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Pulse plating of semiconductors for solar cells

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Abstract

Parameters of rectangular potential pulse electrodeposition which have allowed the obtaining of near-stoichiometric copper indium diselenide layers were determined by means of energy-dispersive X-ray spectroscopy, scanning electron microscopy and the film resistivity measurements. Studies of effects of the pulse electrodeposition modes on structural and substructural parameters, morphology and optical properties of zinc oxide arrays allowed creation of hierarchical nanostructures with large specific surface areas suitable for dye-sensitized solar cells and organic photovoltaic devices. Optimization of pulse electrodeposition modes by means X-ray diffractometry, optical spectrophotometry and atomic force microscopy allowed adjusting sizes of parabolic nipples for creating antireflective moth-eye structure suitable for use in photovoltaic devices.

Keywords: Pulse plating; Photovoltaic device; Diselenide copper and indium; Zinc oxide

1. Introduction

To resolve the problem of global climate changes due to greenhouse gas emission from combustion of fossil fuels, an implementation of alternative renewable clean energy resources is crucial. Solar energy harvesting technologies, such as photovoltaics, are favorable among alternative clean energy sources due to a direct conversion of solar energy into electricity. However, the widespread installation of photovoltaic systems is hindered by their price. The primary objective of solar cell manufacturers is the decrease of production costs in relation to the resulting output power of the produced solar modules. Electroplating (electrochemical deposition) comprises a high potential of decline in value due to a more efficient material consumption and reduces investment costs as compared to production techniques involving high vacuum technologies (Yantara et al., 2012; Jost et al., 2007; Cui et al., 2011; Elias et al., 2009). High efficient electroplated solar cells and

Abbreviations: DSSCs, dye-sensitized solar cells; CIS, Copper Indium Diselenide; CIGS, copper indium gallium selenide; 1D, one-dimensional; FTO, fluorine doped tin oxide; SEM, scanning electron microscopy; EDX, energy dispersing X-ray spectroscopy; XRD, X-ray diffraction; *CSR*s, coherent scattering regions; AFM, atomic force microscopy; JCPDS, Joint Committee on Powder Diffraction Standards; ARCs, antireflective coatings.

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modules based on cadmium telluride (CdTe) are commercial products to date widely available around the world, but the intensive studies for the improvement of their quality are continued. Thin film chalcopyrite solar cells produced from electroplated precursors of $CuInSe_2$ (CIS) have shown the record efficiencies of over 11% (Jost et al., 2007). High-quality ZnO films grown by electroplating can be easily scaled up for organic photovoltaic cells and dye-sensitized solar cells (DSSCs). The interest in the study of organic and dye-sensitized nanocrystalline metal oxide solar cells has grown considerably in recent years because they can be regarded as attractive photovoltaic devices for mass production owing to their simple fabrication and potential low production costs. Aligned ZnO nanowire arrays are considered as a competitor to TiO_2 in DSSCs (Lupan et al., 2010; Klochko et al., 2012a; Guérin et al., 2012). The most papers on using electrochemical techniques employed direct current electrolysis (or direct potential plating, i.e. potentiostatic mode) report on difficulties to control the film orientation (Klochko et al., 2012b; Chandrasekar and Pushpavanam, 2008). On the other hand, the pulse plating has a number of advantages because such pulse parameters as the cathodic average current density or cathode on/off potentials, the pulse length (pulse on-time), the pulse shape and the pulse period can be changed independently over wide ranges in contrast to the direct current plating or potentiostatic electrolysis (Klochko et al., 2012a; Chandrasekar and Pushpavanam, 2008; Nomura et al., 2002). Thus, it is possible that the preferred orientation of films, their morphology and composition of semiconductor compounds may be controlled by changing these pulse parameters.

So, one purpose of this work was the investigation of influence of different pulse plating modes on copper indium diselenide (CIS) films structure, chemical composition, morphology and electrical properties in order to reveal the means for improving quality of the electrodeposited CIS layers. The other aim was to determine the effects of the pulse electrolysis modes on the morphology, structural parameters and optical properties of the zinc oxide (ZnO) layers to implement the controlled growth in the pulsed plating modes of one-dimensional (1D) or hierarchical zinc oxide nanostructures and ZnO arrays with moth-eye effect.

