



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)

# Electroless deposition of Au/Pt/Pd nanoparticles on *p*-Si(1 1 1) for the light-induced hydrogen evolution reaction

M. Metzler<sup>a</sup>, A. Thorwart<sup>a</sup>, S. Zeller<sup>a</sup>, T. Diemant<sup>b</sup>, R.J. Behm<sup>b</sup>, T. Jacob<sup>a,\*</sup><sup>a</sup> Institute of Electrochemistry, Ulm University, Albert-Einstein-Allee 47, 89069 Ulm, Germany<sup>b</sup> Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, 89069 Ulm, Germany

## ARTICLE INFO

### Article history:

Received 21 May 2014

Received in revised form 1 September 2014

Accepted 15 October 2014

Available online xxx

### Keywords:

Metal deposition

Gold nanoparticles

Hydrogen evolution reaction

Silicon–metal–interface

Photoelectrochemistry

## ABSTRACT

Electroless deposition of Au nanoparticles and submonolayer equivalents of Pt and/or Pd on *p*-type silicon are studied with cyclic voltammetry (CV), angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and tapping-mode atomic force microscopy (TM-AFM). The controlled variation of deposition parameters influences the semiconductor/metal interface and the corresponding (photo)electrochemical behavior. The light-induced hydrogen evolution reaction (HER) serves as a model reaction for revealing the distinct changes in the electrode properties dependent on the plating procedure. Improved photoelectrocatalytic activity is observed for Au particles on silicon when decorated with small amounts of Pt (Pd) by means of an additional electroless deposition step, where simultaneous deposition of Pt and Pd leads to the best performance. However, simultaneous deposition of Au and Pt (Pd) results in a complete loss of the photocathode characteristics and therefore yields only dark currents. An interlayer of Pt/Au-silicide, identified with AR-XPS, appears to be responsible for the ohmic behavior.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

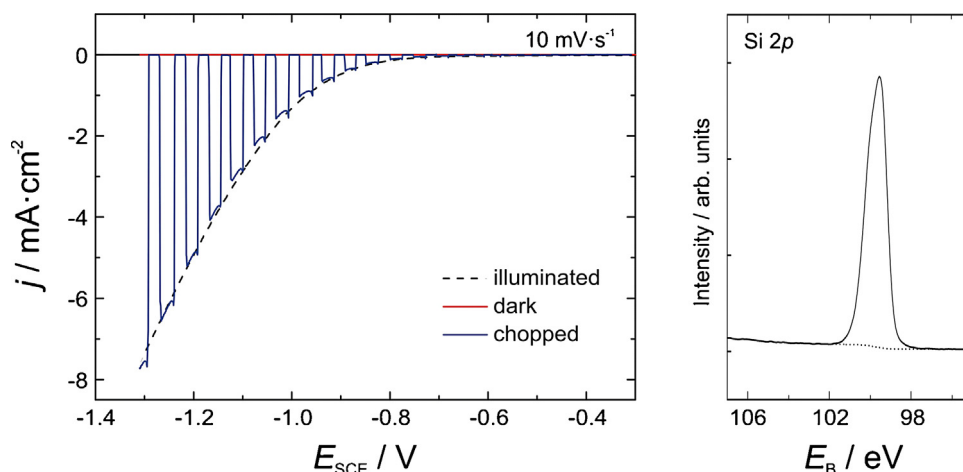
Photoelectrochemical (PEC) production of fuels such as hydrogen out of water and sunlight is one of the technologies on which hopes are pinned in the next decades. The direct conversion of solar radiation into chemical bonds is one possibility for the capture and storage of energy from photons. To make them commercially interesting, PEC cells have to compete with solar-panel-driven electrolyzers, which currently have a combined efficiency of about 11% [1]. Direct photoelectrolysis of water relies on large band gap absorbers ( $E_{\text{gap}} > 2$  eV) to obtain the necessary photovoltages ( $> 1.23$  V). Because photons with energies greater than the band gap are needed to excite electrons from the valence band (VB) to the conduction band (CB) of the semiconductor, photons with lower energies cannot be captured. In contrast, the combination of photoanodes with photocathodes offers the possibility of using materials with lower band gaps to increase the overall efficiency of the PEC system by harvesting more of the incoming photons [2–5].

