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Photoelectrochemical water splitting in a tungsten oxide - nickel oxide thin film material library

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ABSTRACT

A combinatorial thin film library containing WO_3 and NiO was produced using thermal co-evaporation of WO_3 and Ni followed by high temperature reoxidation. Microstructure and crystallographic particularities of the WO_3-NiO library investigated by SEM and XRD revealed three distinct compositional zones: A low Ni concentration zone containing crystalline WO_3 and amorphous NiO, a high Ni concentration zone containing crystalline NiO and amorphous WO_3 and a middle range amorphous zone connecting the extremes. Photo Electrochemical Scanning Droplet Cell Microscopy PE-SDCM was used for locally investigating the photoelectric response of the library as a function of Ni concentration. A substantial photocurrent peak was identified at 6.2 at.% Ni with values in excess of 2.5 mA cm^{-2} while Ni amounts above 9 at.% resulted in a completely photoinactive thin film. XPS surface analysis indicated a surface composition different than the bulk with WO_3 being present up to 45 at.% Ni in the bulk. For bulk Ni amounts above this composition, the surface contained no WO_3 anymore, only an amorphous Ni sub-oxide being suggested.

1. Introduction

Due to depletion of fossil energy resources and serious environmental problems caused by the ever increasing CO_2 content of the atmosphere a lot of scientific research is devoted towards renewable energy sources. Since discovery of semiconductor-based water splitting using solar radiation by Fujishima and Honda in 1972 photoelectrochemical water splitting has attracted great interest of scientists [1]. Up to now, photon to hydrogen conversion efficiencies of up to 4.9% have been achieved by using integrated devices which are combining photovoltaic and photoelectrochemical cells [2]. Mixed transition metal oxides containing materials such as TiO_2 [3–6], α-Fe_2O_3 [7–11] and WO_3 [12–14] are becoming more important for conversion of solar energy into chemical fuels due to their high electrochemical stability, natural abundance and low cost. The photocatalytic properties of these transition metal oxides can be greatly increased upon doping [15]. Semiconducting materials for efficient photoelectrolysis of water will most probably be complex oxides containing various different materials. Even for ternary and quaternary materials, a vast number of materials have to be investigated to find an optimum composition. For this reason, high-throughput combinatorial methods provide the best approach for new photoactive material discovery and development [16–20]. WO_3 is an indirect bandgap semiconductor defined by its different crystal momentum vectors characterizing the minimal and maximal energy states in the conduction and valence bands, respectively. Its numerous crystal structures can be prepared by various different methods like sputtering, thermal evaporation, spray pyrolysis and chemical vapour deposition. Due to its rather large bandgap of 2.7–3.1 eV, WO_3 mainly absorbs radiation in the blue and ultra-violet region of the solar spectrum [21]. Additionally, WO_3 suffers from low electrical conductivity limiting its applicability for photoelectrochemical water splitting devices. In previous studies it was shown that upon doping of WO_3 with transition metals such as Ni and Co, significant increases in photocurrents could be observed [22].

In the present study, a WO_3-NiO thin film material library was prepared by thermal evaporation from two different sources covering a wide compositional range. A detailed investigation of the photocurrents with a compositional resolution of better than 1 at.% was done using Photoelectrochemical Scanning Droplet Cell Microscopy (PE-SDCM) [23]. This allows a very detailed analysis

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of the influence of the Ni concentration on the photocurrents. Additionally, the composition of the prepared material library was investigated using energy dispersive X-ray spectroscopy (EDX), while its microstructure was analysed by scanning electron microscopy (SEM). X-ray diffraction (XRD) provided information about the change of the crystallographic properties along the compositional spread while surface X-ray photoelectron spectroscopy (XPS) was used for a quantitative analysis of the mixed WO_3-NiO compositions.

