Electrochemical and electroless deposition of porous zinc oxide on aluminium

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A B S T R A C T

Metal foils, wires or metalized polymer fibres are of interest as substrate electrode for porous wide band-gap semiconductors in classic dye-sensitized solar cells if protected against corrosion by a passivating oxide layer. Here, aluminium sheets were used as substrate to grow porous ZnO as semiconductor material. To allow growth of ZnO, the insulating Al_2O_3 layer had to be removed by etching in HCl and the surface kept reactive by an intermediate deposition of zinc from a zincate bath. An electroless deposition process of porous crystalline ZnO in the presence of EosinY as structure-directing agent was developed as an alternative to the classic cathodic electrodeposition. By systematic variation of the amount of zinc, the deposition time and by a parallel study of electrodeposition on aluminium or zinc sheets it could be established that the growth reactions in the electroless or electrodeposition processes are identical. Connecting an HCl-etched Al sheet and a zinc wire, e.g. also led to ZnO growth on the Al sheet without any applied potential. We could show that the growth reaction of porous ZnO/EosinY is self-limiting at a film thickness of about 8 μm independent of the aluminium or zinc substrate and independent of electroless growth or electrodeposition.

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1. Introduction

Porous zinc oxide is discussed as an active semiconductor in dye-sensitized solar cells (DSCs) [1]. Because of its rather high chemical reactivity zinc oxide can be easily modified in its structure and morphology and also sensitizers can be anchored to the surface in a wide variety. Zinc oxide is transparent to visible light, has a rather high electron mobility and it can be produced at low temperatures, which makes it a very economic and energy efficient material. A side from well-known preparation by magnetron sputtering [2–4], chemical vapor deposition [5] and pulsed laser ablation [6] also solution-based methods like sol–gel-processes [7–10] or electrochemical deposition [11,12] can be used.

The key advantage of solution-based methods is seen in the fact that it is possible to work at low temperatures (<100 °C) and that no vacuum is needed which make them economic and energy-efficient methods. Film preparation by electrochemical deposition is advantageous in this respect, because crystalline films can be formed at room temperature and no additional annealing step is needed as, e.g. necessary for sol–gel-based films. Electrochemical deposition reactions of ZnO are based primarily on anodic polarisation of a

zinc anode [13] or reduction of a soluble species (O_2, H_2O_2, NO_3^-) leading to an increase of pH which, in the presence of Zn^{2+} ions, leads to precipitation of crystalline ZnO on the substrate [14,15]. In 1996 such electrochemical deposition was described by Izaki and Omi [16,17] and by Peulon and Lincot [18] for the first time. In recent years, numerous studies [19–23] of structure-directing additives and their influence on the film morphology were carried out. ZnO layers which were produced in the presence of the xanthene dye EosinY lead to quite efficient electrodes if the molecules incorporated during film preparation are desorbed [24] and specifically designed sensitizer molecules like the indoline dye D149 are adsorbed [12,25]. Such method delivered porous and crystalline zinc oxide electrodes for dye sensitized solar cells with efficiencies of up to 5.56% [12].

These efficiencies are still lower than those reached with TiO_2 as semiconductor but advantages can be seen for ZnO in the overall cell or module cost performance. State-of-the-art TiO_2-based DSCs are fabricated on a fluorine tin oxide (FTO) glass. Inherent disadvantages of using glass as substrate material are the high material costs, high weight and low mechanical flexibility. Conducting glass is the most expensive part of a DSC and it incurs about 60% of the total cost [26–28]. Based on the described low-temperature processing ZnO cells on the other hand have been prepared also on conductively coated plastic foils at almost preserved efficiency [12]. Metal substrates are of interest to provide excellent conductivity and mechanical flexibility of dye-sensitized solar cells. This may

lead to low-cost, light-weight and flexible DSCs like those using a TCO (transparent conduction oxide) on a plastic foil [12] or those which are produced by the company G24i, using TiO$_2$ on titanium between two laminating plastic foils [29].

Valve metal substrates like aluminium that are protected by a passive layer, can lead to cells containing even an iodine-containing electrolyte without the danger of corrosion [30]. This protective oxide layer, however, also prevents an adhesive coating of ZnO. To temporarily provide a reactive surface essential for the electrode-position of ZnO it is necessary to remove the oxide layer before starting the deposition. Different methods are known to remove the oxide layer. These different methods can be summarised as follows [31]: (i) Mechanical (e.g. grinding, polishing), (ii) metallurgical (e.g. roll cladding), (iii) chemical (e.g. etching), (iv) electrochemical (e.g. electroplating, anodising), (v) physical (e.g. flame spraying). One of the best known methods is the pre-treatment of aluminium in an alkaline zinc hydroxide solution ("zincate stain"). When immersing the substrate into the zincate stain, the aluminium surface is activated and the naturally grown oxide layer is removed. A thin conductive zinc layer is grown on the surface, which prevents a reoxidation of the aluminium which allows to transfer the substrate into the deposition bath and which subsequently leads to a good adhesion between the substrate material and the coating. In this method zinc is grown on the aluminium surface by the following reactions [32]:

a) Oxidation of aluminium

$$Al + 3OH^- \rightarrow Al(OH)_3 + 3e^- \qquad (1)$$

$$Al(OH)_3 \rightarrow AlO_2^- + H_2O + H^+ \qquad (2)$$

b) Reduction of zinc:

$$Zn(OH)_4^{2-} \rightarrow Zn^{2+} + 4\,OH^- \qquad (3)$$

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad (4)$$

Aluminium is oxidized to aluminate allowing to reduce zincate to metallic zinc deposited on the aluminium surface. In addition, the formation of hydrogen can occur as a side reaction:

