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Low temperature electrodeposition of SiO_x films photoactive in water solution

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ABSTRACT

We report a low temperature, an electrochemical way of preparation of a photoanode made of n-type silicon oxide based films, at which surface photoelectrochemical oxygen evolution was observed with no need to deposit of other materials. Conditions of electrosynthesis, under which the electrochemical reduction of silicon chlorides in non aqueous solutions leads to silicone oxide based films are described. The photoactivity of prepared photo-anodes was reproducible and the observed photocurrent sustained for many hours. The most stable photocurrent was observed for films deposited at −2.7 V. Water oxidation was observed while occurring at the onset potentials smaller than 0.2 V comparing to the dark water splitting potential. The highest photocurrent was observed at −0.3 V (thermodynamic value 1.02 V vs. Ag wire), which means energy saving corresponding to ca. 1.3 V. The results demonstrate that a low temperature electrodeposition of silicon oxide based films can be an alternative route for fabrication of photoanode for water photosplitting devices.

1. Introduction

The water photosplitting process is an approach to electrochemical direct solar energy conversion into electricity, hydrogen fuel and chemical energy. This idea is among key technologies using renewable energy sources, such as solar energy with almost zero warming gas emission. A rising global energy demand has prompted an enormous interest in technology to harness energy from renewable sources while decreasing addiction to fossil fuels and the earth climate non-neutral sources. One interesting approach is to produce hydrogen from water by splitting water molecule using of solar energy and semiconductive (SC) electrodes as the source of electrons.

$$2H_2O + SC + \text{solar energy} \rightarrow 2H_2 + 1/2O_2 + SC \qquad (1)$$

The water photosplitting process requires oxidatively robust and inexpensive photoanodes. The obvious source of such a photoanode is silicon because of its semiconductive properties and a wide prevalence of silicon in the lithosphere.

The present main source of silicon is a reduction of silica by carbon at ca. 1900 °C [1], followed by Siemens' purification method, and further reduction in hydrogen atmosphere at 1100 °C [1]. The next step of the production of silicon required for electronic, photovoltaic (solar cells) and photogalvanic (photoelectrochemical cells) applications is the preparation of silicon in the form of single crystal [1]. All these processes are a high temperature ones and environmentally harmful method.

Methods of silicon based films electrodeposition might be considered as low energy consumption and a low-cost alternative for the standard high temperature methods. There are several advantages of the electrochemical methods: an electrically driven process offers a precise control, the growth in range of temperatures below melting point, the solvents can dissolve impurities, purification might occur during electrodeposition because of differences in deposition potentials between major and minor ones. Electrolysis can be convenient for epitaxial deposition of silicon based films since the growth occurs chemically uniformly over the sample area.

Electrochemical preparative methods can be easily divided into two categories: high temperature techniques (molten salt solutions) and low temperature techniques (ionic liquid and organic electrolyte solutions). The interests in the possibility of silicon electrodeposition started in the mid 1800's with the work of St.Claire De Ville [2]. It was a high temperature electrodeposition from molten $NaAlCl_4$ but material obtained in that work did not oxidize so that claim might be questionable. Gore claimed that he had deposited silicon at low temperature from water solution of K_2SiO_3 [3]. That claim has never been confirmed. Moreover, there is no proof that silicon has ever been deposited by other authors from any aqueous solution. Ullik was probably the first to deposit elemental silicon by an electrochemical method from the molten solution of K_2SiF_6 and KF [4]. Warren deposited silicon under low temperature

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conditions and showed suitability for halides and organic solvents in the process [5].

The methods of low temperature electrodeposition of silicon can be divided into two sub groups; electrodeposition from ionic liquid solutions and from organic solvent solutions. The electrodeposition from ionic liquid solutions although promising is difficult to carry out because of a high demand for the non-water conditions and a high price of the required reagents. The deposition from organic solvents requires less limiting conditions and it was reported by Austin and Agrawal [6,7]. A serious problem reported concerning the silicon films obtained under low temperature conditions is their instability in air as well as in water [8,9], which constrains the use of these materials in photovoltaic and photogalvanic devices. A more complete discussion on the silicon electrodeposition methods was given by D. Elwell and Rao [10] and Elwell and Feigelson [11].

Although silicon deposition has been reported by different authors [6–9,12–14] the reports on its photoactivity are especially exceptional. The difficulties in the electrodeposition of photoactive silicon have already been described [12,15] so it can be stated that there have been only few successful attempts to register the deposits' photoactivity illuminated in organic solution [13,16,17] and none in water solution. The reason for such an obstruction are impurities persisting at low concentration from the deposition process. They can work as a photo generated charge scavenger states. The dangling hydrogen formed during a silicon salt reduction is probably the reason for instability in time of the produced films [12]. A frequent absence of photoactivity is a serious problem in promoting electrodeposition as a cheap and efficient method of silicon based films production for photovoltaic and photogalvanic cells.

Here, we propose to change the approach to the difficulties discussed. In our proposition we consider the mixture of silicon and silicon oxides as a film working under photoelectrochemical conditions instead of the pure silicon.

