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Micro- and nanotopographies for photoelectrochemical energy conversion. II: Photoelectrocatalysis – Classical and advanced systems

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ABSTRACT

The present trends on water photolysis are shortly reviewed. For application in monolithically integrated structures, photoelectrocatalytically active half cell developments with p-Si are described. Using the concept of nanoemitter minority carrier harvesting, it is shown that the introduction of traces of noble metal catalysts that allow collection of light-induced carriers does not result in cost or scarcity limitations. The issue of charge transfer through an interfacial oxide and ballistic electron injection into the electrolyte vs. thermalization is discussed. The experimental data shows that the nanoemitter system can sustain the high current densities resulting from injected light-induced excess carriers from the semiconductor at low overvoltages. Limitations of planar systems with Si are discussed and possible improvements are outlined. First tests of Si rod-like microstructures are presented and the influence of localized surface plasmon excitation on light-induced H_2 evolution with p-Si is investigated.

1. Introduction

Presently, the situation in light-induced catalysis, and, in particular in water photolysis, is characterized by a simultaneous advancement of two main approaches, e.g. the use of electrolysers coupled to solid state high efficiency concentrator photovoltaic cells [1,2] and the integrated approach is pursued intensively [3–6]. As the latter appears more cost- and resource efficient [7], this route is followed here. Water splitting is characterized by multi-electron transfer processes for which theories have not yet been developed and experiments were mostly based on empirical or combinatory approaches [8,9]. The overvoltages for the four-electron oxygen evolution reaction and for hydrogen evolution of about 0.5–0.6 V, losses for driving force, carrier thermalization and transport in solution have to be added to the thermodynamic value of +1.23 V vs. the normal hydrogen electrode (NHE) for the dissociation of water [10]. For a semiconducting absorber, the energy gap has to exceed 2.1–2.2 eV [11] to drive the water photolysis reaction, thereby limiting theoretical efficiency values under AM 1 irradiation conditions to ~15% [12]. Two major development strategies can be followed: (i) the use of abundant low cost materials for water splitting with a single junction structure that is inherently limited in efficiency and (ii) the preparation of multiple junction (tandem) structures where the theoretical efficiency exceeds 40% already for a two-component structure [13,14]. The Z-scheme of photosynthesis [15] points to the use of the latter concept in nature and intense efforts have been made in the field of artificial photosynthesis to mimic the basic processes of photosynthesis using simpler and more robust components [16–18]. Hitherto, however, these efforts have yet to await a major breakthrough and therefore, we follow the route of developing tandem structures by analyzing their components.

The fields of photoelectrochemistry and photoelectrocatalysis are characterized by a strong chemical approach in materials development, particularly when nano-grain films are prepared. Considerations from semiconductor and device physics are less established and therefore, the development of efficient systems has to rely on existing advanced semiconductors that have originally been developed for other purposes. Such semiconductors have to be technologically advanced such that tunnel junctions can be fabricated and that doping with foreign materials can be controlled [19]. This allows fabrication of monolithically integrated structures where photon absorption and photocatalytic reactions take place within a single structure (device).

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In the present article, the properties of Si as a half cell absorber of a tandem structure are investigated. For light-induced H_2 evolution, p-type Si is not an ideal candidate because of its limited contact potential difference with regard to the hydrogen redox couple and due to its susceptibility to chemical corrosion and photocorrosion [20]. On the other hand, this apparent disadvantage allows to investigate stabilization approaches and routes to increase the contact potential difference and, also, with Si incorporated in a tandem structure, efficiencies above 40% can be theoretically achieved [14,19]. A further advantage is the accumulated knowledge on the surface and interface behaviour of Si [20–23] and the experience of the semiconductor industry gained in fabrication of ultrathin interfacial films in Si, including foreign materials for the CMOS technology [24,25]. Therefore, the investigation of Si as photonic component in a photoelectrocatalytic device points to limitations and approaches to overcome them. Physical stabilization by interfacial anodic oxides emphasizes the use of nanoemitter structures (Section 3.1.1) [26]. The weak absorption leads to design of alternative absorber structures (Section 3.1.2) and to ways to enhance the coupling of light using the scattering behaviour of localized surface plasmons (Section 3.1.3) [27,28]. More generally, ways to overcome transport limitations in classical systems where electron drift and diffusion is a major issue, are of interest and a possible device structure based on Förster excitation energy transfer will be suggested.

2. Experimental

p-Si (1 0 0) samples, B-doped to a level of 10^{15} cm^{-3} have been used with a nominal miscut of 0°. Back contacts were made by removing the native oxide and Au deposition. Electrochemical experimentation and surface analyses were done as described in article I. Noble metal photoelectrodeposition was made using white light from a *W*-I lamp. The Pt and Rh carrier solutions were prepared using reagent grade and, when available, ultrapure chemicals and Milli Q water (18 MΩ).

The preparation of Au nanoparticles for adsorption and investigation of possible plasmonic enhancement effects has been described elsewhere in detail [29,30]. The procedure results in spherical particles of small size dispersion with about 20 nm diameter and of a variety of non spherical and agglomerated particles (see Section 3.1.3).

