

Electrochemically Induced Growth of Zinc Oxide on Microelectrodes

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Zinc oxide (ZnO) is a promising electrode material for the application in dye-sensitized solar cells (DSCs) and devices for transparent electronics. Electrodeposition from aqueous precursor solutions can serve as an energy-efficient, environmentally friendly and low-cost method of preparing compact or porous crystalline ZnO thin films even on temperature-sensitive substrates such as polymer foils or fibers [1].

ZnO film preparation on micro-structured electrode arrays consisting of two sets of individual gold bands of 5 to 40 μm width and distance or on gold wires with a diameter of 250 μm served to characterize microelectrode effects in the growth of compact ZnO from unstirred zinc nitrate solutions at 70°C. The substrates served as models for conductively coated interdigital textile threads which are discussed as substrates in textile-based solar cells [2]. Galvanostatically controlled pulses were applied to reduce nitrate, produce OH⁻ ions and thereby precipitate crystalline ZnO. The current density, the pulsating times and the total deposition time were varied among samples as decisive pulse parameters. The established potential during deposition was measured. Three significant stages (I-III) in the chronopotentiograms of the micro-structured arrays were detected (Figure 1a), similar to the potential characteristics observed for depositions at constant current [3]. The first stage (I) was defined by a uniformly pulsating potential between two constant values, roughly -1.3 and -1 V, and represented the initial stage of ZnO deposition on the pure metal. Following a short oscillatory period, the potentials shifted to less negative values (stage II) at a characteristic time of deposition (vertical line). This change occurred at later times for increased current density (Figure 1b). Following the transition (stage II), the potential was characterized by a uniformly pulsating potential (stage III) between two constant values, -0.95 and -0.8 V.

With the help of scanning electron microscopy, it was determined that the transition in stage II was indicative of a completed coverage of the active electrode area by a dense ZnO layer. For small current densities, the films grew homogeneously and the time for complete coverage was short compared to depositions at high current densities, where dendrite formation was typical [4]. In stage III, the reaction was stabilized at widely constant potentials and ZnO grew continuously on top of a completed ZnO layer.

Depositions were also carried out with only one set of electrode bands contacted to the galvanostat. These experiments confirmed the correlation between the observed potential and the electrode coverage in the three stages (I-III) of the depositions. A first abrupt shift to less negative potentials (II) was observed once the contacted electrode bands were completely covered with ZnO. Due to the continuous growth of ZnO, the semiconductor eventually bridged the insulating gaps to the adjacent non-contacted bands, establishing electrical contact and leading to deposition also on the latter (Figure 2). As soon

as a full ZnO layer was also deposited on the second set of bands, a second shift to less negative potentials (II') was measured and stage III was reached for the whole band array.

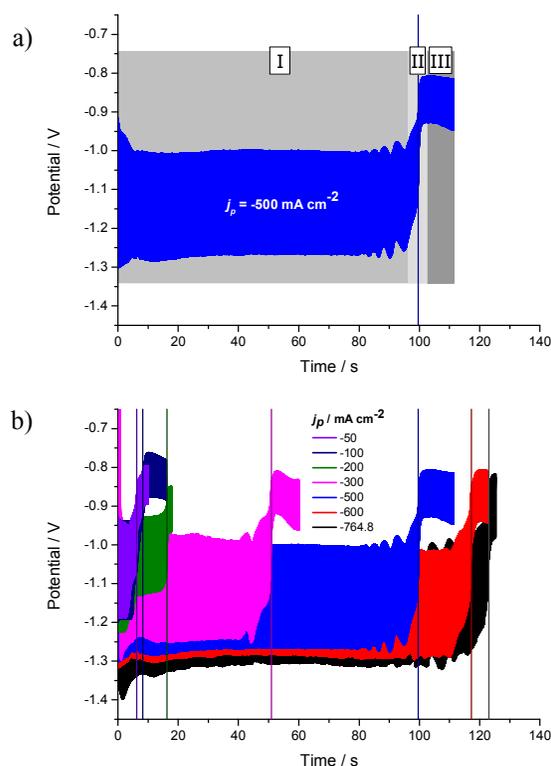


Figure 1. Chronopotentiograms of depositions onto micro-structured arrays divided into three stages I-III (a) and carried out at different current densities (b).

On gold wires, the chronopotentiograms during electrodeposition of ZnO showed similar characteristics to those measured for the micro-structured substrates. However, due to the different diffusion profiles of the reacting species on both substrates, the time of potential shift (stage II) for the wires differed from the micro-structures. These characteristics will be analyzed in the contribution. The significance of each stage in the chronopotentiograms for a systematic electrodeposition of compact and porous ZnO layers on wires, threads or fibers as microelectrodes will be discussed in view of their possible application in DSCs.

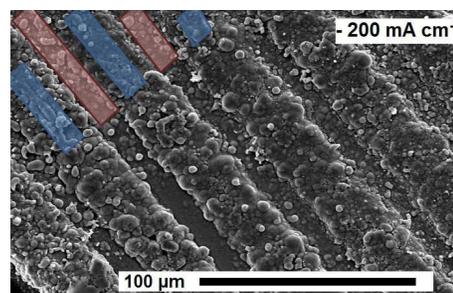


Figure 2. SEM image of a ZnO film deposited on a micro-structure when contacting only one set of electrode bands (indicated in blue). Bands which were not contacted initially are indicated in red.

References

- [1] T. Yoshida, J. Zhang, D. Komatsu, et al., *Adv. Funct. Mater.*, **19**, 17 (2009).
- [2] T. Loewenstein, M. Rudolph, M. Mingeback, et al., *Chem. Phys. Chem.*, **11**, 783 (2010).
- [3] R. Salazar, C. Lévy-Clément, V. Ivanova, *Electrochim. Acta*, **78**, 547 (2012).
- [4] M. Stumpp, C. Lupo, D. Schlettwein, *J. Electrochem. Soc.*, **159**, D717 (2012).