



Zinc oxide–nickel cermet selective coatings obtained by sequential electrodeposition

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Abstract

The investigation of pulse electrodepositing modes influence on crystal structure, morphology and optical properties of ZnO has revealed the conditions in which quasi-one-dimensional (1D) ZnO nanorod arrays are formed as separate nanorods. Due to a sufficiently high resistance of zinc oxide, the electrodeposition of nickel on the fluorine doped tin oxide (FTO)/ZnO surfaces carried out in space between the ZnO nanorods. An incomplete filling of the gaps between nanorods by the nickel nanoparticles through subsequent Ni electrodeposition ensured the creation of ZnO–Ni graded cermets. The cermets, in which electrochemical filling of the spaces between ZnO nanorods by Ni, was performed in the pulse mode. It provided higher absorption of visible and near IR light. It was shown that the manufactured ZnO–Ni graded cermets have high light absorption combined with comparatively low thermal losses, so these cermets are promising cheap and affordable selective coatings for solar heat collectors.

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1. Introduction

The efficiency of solar energy conversion into heat is mainly determined by the optical properties of an absorber surface. The efficient selective solar absorber surface should have the good optical properties, i.e. high absorption A_s

over the spectral range of solar spectrum (0.3–2.5 μm) combined with low thermal losses ε because of re-radiation at longer wavelengths (beyond 2.5 μm). Several solar absorber materials based on cermets have been reported by various authors (Grainghead et al., 1979; Klochko et al., 2005; Cheng et al., 2013; Nuru et al., 2014; Li et al., 2012; Nuru et al., 2015; Feng et al., 2015). The highly absorbing cermet coatings (metal-dielectric composites), consist of metal or carbon particles in a dielectric matrix. The other cermets are the porous oxides impregnated with metals. These coatings are transparent in the thermal infrared region and they are strongly absorbing in the solar spectrum region because of the interband transitions in the metal and the small

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particle resonance. A variety of techniques, such as magnetron sputtering (Cheng et al., 2013; Feng et al., 2015), electron-beam evaporation (Nuru et al., 2014, 2015), sol-gel technique (Katumba et al., 2008), electroplating (Klochko et al., 2005), coating by the aqueous solution-chemical method (Li et al., 2012), metal pigmentation of anodically oxidized porous surfaces (Kadirgan et al., 1999) can produce the composite coatings. The absorbing cermet layer may have either uniform or graded metal (or carbon) content. Early (Katumba et al., 2008) cermet selective surfaces for solar thermal collectors were prepared by uniform dispersion of 55–62 nm carbon nanoparticles in zinc oxide (ZnO) matrices. Guided by the double interference absorption theory (Grainghead et al., 1979) in the graded cermet, the reflectance from the cermet is reduced by gradually increasing the metal volume fractions; hence the refractive index decreases as a function of depth from the surface to the base of the film. So, it provides improved absorption of visible light due to the additional antireflection effect caused by the graded refractive index profile. Graded metal-pigmented alumina selective coatings are used. As a rule, oxide coatings were obtained by anodization of aluminum. The oxide coating was the porous alumina layer whose pores are perpendicular to the aluminum substrate and coating was partly impregnated with Ni, V, Cr, Co, Cu, Mo, Ag, or W in form rod-like particles 30–50 nm in diameter. The high visible absorptance of the cermet is both intrinsic and also geometrically enhanced, since typical structure of this coating from surface to substrate consists of the antireflection layer composed of a transparent oxide material that enhances solar absorption, a low metal volume fraction cermet solar absorbing layer and a high metal volume fraction cermet solar absorber layer (Cheng et al., 2013).

Zinc oxide, which proved to be successful component of the cermet selective coatings for solar thermal collectors (Katumba et al., 2008) is a promising widespread inexpensive material with high resistivity in its intrinsic form. ZnO is the wide bandgap semiconductor with a direct bandgap of about 3.37 eV. It has attracted increasing interest due to its unique ability to form a variety of nanostructures. A special attention is focused on the ZnO in the form one-dimensional (1D) nanorod arrays vertically arranged with respect to the substrate. The ordered 1D ZnO nanostructures are successfully manufactured by various methods and already used in various technologically important devices such as short-wavelength lasers, electroluminescent devices, sensors, photocatalytic systems and third generation of solar cells (Skompska and Zarębska, 2014). Electrochemical deposition has a high potential due to a more efficient material consumption and reduces investment costs as compared to production techniques involving high vacuum technologies (Yantara et al., 2012; Sokol et al., 2014). The pulse electrodeposition has a number of additional advantages because the preferred orientation of ZnO films and their morphology may be controlled by changing such pulse parameters like

the cathodic average current density or cathode on/off potentials, the pulse length (pulse on-time), the pulse shape and the pulse period. These parameters can be changed independently over wide ranges in contrast to the direct current plating or potentiostatic electrolysis. Early (Klochko et al., 2014) it was optimized the pulse electrodeposition conditions for the fabrication of antireflective 1D ZnO coatings with parabolic nanonipples, which demonstrated the moth-eye effect. Since pulse plating can produce 1D ZnO nanostructured antireflective arrays (Klochko et al., 2012; Sokol et al., 2014; Klochko et al., 2014), in this work for the first time it was investigated the possibility of creating the graded cermet selective coatings using two sequential processes of electrochemical deposition, namely, electrodeposition of nickel nanoparticles in the spaces between previously electrodeposited ZnO nanorods. It should be noted that for this the electrodeposited zinc oxide must have sufficiently large resistivity and has to be in the form the array of separate 1D ZnO. So, the purpose of this work was to investigate the crystal structure, morphology, optical and electrical properties of the pulse electrodeposited ZnO arrays and to study the influence of Ni potentiostatic and pulse plating modes on structure, optical properties, morphology and optical selectivity of graded ZnO–Ni cermets obtained by successive ZnO and Ni electrodeposition in order to create cheap and affordable selective coatings for solar heat collectors.

2. Experimental procedures

Zinc oxide arrays were obtained by cathodic electrochemical deposition using a three-electrode electrochemical scheme with not stirred aqueous electrolyte containing 0.01 M $\text{Zn}(\text{NO}_3)_2$ and 0.1 M NaNO_3 on the $\text{SnO}_2:\text{F}$ /glass cathode substrates (FTO, TEC 7 Pilkington Company, USA). Both potentiostatic and pulse plating modes of ZnO operation were realized in the standard thermostatic three-electrode electrochemical cell by using platinum spring as counter-electrode and saturated Ag/AgCl reference electrode. The pulse plating mode for the ZnO nanorods electrodeposition was performed by applying rectangular potential pulses, so that the lower and upper potential limits were, respectively, U_{off} and U_{on} (Table 1). The values of cathode potentials provided by a programmable impulse potentiostat PI-0.5–1.1 were measured vs. Ag/AgCl electrode. According to Skompska and Zarębska (2014) the seeding stage in general enhances formation of the vertically aligned ZnO nanorods and allows controlling their diameter and density in electrochemical deposition. So, in a first electrodeposition step in some cases ZnO seed layers were formed by potentiostatic electrochemical deposition in the same electrolyte during short time $\tau = 30$ s at potential $U = -1.3$ V. After that the pulse plating of ZnO nanorods was carried out during time τ (Table 1). A duty cycle (Dc) was given as relation $T_{\text{on}}/(T_{\text{on}} + T_{\text{off}})$, where T_{on} is a time at potential U_{on} and T_{off} is a time at potential U_{off} . Potential pulse frequency f

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