MnO_2 Nano-films for the Enhancement of Transparent Nanocoral ZnO-Based Supercapacitor Performance

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We present thin MnO_2 films deposited by magnetron sputtering applied as capacitance-enhancing material to nanocoral ZnO-based transparent supercapacitors. The films were deposited using magnetron sputtering of a MnO_2 target in an Argon-oxygen mixture under 125 W RF power. The communication discusses the liaisons between the process parameters, MnO_2 structural properties and resulting device performance. Since very few literature works on the growth of MnO_2 by sputtering exist, a wide array of process parameters was studied. For the deposition, an argon flow of 10 sccm was used with the oxygen flow changing from 10 to 0 sccm in the experiment. Furthermore, total gas pressures ranging from 12 to 1.5 mtorr were applied. The growth rates of the MnO_2 were found to be very low, therefore the structural analysis was performed by electron diffraction in a transmission electron microscope for 10 nm thick samples, as scaled using X-ray reflectometry and deposited on TEM carbon grids.

We found that depending on the deposition parameters, the MnO_2 films can contain three MnO_2 crystalline phases: γ, β and λ. We selected the material containing each phase for tests in supercapacitor constructions. Symmetric supercapacitor electrodes were fabricated on fluorine-doped indium tin oxide covered glass. A 150 μm sealing tape was used as a separator and a LiCl/poly(vinyl alcohol) gel electrolyte was applied.

Supercapacitors were characterized in the range 0-1V using cyclic voltammetry, cyclic charge-discharge curves and electrochemical impedance spectroscopy. We show that only the λ-MnO_2 phase leads to capacitance enhancement as related to pure ZnO (30 $\mu F/cm^2$ v.s. 20 $\mu F/cm^2$). Furthermore, the device with λ-MnO_2 undergoes a chemical reaction in the first 100 cycles, increasing its capacitance to 80 $\mu F/cm^2$ and retaining it for the next 4900 charge-discharge cycles. It is put forward that a reaction from λ-MnO_2 to the isostructural $LiMn_2O_4$ spinel takes place, enabling more efficient Li ion intercalation leading to increased capacitance values. The device shows also a high optical transmission of 60% at 500 nm.

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