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \qquad (5)$$

The use of aluminium as substrate material in dye sensitized solar cells has to consider that light cannot penetrate the metal and therefore the cells have to be illuminated through the electrolyte. Initial concepts for this kind of DSCs like those using TiO$_2$ on Ti [29] have already been tested and it could be shown that cells illuminated through the electrolyte could be constructed that showed only slightly lower efficiency than standard DSCs [33].

In this work the electrochemical and electroless deposition of porous zinc oxide films on aluminium was studied in detail. The electrochemical deposition was transferred from known reactions on FTO and adapted to Al by appropriate pre-treatment. Electroless depositions are technically attractive since they avoid the non-trivial task to provide a well-defined field distribution which is essential in electrochemical large-area processes. Electroless metal depositions such as the electroless deposition of nickel [34], copper [35], silver [35], gold [36] or palladium [37] are well known processes. In these reactions (1) a reducing agent in solution can be used if a catalytic surface is provided for metal growth or (2) a less noble metal on the substrate surface can be used in galvanostatic replacement reactions. Electroless depositions also of ZnO from aqueous Zn^{2+}-solutions have been described in analogy to approach (1) using dimethylaminoborane as reducing agent in solution, Au or Pd as catalysts on the surface and nitrate as oxidant which yields

the OH$^-$-ions needed for the precipitation of ZnO [38–40]. In this paper an electroless deposition method of the semiconductor ZnO will be established that shows some analogy to approach (2) above: the reducing component consists of a base metal on the substrate and no catalyst is needed. Further, we use oxygen as oxidant rather that nitrate to approach the successful structures established by electrodeposition [12] also in an electroless deposition.

2. Experimental

Porous zinc oxide films were prepared by electrochemical or electroless deposition on aluminium substrates in the presence of the xanthene dye EosinY (50 μM, Kanto Chemical, $\geq$85%) as structure directing agent from an oxygen saturated 0.1 M KCl (Merck, >99%) and 5 mM ZnCl$_2$ (Merck, $\geq$98%) aqueous solution. The saturation by oxygen was established by purging the gas 10 min before and during the deposition.

Aluminium sheets (Alpha Metall, 99.5%) were used as substrates. These were pre-treated either by polarization (500 rpm) at -2 V vs. Ag/AgCl in 0.1 M KCl, by chemical etching in highly-concentrated (37%) hydrochloric acid (Roth) for 2 min, or by a combination of chemical etching in 37% HCl (Roth) and subsequent treatment in zincate stain for 120 s. For electrochemical deposition (-1060 mV vs. Ag/AgCl) a three-electrode arrangement consisting of the horizontally oriented aluminium sheet working electrode mounted into a rotating holder (500 rpm), a Zn (Sigma-Aldrich, 99.99%) counter electrode and a Red Rod reference electrode (0 mV vs. Ag/AgCl, Radiometer Analytical) was positioned in a thermostatic bath, adjusted to 70 °C.

The electroless deposition was realized on zinc coated aluminium sheets pre-treated by the combination of chemical etching in 37% HCl and subsequent treatment in zincate stain for 10 s to 300 s. The pre-treated sheets were horizontally placed in a 5 mM zinc chloride solution, saturated with oxygen, including 0.1 M KCl and 50 μM EosinY. For this kind of deposition the mounted aluminium sheet was simply placed into the deposition bath without any electrical connections. The zincate stain used in the pre-treatment was prepared by dissolving 50 g/L zinc oxide powder (Sigma-Aldrich, >99%) in hot 750 g/L NaOH (Roth, >99%) in deionised water. The aluminium sheets were placed into this solution at room temperature.

The films were characterized by optical microscopy (*Nikon OptiPhot*), scanning electron microscopy (*Philips* 525 M) and by X-ray diffraction in Bragg–Brentano (Θ/2Θ) geometry (*Siemens D5000 Diffractometer*) using Cu K_α radiation. A *Tencor Instruments α-Stepper 10-00020* profilometer was used to determine the average film thickness across the edge of the grown film which was defined by a tape mask or across a scratch in the zincate-treated substrates. A test for film adherence on the substrate was performed by attaching a *3 M Scotch® Magic*^{TM} tape to the film, pressing it on by finger until the joint cleared and then detaching the tape from the substrate. In the successful tests the film remained on the substrate rather than on the tape.

3. Results and discussion

3.1. Electrochemical deposition of porous zinc oxide on aluminium

The dependence of the observed current density on time during a potentiostatic deposition (-1060 mV vs. Ag/AgCl) of porous zinc oxide following a standard method [12] for each type of pre-treatment are shown in Fig. 1a and b. The characteristics during the pre-treatment (first 120 s) are also shown in Fig. 1a. As pre-treatment a polarization at -2 V in 0.1 M KCl was used.