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Metal oxide heterojunction (NiO/ZnO) prepared by low temperature solution growth for UV-photodetector and semi-transparent solar cell

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ABSTRACT

Wide bandgap inorganic metal oxide heterojunctions *p*-NiO/*n*-ZnO have been prepared by two low temperature solution growth techniques. Namely, one-dimensional ZnO nanostructure arrays electrodeposited in a pulsed mode, and nanocrystalline NiO films synthesized via Successive Ionic Layer Adsorption and Reaction (SILAR). The crystal structure, morphology, and optical properties of NiO films and NiO/ZnO heterostructures were investigated both before and after annealing in air. The analysis of the dark current vs. voltage characteristics and temporal response curves of the NiO films and corresponding NiO/ZnO heterostructures have shown the promise of their use in the effective UV-photodetectors. Poor photovoltaic characteristics of the test samples on the base of obtained NiO/ZnO heterostructures probably associated with their not quite optimal design, and with too large series resistances and diode ideality factors of the manufactured *p*-NiO/*n*-ZnO heterojunctions, that will be corrected by scrutinizing the defects in the metal oxides and through the improvement of the NiO/ZnO heterostructure design. Solving these problems will provide the effective application of the wide bandgap metal oxide NiO/ZnO heterostructures prepared by low temperature solution growth in the UV-active semi-transparent solar cells.

1. Introduction

Transparent, or at least semi-transparent, solar cells (SCs) which optimize both visible transmission and power conversion efficiency would open up new possibilities for energy conversion through their widespread adoption in buildings, windows, electronic device displays, and automobiles (Yang et al., 2017; Sun and Jasieniak, 2017; Patel et al., 2017; Karsthof et al., 2016). Modern semi-transparent photovoltaic technologies are grouped into variants that are either wavelength-selective or non-wavelength-selective in their absorption of sunlight. Non-wavelength-selective technologies produce electricity from broad absorption of the solar spectrum (including visible photons) and achieve some average visible transmission either by segmenting opaque solar cells (Yang et al., 2017), or via using of sufficiently thin or diluted photoactive materials (Sun and Jasieniak, 2017; Patel et al., 2017). Over the past three decades, a host of inorganic, organic, dye-sensitized and hybrid perovskite photovoltaic technologies have emerged that can be integrated into semi-transparent solar cells. These inorganic SCs include hydrogenated amorphous silicon and its alloy with germanium (a-Si:H and a-SiGe:H, respectively) (Karsthof et al., 2016), non-wavelength-selective amorphous silicon-, kesterite-, chalcopyrite-, cadmium telluride-based systems (Sun and Jasieniak, 2017; Patel et al., 2017). Wavelength-selective transparent and semi-transparent SCs employ photoactive materials that preferentially harvest ultraviolet (UV) or near-infrared (NIR) light, while selectively transmit the visible spectrum. Recently, organic solar materials and perovskites were applied for the utilization of infrared segment (Yang et al., 2017; Patel et al., 2017). However, according to Patel et al. (2017), the promise of the based on organic materials transparent solar cells is behind from the expectation due to the complex processes, cost-burden and uncertain stability. Use of wide bandgap inorganic materials is one of the possible ways to realize transparent solar cells, which actively absorb UV rays, while allowing the transmission of visible light and eliminating concern against the unwanted excessive UV exposure (Warasawa et al., 2013; Kawade et al., 2014; Karsthof et al., 2016; Lupan et al., 2016; Patel et al., 2017). For example, UV-active semi-