2. Experimental

2.1. Thin film combinatorial library fabrication and basic characterization

For investigating the properties of the WO_3-NiO mixtures, a combinatorial approach was used based on the idea of co-deposition from two separate thermal sources in vacuum. The great advantage of such approach is found in the possibility of analysing virtually any possible alloys between WO_3 and NiO deposited in the same time on the same sample, therefore having the same history with directly comparable properties. For this purpose, a wide compositional range WO_3-Ni thin film combinatorial library was produced first. Two thermal sources, able to provide heating powers up to 3.3 kJ s^{-1}, were simultaneously used for co-deposition of WO_3 and metallic Ni using a state of the art thermal co-evaporator. The base pressure of the vacuum chamber was in the range of 10^{-5} Pa. A tungsten boat was used as Joule heating element for evaporation of WO_3 due to the good stability of the oxide on the surface of its own metal during its sublimation at approximately 1070 K (at 10^{-4} Pa). A boron nitride crucible heated by a tungsten filament was found suitable for Ni evaporation due to the high reactivity of molten Ni before reaching its evaporation temperature of approximately 1370 K (at 10^{-4} Pa). The necessary electrical power for the deposition processes was delivered to the thermal sources via pairs of oxygen-free high purity Cu rods, 2 cm in diameter, connected by high pressure gas tight electrical connectors and ultra low resistance cables. For thermally stabilizing the Cu rods during the deposition, air-air heat exchangers with a nominal cooling power of 300 W were attached to each single Cu rod externally to the vacuum chamber. Two DC power sources (N8734A–Agilent Technologies) each able to deliver up to 165 A at maximum 20 V were involved in the process of Joule heat generation. The bulk materials used for the deposition of WO_3 and Ni were high purity powders (99.9 %, Sigma-Aldrich and ChemPur, respectively). In order to tune the compositional gradient along the WO_3-Ni thin film library, quartz crystal thickness monitors (QCM) placed above each thermal source were used (Inficon–SQM242 acquisition board). Using appropriate shielding at each QCM for allowing only detection of species coming from the monitored source, the evaporand flux of each material was individually controlled and the desired compositional gradient was obtained by adjusting the evaporation power through a software implemented PID controller (LabView software). The substrates used for the WO_3-Ni thin film library were borosilicate glass slides (76×26 mm^2) covered by an ITO layer (15 Ω/□, Kintec Co.) for improving the electrical conductivity and the deposition distance was 120 mm. Two consecutive depositions were carried out on separate substrates, each having a natural compositional gradient of approximately 35 at.%. Evaporation rates ranging between 0.002 nm s^{-1} and 1 nm s^{-1} were used for each source in order to obtain a total compositional gradient of 58 at.% across the complete thin film library containing both substrates. In order to maximize the individual film thickness gradients (as dictated by the cosine law of evaporation) both WO_3 and Ni sources were placed off centre directly under the short edges of the glass substrates. All depositions were started at room temperature, the substrate reaching up to 470 K until the end of the deposition due to thermal radiation from the heating elements. A total WO_3-Ni thin film thickness of approximately 600 nm was measured at the centre of each substrate after the deposition.

For obtaining the final WO_3-NiO combinatorial library, a heat treatment was applied to the as-deposited WO_3-Ni library. Usually, a thermal heat treatment ensures reoxidation of the vapour-deposited WO_3 which tends to condense in slightly subvalent states due to a partial decomposition during the evaporation process leading to oxygen losses [24]. Additionally, this heat treatment ensures conversion of Ni into NiO. The heat treatment process on the as-deposited WO_3-Ni material library was done in pure oxygen atmosphere for 18 hours at 673 K with cooling and heating rates of 3 K min^{-1}. Mapping of the elemental composition of the WO_3-NiO thin film material library after heat treatment was done using a Zeiss 1540-XB scanning electron microscope with a built-in EDX analyser (INCA X-sight, Oxford Instruments). The EDX-detector was calibrated prior to measurements using a high purity Co-standard (Micro-Analysis Consultants, United Kingdom). Processing of obtained EDX-data was done using INCA-software. Results were calculated from spectra measured with 18 kV acceleration voltage and an acquisition time of 120 s for each spot. The origin (zero) point of each scanned line was located at the short side of each glass/ITO slide which was closest to the WO_3 evaporation source. On each of the two individual substrates, which together are representing the entire thin film material library, a line of equally spaced spots was automatically measured. Surface microstructure mapping of the material library was achieved using a ZEISS 1540-XB scanning electron microscope (SEM). The crystallographic properties of the WO_3-NiO combinatorial library were locally investigated by X-ray diffraction (Philips X'Pert Pro, Cu$K\alpha$ radiation) and were mapped along the compositional gradient. Elemental composition of the surface of the entire material library was mapped using a Theta Probe X-ray photoelectron spectrometer (XPS) from Thermo Fisher with Al anode at Kα energy of 1486.7 eV and a spot size of 400 μm. The properties were mapped along the compositional gradient using the position information obtained from the EDX investigations.

2.2. Photoelectrochemical Scanning Droplet Cell Microscopy

The photoelectric properties of the WO_3-NiO combinatorial library were mapped as a function of the composition. All photoelectrochemical measurements were carried out using a photoelectrochemical scanning droplet cell microscope (PE-SDCM) [23].

The main body of the cell was made from an acrylic block ($22 \times 22 \times 12$ mm^3) into which three connected channels (3.3 mm in diameter) were drilled. These details are observable in Fig. 1 which is schematically describing the PE-SDCM. Each channel was sealed using polypropylene (PP) screws with an O-ring underneath the head of each screw. A μ-Ag/AgCl system was used as a micro reference electrode (μ-RE). To prepare this reference electrode AgCl was electrodeposited on the first 10 mm of a longer 100 μm in diameter Ag wire in 1 M HCl. A detailed description of the deposition process can be found elsewhere [25]. This partially coated wire was inserted into a small glass capillary (<1 mm in diameter). Next, the small glass capillary was filled with an agar immobilized 3 M KCl solution and afterwards sealed at the top end using epoxy glue. The measured potential of this electrode was 0.227 V vs. standard hydrogen electrode (SHE). The counter electrode (CE) used for the PE-SDCM was made from a flattened 100 μm in diameter Au wire (99.999 %, Wielandt Dentaltechnik, Germany).

The lower part of the PE-SDCM, where the electrolyte droplet is released from, was made using a second borosilicate glass capillary with an outer diameter of 2.5 mm. It was manufactured using a