

Epitaxial layers of BP on (100) Si substrates can be obtained by Chemical Vapor Deposition (CVD) using a cold wall reactor. A Si wafer is placed on a carbon susceptor which is heated inductively to 900 ^{o}C. Evaporated BBr_3 and

PBr_3 reactants are diluted with purified hydrogen and fed into the furnace in a molecular ratio of 1 to 20. A growth rate of typically 1 μm per hour has been achieved. Details on the CVD process of BP can be found in reference [6] and in the extended abstract of Kelder et al. in this proceedings volume.

In Figure 1 the Auger depth profile of the elements in the laminate composite is presented. The interfacial region is sharp and the stoichiometry in the bulk of either Si or BP is well defined.

The obtained heterostructures are prepared as photoelectrodes and brought into contact with either of the indifferent aqueous electrolytes: H_2SO_4 (0.5 M), buffered KCl (1 M), and KOH (1 M).

When the electrode is irradiated with tungsten–halogen light, 70 mW cm^2, and the potential sweeped slowly from +1 to –1 V vs SCE a photocurrent can be observed. For n–Si/n–BP heterojunctions an anodic photocurrent in the μA cm^{-2} range sets on at +0.8 Volt. For p–Si/n–BP electrodes large cathodic photocurrents in the mA cm^{-2} range are observed for voltages below –0.5 Volt. Here H_2SO_4 (1M) is used as electrolyte.

The excitation spectrum of the photogenerated minority carriers was detected by recording the photocurrent at a fixed potential. In this experiment a completely different behavior is observed for the two studied configurations. n–Si/n–BP electrodes revealed an anodic photocurrent that was generated by photons with $h\nu > 2$ eV. p–Si/n–BP electrodes showed a cathodic photocurrent generated by photons with $h\nu > 1.1$ eV. The excitation spectra for the two studied configurations are presented in Figure 2.

The small signal a.c. response of the PEC cell was recorded at 40 frequencies between 10 Hz and 65 kHz and could be fitted to a simple equivalent circuit comprising one or two series connections of a parallel RC combination. The Faraday resistance and the space charge capacitance, C_{sc}, of BP at the BP/electrolyte interface were obtained as a function of the cell's d.c. potential. From the C_{sc} values the Mott–Schottky (MS) plots of $(C_{sc})^{-2}$ versus the d.c. bias, V, were constructed. Linear frequency independent MS–plots were obtained. The extrapolated bias intercept was identical for both electrode configurations and read –0.35 V vs SCE in H_2SO_4 (1M) electrolyte. The flatband potential was observed to possess the usually found –60 mV/pH Nernstian pH dependence. For both electrode types the MS–plot slope was positive. From the slopes donor concentrations between 1 and 5 x 10^{19} cm^{-3} were determined for all studied samples.

Discussion

n–Si/n–BP heterojunction electrodes produce small anodic photocurrents when irradiated with high energetic photons, $E_{ph} > 2.0$ eV. Obviously this photocurrent is generated in the window material n–BP and not in the n–Si substrate. Apparently the holes created in the Si are unable to reach the BP/electrolyte interface.

p–Si/n–BP configurations produce large cathodic photocurrents when irradiated with low energetic photons, $E_{ph} > 1.1$ eV . Here the photogenerated minority carriers in Si do cross the Si/BP interface and reach the electrolyte to drive a cathodic reduction reaction there.

The band structure of the Si/BP heterojunction apparently prevent holes in Si to cross the Si/BP interface, but does make it possible for Si conduction band electrons to pass through.

From MS–plots the band structure of a semiconductor can be elucidated. Normally the flatband potential is related to the intercept of linear MS–plots with the potential axis. For both structures this intercept reads –0.32 V vs SCE at pH 0. The Point of Zero Charge (PZC) of BP was determined with the method proposed by Ginley et al. [7] and lies at a pH value of 6.4. The energy positions of the conduction and the valence band of BP on the absolute energy scale are determined experimentally to be:

E_c (BP) = (+0.32 – 0.06•pH) eV vs SCE
E_v (BP) = (–1.68 – 0.06•pH) eV vs SCE
PZC (BP) lies at a pH of 6.4
SCE ≈ 4.75 eV below vacuum level.

Si is known to have a conduction band energy of about +0.7 eV and a valence band at –0.4 eV vs SCE. Hence, the conduction band of Si matches excellently to the corresponding BP band allowing conduction band electrons to pass easily through the Si/BP interface. However, the valence band energies of Si and BP differ considerably. Valence band holes face a 0.8 eV potential barrier at the Si/BP junction and recombine with electrons instead of crossing. The band structures of n–Si/n–BP, and p–Si/n–BP heterojunction configurations are presented in Figure 3.