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transparent solar cells have been lately fabricated on gallium nitride and indium-gallium nitride (GaN/InGaN) junctions (Karsthof et al., 2016). Amongst the different inorganic wide bandgap materials studied thus far for UV detection applications, zinc oxide (ZnO) as a widely used *n*-type semiconductor (energy gap $E_g = 3.37$ eV according to Newton and Shaikhaidarov (2009)) and *p*-type semiconductor nickel oxide (NiO) (E_g = (3.6–4.0) eV according to Jung et al. (2013); E_g = (3.6–4.3) eV according to Patel et al. (2015); E_g = (3.6–3.8) eV according to Lupan et al. (2016)) have specific importance. The enhanced optoelectronic properties of NiO and ZnO allowed a creating of high-performing metal oxide *p*–*n* heterojunction based light emitting diodes (LEDs) (Xi et al., 2008; Jung et al., 2013) and highly sensitive photodetectors with fast responses and recovery speeds for efficient detection of soft UV light (Newton and Shaikhaidarov, 2009; Tsai et al., 2011; Abbasi et al., 2013; Grundmann et al., 2014; Jlassi et al., 2014; Tyagi et al., 2014; Debnath et al., 2015; Echresh et al., 2015; Patel et al., 2015; Luo et al., 2016; Lupan et al., 2016). Recently, *p*-NiO/*n*-ZnO heterojunctions have been also used in both visible-transparent (Warasawa et al., 2013; Patel et al., 2017) and semi-transparent (Karsthof et al., 2016) UV-active solar cells, which are attractive not only because of their optical transparency permits greater flexibility of installation location. They have the further advantages of absorbing UV light of the solar spectrum, which is harmful to humans, the metal oxides NiO and ZnO are available, stable, inexpensive and can be manufactured using various methods.

According to Kawade et al. (2014), the first step in the realizing of any transparent semiconductor device is fabricating of the visible light-transparent *p*-*n*-junction by a simple, conventional, and economical deposition technique. But so far all *p*-NiO/*n*-ZnO based SCs have been prepared through utilization of expensive and complex physical techniques, such as solid-state sputtering (Patel et al., 2017), reactive RF sputtering (Warasawa et al., 2013), pulsed laser deposition and magnetron sputtering (Karsthof et al., 2016). At the same time, a lot of uncomplicated, affordable and suitable for large-scale production chemical approaches have been successfully implemented in the manufacture of the visible-transparent or semi-transparent UV-active devices on the base of *p*-NiO/*n*-ZnO heterojunctions (Dhara and Giri, 2013). Among them, chemical vapor transport (Newton and Shaikhaidarov, 2009), hydrothermal growth (Abbasi et al., 2013; Echresh et al., 2015; Luo et al., 2016), sol–gel technique (Jlassi et al., 2014; Debnath et al., 2015) and electrodeposition (Xi et al., 2008; Lupan et al., 2016). According to Lupan et al. (2016), low-temperature solution syntheses of semiconductor transition-metal oxides and related heterostructures have attracted a tremendous research activity in recent years due to their importance for various advanced optoelectronic applications. The authors Lupan et al. (2016) note that the electrodeposition technique is of special interest, since it is (i) well-suited for scaling-up, (ii) high-quality crystal layers can be prepared even without annealing, (iii) homogeneous deposition can be performed on arbitrary substrate shapes, (iv) the morphology and size can be tuned by manipulating the deposition parameters, (v) the precise control of deposition position by selective patterning of the substrate is possible, (vi) the electrical contact between structures and substrate is excellent and (vii) there is a minimum inter-reaction or inter-diffusion between the electrodeposited layer and substrate due to the low deposition temperature.