3. Results and discussion

3.1. Nanoemitter structures for photoelectrocatalysis

3.1.1. Planar electrodes

The dark current–voltage behaviour of p-Si in dilute NH_4F solution is displayed in Fig. 1. At potentials between −0.1 V and slightly above 0 V, i.e. shortly before the current maximum of 610 μA cm^{-2} is reached, the Si dissolution is divalent. This nomenclature is somewhat misleading since actually Si is dissolved as SiF_4 or $SiF_6{}^{2-}$ and shall indicate that only two charges are necessary to remove a Si atom [30]. This is the potential range where porous Si is formed [31,32]. Near the first current maximum at 0 V, the character of the dissolution changes to tetravalent, resulting in surface oxidation [33]. This potential regime is first characterized by electropolishing where ultrathin oxides reside on the surface [34] and, at larger potentials a thicker but porous oxide is formed. Above approximately +4 V, oscillations set in which are better visible in chronoamperometry as indicated in figure. The oscillatory regime is characterized by thicker oxides ($d \sim 10$ nm) which also vary periodically in their average thickness, phase shifted with regard to the current. The volume mismatch between Si and the anodic oxide results in tensile (oxide) and compressive (Si) stress at the interface which is relaxed by the formation of pits and cracks that, under silicon oxide etching conditions, develop into nanopores [35,36]. A HRSEM image of a Si surface after current oscillations is shown in Fig. 2 where the pores are clearly discernable.

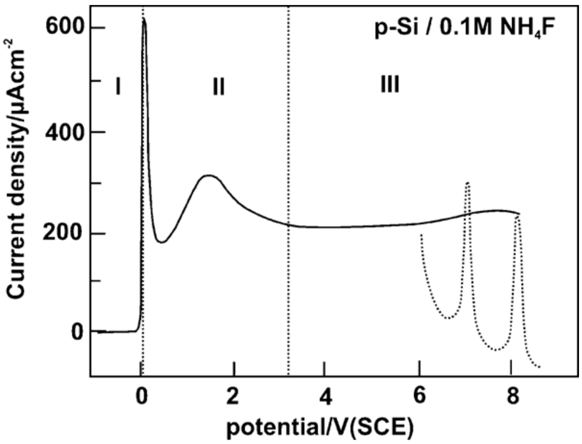

Fig. 1. *I–V* characteristic of p-Si(1 0 0) in dilute ammonium fluoride electrolyte: solution: 0.1 M NH_4F, pH 4; regions I–III indicate different surface conditions; I: divalent dissolution; II: electropolishing; III: oscillation.

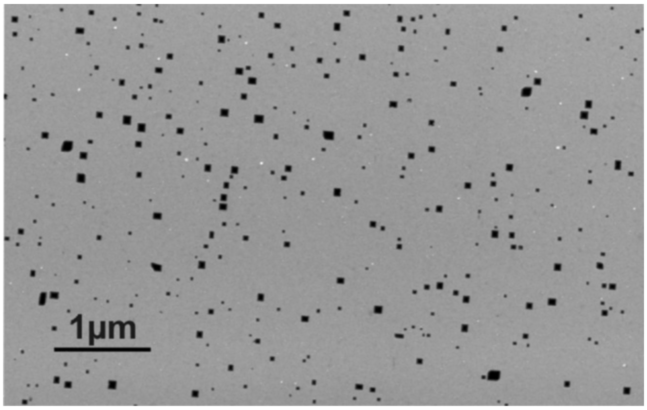

Fig. 2. HRSEM image of nanopores in the anodic oxide of p-Si(1 0 0) after dark current oscillations at +6 V (SCE); note the rectangular pore shape.

In analogy to the development of photovoltaic nanoemitter solar cells with n-Si in contact with aqueous electrolytes [37], photoelectrodeposition of noble metals such as Pt, Ir and Rh has been carried out to examine the nanoemitter concept (see article I) for its applicability in photoelectrocatalytic structures. Fig. 3 shows the protocol of Pt photoelectrodeposition into the nanoporous oxide

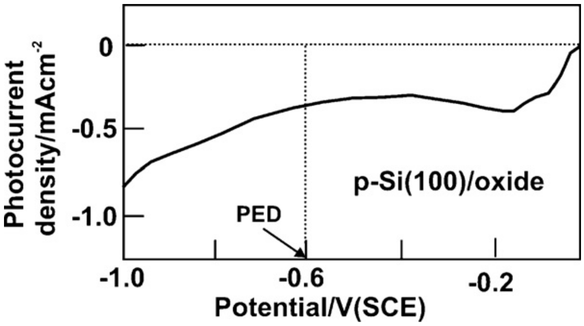

Fig. 3. Photoelectrodeposition of Pt from a Pt hexa-chloro solution (1 mM) into a nanoporous matrix as shown in Fig. 2; illumination intensity: 130 mW cm^{-2}, white light, W-I lamp; deposition potential: −0.6 V as indicated in figure (PED).