2. Experimental procedures

Both potentiostatic and pulse plating modes of operation were realized by using a three-electrode cell contained cathode (conducting substrate), platinum counter-electrode and saturated Ag/AgCl reference electrode. We used molybdenum coated glass sheets or glass sheets covered by transparent conductive oxide SnO_2:F (FTO, Pilkington Corp., USA) substrates. The values of cathode potentials provided by a programmable impulse potentiostat PI-0.5–1.1 presented in this paper were measured vs. Ag/AgCl. The all CIS films were plated on cathodes at room temperature in aqueous acidic chloride electrolyte contained 0.9 mM CuCl, 4.5 mM $InCl_3$, and 1.5 mM SeO_2 (pH 1). CIS films with thickness up to 2 μm were electrodeposited under potentiostatic regime, i.e. at constant cathode potential $U = -0.60$ V, or the electrodeposition was carried out under pulse plating conditions. Some pulse electrodeposited films were obtained under current pulse plating modes, namely, in straight full-wave rectified and reverse full-wave rectified modes with sinusoidal shape of current pulses (in the latter case the ratio of durations of direct and reverse pulses was 10:1). Other patterns were obtained in potential pulse plating modes with rectangular potential pulses. The lower cathode potential was $U_{off} = 0.2$ V, the upper cathode potentials U_{on} were in interval from −0.4 V to −0.8 V, that is the amplitudes of the rectangular potentials changed from 0.6 V to 1.0 V, respectively. Potential pulse frequency varied from 0.7 Hz up to 7 kHz. A duty cycle (Dc) was given as relation $T_{on}/(T_{on} + T_{off})$, where T_{on} is a time at potential U_{on}; T_{off} is a time at potential U_{off}; f is the frequency, defined as the reciprocal of the cycle time ($T_{on} + T_{off}$). At CIS pulse plating Dc was varied from 0.17 up to 0.91. As Dc value increased the checked by mechanical surface profiler "Alpha-step 200" thickness of the deposited during 15 min CIS films growths from 0.2 μm up to 1.9 μm. During the electrodeposition the electrolyte was agitated by a magnetic stirrer. Surface morphology of CIS films and their bulk chemical composition were investigated by means of scanning electron microscopes "REM100U" and "LEO 1530" using scanning electron microscopy (SEM) and energy dispersing X-ray spectroscopy (EDX) regimes. Investigation of CIS film phase composition was carried out by X-ray diffraction (XRD) method by using of the "Philips PW 1820" goniometer with Cu Kα-radiation (the wavelength $\lambda_{CuK\alpha} = 1.5406$ Å) under Bragg–Brentano focusing (θ–2θ). Annealing of the CIS films fulfilled during 1 h in dry pure argon flow at 400 °C under argon pressure 760 Pa and partial pressure of residual gases in the chamber less than 10^{-2} Pa. Cross resistances of as-deposited CIS films $R_{\perp}$ were investigated by one probe method. Hot probe measurement technique was used to determine the conductivity type of the films.

Zinc oxide arrays were obtained by cathodic electrochemical deposition in the three-electrode electrochemical cell with not mixed the aqueous electrolytes containing 0.01 M or 0.05 M $Zn(NO_3)_2$ and 0.1 M $NaNO_3$ on the FTO cathode substrates in a pulse plating mode by applying rectangular potential pulses, so that the lower and upper potential limits were, respectively, $U_{off} = -0.8$ V and $U_{on} = -1.2$ V or $U_{on} = -1.4$ V. The optical properties of the arrays of zinc oxide nanocrystallites were studied by using an "SF 2000" spectrophotometer. FTO substrates were used as reference samples when measuring the optical transmittance T spectra. The optical band gap of the zinc oxide layers E_g and their Urbach energies E_o were determined according to Klochko et al. (2012a); Pradhan and Leung (2008). To analyze ZnO layer structure, X-ray spectra were obtained using a "DRON-4M" diffractometer in