Currently, semiconducting nanoscale crystalline structures are studied especially extensively, as their unique optical and electronic properties have potential use in the various device applications. For example, one-dimensional (1-D) ZnO nanostructures with high surface to volume ratio have a capability of excellent transport of charge carriers, therefore resulting in enhanced working performance of the 1-D ZnO based devices (Klochko et al., 2017b). Thus far, light emitting diodes, lasers, waveguides, and photodetectors made from these nanostructures have been successfully demonstrated (Newton and Shaikhaidarov, 2009). Most of the efforts for the development of the *p*-NiO/*n*-ZnO heterojunction UV photodiodes and light emitting diodes are also directed towards the synthesis of nanomaterials of these wide bandgap semiconductors *p*-NiO and *n*-ZnO (Xi et al., 2008; Abbasi et al., 2013; Jung et al., 2013; Tyagi et al., 2014). Recently, nanocrystalline NiO thin films were synthesized by Akaltun and Çayır (2015) and Taşköprü et al. (2015) using a low temperature solution growth by means of Successive Ionic Layer Adsorption and Reaction (SILAR) technique. According to Taşköprü et al. (2015), SILAR method has various advantages such as (i) low cost, (ii) low deposition temperature, (iii) high feasibility for large area deposition, (iv) availability, (v) good reproducibility, (vi) layer-by-layer growing feature, (vii) good control over the deposition process and film thickness, (viii) separate precursors of anionic and cationic solutions comprise material utilization efficiency. In Klochko et al. (2017a) and in Klochko et al. (2017c) we used SILAR for a wet chemical synthesis of pinhole-free and uniform *n*-Bi_2S_3, *p*-CuI and *n*-ZnS nanostructured semiconductor layers for thin-film solar thermoelectric generator and for kesterite solar cell, respectively. In Klochko et al. (2017b) we presented a *p*-CuI/*n*-ZnO barrier heterostructure with cuprous iodide film fabricated by SILAR technique and 1-D ZnO nanostructured array electrodeposited in the pulsed mode, which showed that above-mentioned wide bandgap heterojunction is sensitive to UV irradiation and can be used as a basis diode structure for a semi-transparent UV-photodetector.

In this research work, we present metal oxide heterojunction *p*-NiO/*n*-ZnO prepared by two low temperature solution growth techniques. We used 1-D ZnO nanostructure arrays electrodeposited in a pulsed mode, as this low cost method is suitable for large-area non-vacuum productions of nanostructures suitable for manufacturing of solar cells (Klochko et al., 2015) and UV-photodetectors (Kopach et al., 2016; Klochko et al., 2017b). Nanocrystalline NiO films have been synthesized via SILAR technique, their morphology, crystal structure, type of conductivity and optical properties investigated both before and after annealing in air. Dark current-voltage characteristics and temporal response curves under the influence of UV and visible light have been researched for the obtained nickel oxide films of different thicknesses both before and after annealing in air, and for the corresponding *p*-NiO/*n*-ZnO heterostructures for the purpose of their use as basics of UV-photodetectors. Dark and light current-voltage characteristics were investigated to determine the possibility of using as a basic of the UV-active semi-transparent solar cells of *p*-NiO/*n*-ZnO heterojunctions with NiO films obtained via SILAR and 1-D ZnO arrays electrodeposited in a pulsed mode.

2. Experimental procedures

Nanostructured 1-D ZnO arrays were obtained by cathodic electrochemical deposition using a standard thermostatic three-electrode electrochemical cell with platinum spring as counter-electrode and saturated Ag/AgCl reference electrode in unstirred aqueous electrolyte containing 0.01 M $Zn(NO_3)_2$ and 0.1 M $NaNO_3$ on SnO_2:F/glass (FTO, TEC 7 Pilkington Company, USA) substrates with 1.5×2 cm^2 area. Temperature of the electrolyte was 70 °C. Schematic illustration of the zinc oxide electrodeposition is presented in Fig. 1. Firstly, ZnO seed layers were formed via potentiostatic electrochemical deposition provided by a programmable impulse potentiostat PI-0.5–1.1 during short time (30 s) at potential $U = -1.3$ V (here and below, vs. Ag/AgCl) (Fig. 1(a)). After that, plating of 1-D ZnO was carried out in the same electrolyte during the half-hourly electrodeposition in the pulsed mode by applying rectangular potential pulses. The lower and upper potential limits were, respectively, $U_{off} = -0.7$ V and $U_{on} = -1.3$ V. A duty cycle ($Dc = 0.4$) was given as relation $T_{on}/(T_{on} + T_{off})$, where T_{on} is a time at potential U_{on}, and T_{off} is a time at potential U_{off}. Potential pulse frequency *f* was 2 Hz. As a result, 1-D ZnO arrays with average length about 1.1 μm were grown on FTO surfaces, so, the thickness of the obtained ZnO layer $D_{ZnO} \approx 1.1$ μm (Fig. 1(b)).

In this study, NiO thin films were synthesized by SILAR method on glass substrates (NiO/glass samples), on FTO (NiO/FTO samples) and