Silicon ( $E_{\text{gap}} = 1.12$  eV) [6] is a promising material for such tandem systems, because it is not only abundant and stable under

cathodic conditions, but in its *p*-doped state also has a conduction band, which supports the photoelectrochemical HER with excited electrons. In bare silicon surfaces, recombination competes with the kinetically unfavored reduction of protons in solution, so that a high external bias is needed to drive hydrogen production, resulting in an inefficient process. The deposition of a co-catalyst is typically used to overcome these difficulties and various plating techniques for synthesizing such photoelectrocatalysts are discussed in the literature. Methods for metalizing silicon include electron beam evaporation techniques [7,8], (photo)electrochemical methods [9], electroless deposition from fluoride solutions and reversed micelle microemulsions [10]. Interestingly, the same metals on the same substrates deposited in different ways can lead to drastic changes in PEC performance [10]. High dark currents and a substantial loss of photovoltage is observed just by changing the Pt salt precursor from Pt(IV) to Pt(II) while using the same deposition technique [11]. Hence, the preparation method, the involved precursor chemicals as well as the solvent can influence the formed silicon/metal interfaces and with that their (photo)electrochemical properties. In order to better understand this dependence, the present work investigates silicon/metal interfaces, synthesized by means of electroless metal deposition, and their (photo)electrochemical performance. In this context, the term *electroless* is referred to deposition under OCP (open circuit potential) conditions, which should not be confused with deposition supported by reducing agents in solution.

\* Corresponding author.

E-mail address: [timo.jacob@uni-ulm.de](mailto:timo.jacob@uni-ulm.de) (T. Jacob).



**Fig. 1.** Electrochemical HER on a hydrogen-terminated  $p$ -Si(111) electrode in 0.1 M  $\text{H}_2\text{SO}_4$  shown for a chopped measurement (blue curve), under continuous illumination (dotted) and in the dark (red); scan rate:  $10 \text{ mV}\cdot\text{s}^{-1}$ . The XP core level spectrum of the Si-2p region shows an oxide-free surface (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

The electroless deposition technique from fluoride-free solutions has been chosen because it is a fast and facile method for obtaining homogeneously distributed Au nanoparticles ( $t_{\text{dep}} = 5 \text{ s}$ ). Furthermore, studies on bulk electrodes have shown that it is possible to improve the catalyst by depositing submonolayers of Pt/Pd on Au [12,13]. The light-induced HER serves as an electrochemical test reaction on the influence of changing deposition parameters. The TM-AFM images display the electrode topography and the AR-XP core level spectra help identifying the species at the electrode surface and their vertical distribution on or in the surface.

## 2. Material and methods

Silicon samples were cut from 1 to  $10 \Omega\text{cm}$   $p$ -type Si(111) wafers as purchased from Si-Mat (Germany). Wafers were cleaned in an ultrasonic bath for 5 min in acetone, ethanol, and ultrapure water (Milli-Q,  $\text{toc} < 3 \text{ ppb}$ ,  $18.2 \text{ M}\Omega\text{cm}$ ), respectively. Hydrogen termination was achieved by etching the native oxide in HF (50%, BASF) for 1 min. Electroless metal deposition was carried out in aqueous, HCl or  $\text{H}_2\text{SO}_4$  (suprapur, Merck) solutions of  $\text{AuCl}_3$  ( $\geq 99.99\%$ , Sigma-Aldrich),  $\text{H}_2\text{PtCl}_6$  ( $\geq 99.995\%$ , Sigma-Aldrich),  $\text{PdSO}_4$  and  $\text{PdCl}_2$  (99.995% and 99.9%, Alfa Aesar). All cleaning, etching and deposition steps were followed by careful rinsing with ultrapure water. Electrochemical measurements were performed in degassed (Ar 5.0) 0.1 M  $\text{H}_2\text{SO}_4$  using a three-electrode configuration with the Si wafer as the working electrode, a Pt wire as the counter electrode and a saturated calomel reference electrode (SCE). All potentials reported here are referenced to this electrode. For the light-chopped measurements a 150 W halogen lamp was used. TM-AFM measurements were performed with a Veeco Multimode 8 in air. XP spectra were obtained from a Physical Electronics PHI 5800 Multi ESCA System with monochromatized Al  $K_{\alpha}$  radiation at  $45^\circ$  electron emission and 29.35 eV pass energy for detail spectra, if not otherwise specified.