In order to verify this band model, a p–Si/n–BP photoelectrode, was placed in an electrolyte comprising a V^{2+}/V^{3+} redox couple. This couple reaches a redox potential of –0.45 V vs SCE when properly de–aerated. Irradiated with 100 mW cm^{-2} tungsten–halogen light results in a 20 mA cm^{-2} short circuit current. The open circuit potential was recorded to be 0.4 V. The short circuited PEC cell operated for over 1000 hours of continuous operation without any noticeable deterioration of the electrode. After this period the experiments were terminated. During this test more than 30,000 Q

cm^2 charge passed through the device which means that for every atom present in the thin coating, i.e. B or P, more than 40,000 electrons were crossed.

Conclusions

The utilization of optical windows on corrosion sensitive semiconductor photoelectrodes in PEC solar cells can stabilize the photoelectrodes without concomitant loss of the cell's efficiency. In order to achieve an efficient solar cell, the following four conditions must be fulfilled.

Firstly the window material must possess a significant larger bandgap than the substrate semiconductor. Secondly, the window material must have a high conductivity in order to avoid ohmic losses in the cell. Thirdly, if the substrate material is chosen to be p–type and the window material to be n–type, photoholes are absent at the sc/el interface in all circumstances which ensures a durable cell operation. In the dark the n–type window inhibits the holes from the p–substrate to flow towards the surface. Upon irradiation, the minority photoholes from the window are annihilated by the photoelectrons from the substrate. Fourthly, a p–substrate/n–window configuration can only be conductive for the minority carriers of the substrate if a good bandmatch between the conduction bands of the two materials is present.

All four requirements are fulfilled by the p–Si/n–BP heterojunction configuration. Consequently, employing such electrodes makes efficient and durable solar energy conversion in PEC cells within reach.

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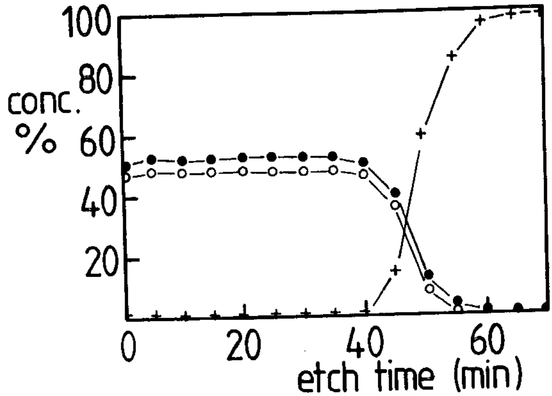

Fig. 1 : Auger depth profile of the elements in Si/BP composites.
• = boron, o = phosphorus, + = silicon.

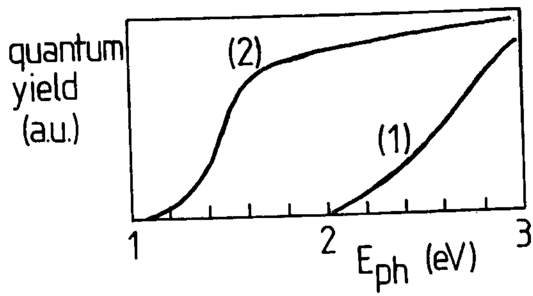

Fig. 2 : Quantum Yield spectra of n–Si/n–BP (1), and p–Si/n–BP (2) heterojunction photoelectrodes.

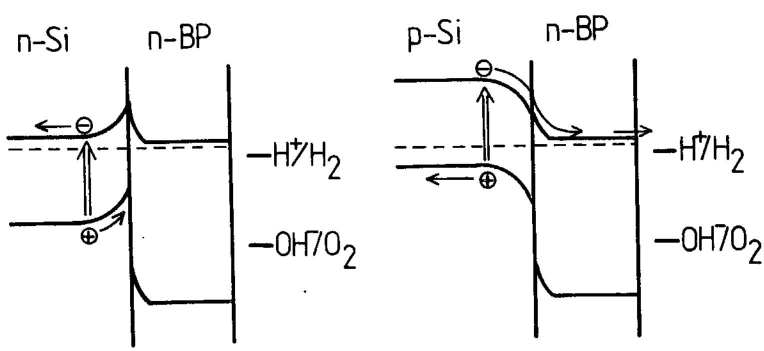

Fig. 3 : The band structure of Si/BP heterojunctuions.