In the seventies and eighties it was proved that different bulk silicon oxide types (SiO_x) exist [18,19]. These compounds are semiconductive and their electronic energy band gap is between 1.12 eV, for the bulk silicon, and 8.9 eV, for the bulk silica [20] Furthermore, it was shown that silicon monooxide, SiO, might increase photoeffect of a mono crystalline silicon electrode and might protect such an electrode against corrosion in water solution [21,22]. These are reasons why we have assumed that the efficient way to solve the problem of the missing photoactivity of electrodeposited silicon isn't to decrease water and oxygen concentration in the electrodeposition cell to the most minimal amount possible. The way is to find electrochemical conditions with the use of reagents usually available on the market, which would lead to the production of the photoactive material based on the silicon and silicon oxides, SiO_x [22–24].

Here we report a low temperature, cheap electrochemical way of preparation of a photoanode made of silicon oxide based films which consist mainly of n-type silicon oxide, at which surface photoelectrochemical water oxidation was observed with no need for deposition of other materials. We determined the conditions of electrosynthesis under which the electrochemical reduction of silicon chlorides in non-aqueous solutions leads to silicone based films stable in water solution. The photoactivity of prepared photoanodes was highly reproducible and the observed photocurrent sustained for many hours. Photoelectrochemical water oxidation was observed while occurring at the onset potentials smaller than 0.2 V comparing to the dark water splitting potential, (1.23 V), which means energy saving corresponding to ca. 1 V. Our results demonstrate that low temperature electrodeposition of silicon oxide based films can be a route to water photosplitting device construction.

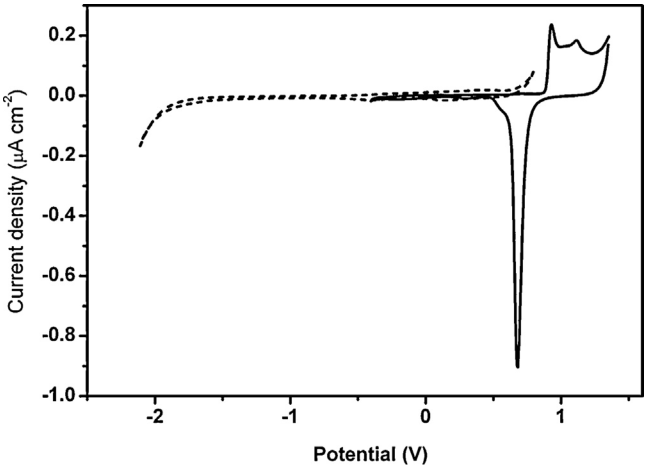

Fig. 1. Cyclic volammograms for gold electrode registered in 0.1 M TBAB/PC solution, and in 0.1 M $HClO_4$ solution, dashed line and solid line, respectively. Sweep rate: 50 mV sec.

2. Experimental

A three-electrode Teflon cell equipped with a quartz window was used. The working electrode was a polycrystalline 4 N gold disk of a working diameter ca. 3 mm. The electrode was polished with alumina down to 0.5 μm, cleaned in an ultrasonic bath and dried before being used. Platinum and silver wire was used as counter and reference electrodes, respectively.

All parts assumed to have had any contact with the solution were cleaned with concentrated aqueous KOH (Chempur, pure p.a.) solution to remove the SiO_x residues remained after the previous experiments, thoroughly rinsed with water and dried under air atmosphere. The counter and reference electrodes were cleaned first in water and then with H_2SO_4 (POCH, 95–98%) and $HClO_4$ (Aldrich, 70%, A. C. S. Reagent), respectively.

The electrodeposition was performed from 0.1 M *tert*-buthyl ammonium bromide, TBAB, (Fluka, puriss ≥99%), dissolved in propylene carbonate, PC, (Sigma-Aldrich, anhydrous 99.7%). Films were deposited till the steady current value had been attained. The potentials applied and the deposition time were checked for the ranges from -2.00 V to −2.85 V vs. Ag wire and from 6 min to 75 min, respectively. The electrodeposition charge was calculated by integration of *i*–*t* dependencies after the subtraction of background current. For the dependencies presented in this article the charges were 0.085 C cm^{-2}, 0.13 C cm^{-2}, and 0.26 C cm^{-2} for deposition potentials equal to −2.5 V, −2.7 V and −2.85 V, respectively.

$SiHCl_3$ (Aldrich Chemistry, 98%) was used as a silicon precursor at the concentration 0.5 M. TBAB was dried under atmospheric pressure at 85 °C prior to use for 24 h, PC and $SiHCl_3$ were used as received with no drying. The electrochemical activity of the working electrodes surface and the purity of the solutions were studied by a cyclic voltammetry. Obtaining well defined CV curves in water and PC solution (Fig. 1) was the condition to start the deposition process. Si based films were obtained potentiostatically. The deposition potential values were determined by the position of the peak corresponding to Si reduction. The deposits were studied for their photoactivity in TBAP/PC and then in $HClO_4$/water solutions. Solution of 0.1 M $HClO_4$ was prepared by mixing appropriate amount of water (MilliQ) and $HClO_4$ acid.

1000 W Xenon lamp (Lot Oriel) for illumination of a sample was used. A water filter to avoid the sample heating was applied. The light intensity measured at the sample position with IL 1700 light meter (International Light) equipped with a SEL033/F/W detector was 40 mW cm^{-2}.