## 3. Results and discussion

### 3.1. Substrate characterization

Etching clean silicon samples in HF solutions leads to the removal of a native oxide layer and results in a flat surface but with inconsistent hydrogen termination, showing mono-, di-, trihydrides [14,15]. The XP core level spectrum around the Si-2p

region shown in Fig. 1 confirms an oxide free surface after the fluoride treatment. The Si- $2p_{3/2}$  ( $2p_{1/2}$ ) spin-orbit doublet is located at 99.5 eV (100.1 eV) with a branching ratio of 2:1 after a Shirley-type background (dotted line) has been subtracted. The survey scan was free from any metal contamination. Such a bare silicon electrode is not very suitable for the photoelectrochemical HER, as is shown by the illuminated CV measurements in Fig. 1 (dotted curve), where considerable reaction rates occur only for high overpotentials ( $< -0.8 \text{ V}_{\text{SCE}}$ ). Corresponding dark currents are very low ( $< 5 \mu\text{A}\cdot\text{cm}^{-2}$ , red line) as expected for  $p$ -type silicon. In a chopped measurement (blue curve) dark- as well as photo-currents can be observed in a single cathodic scan.

### 3.2. Electroless Au deposition on $p$ -Si(111)

An improvement of the rather poor kinetics on the hydrogen-terminated surface is necessary for achieving considerable reaction rates. Electroless metal deposition is a convenient and well established method to metalize silicon surfaces [16,17]. For non-fluoride solutions, according to the Gerischer model [18], an injection of holes from vacant metal salt solution acceptor states into the silicon VB leads to a reduction of Au ions forming metal clusters on the electrode surface, which is accompanied by the formation of a thin oxide layer. In fluoride-containing solutions, the emerging oxide would be partially dissolved by the attack of fluoride ions. The standard potential of the redox couple  $\text{Au}^{3+}/\text{Au}$  ( $+1.5 \text{ V}_{\text{NHE}}$ ) [19] is considerably more positive than the VB edge of silicon ( $+0.62 \text{ V}_{\text{NHE}}$ ) [20], providing sufficient overlap of occupied and empty states. As a result few seconds of exposure to the plating solution is enough to obtain homogeneously distributed Au nanoparticles on silicon. The corresponding standard potentials for Pt and Pd are not as positive as for Au, so only traces of these metals can be deposited under the same conditions (hardly detectable by XPS). Thus, the PEC performance of such electrodes shows minimal improvement over bare silicon.

The gold decorated electrode exhibits a distinct shift in the onset potential of about 0.5 V (Fig. 2, black curve) compared with bare silicon (blue curve). These findings demonstrate the importance of a metal co-catalyst to perform light-induced HER on silicon electrodes. The presence of an electrocatalyst is inevitable to benefit from the photovoltage provided by the semiconductor electrode. The red CV represents the onset of the HER on a Au(111) single crystal, located at a potential of about 0.3 V more negative. Optimal conditions for the electroless Au deposition on silicon were

Download English Version:

<https://daneshyari.com/en/article/6505219>

Download Persian Version:

<https://daneshyari.com/article/6505219>

[Daneshyari.com](https://daneshyari.com)