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UV detection properties of hybrid ZnO tetrapod 3-D networks

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ABSTRACT

Hybridization of micro- and nanostructures of semiconducting oxides is known to be an efficient way to greatly improve their sensing properties and photocatalytic activity. In this work, zinc oxide (ZnO) tetrapod (T) three-dimensional (3-D) highly porous networks were hybridized with Me_xO_y and $Zn_xMe_{1-x}O_y$ compounds (Me = Sn, Fe, Bi, Cu or Al), and their ultraviolet (UV) sensing properties were investigated. Additionally, individual Al-doped ZnO-T (ZnO-T:Al) with different diameters were integrated into devices using a FIB/SEM system to study the influence of diameter on the UV sensing properties. ZnO-T–CuO hybrid networks demonstrated the highest increase in UV response (with about 2.5 times) and decrease in response and recovery time ($\tau_{r1} = \tau_{r2} \approx 0.03$ s and $\tau_{d1} = \tau_{d2} \approx 0.045$ s) compared to pristine ZnO-T networks before hybridization, which is quite promising for applications in fast optical communication. The ZnO-T–Zn_2SnO_4 hybrid networks showed only a slight increase in UV response while other types of hybrid networks showed a considerable decrease in UV response, especially in the case of ZnO-T–Bi_2O_3 hybrid networks, which could be attributed to the fast recombination of photoexcited electrons and holes in Bi_2O_3 under the UV light illumination. The results demonstrate that hybridization with *p*-type materials is more efficient due to higher photogenerated charge separation properties. In the case of individual structures the device based on a microwire with lower diameter showed higher stability and good repeatability with a relatively high UV response of about 5.5. The excellent UV sensing properties combined with ultra-low power consumption make such devices very attractive for real applications like portable UV dosimeters. This work demonstrated the high efficiency of ZnO-T hybridization with *p*-type metal oxides for improvement of UV sensing properties.

1. Introduction

Detection of UV light is highly desirable nowadays due to an intensified ozone layer depletion [1]. Almost everyone is exposed to ultraviolet radiation from the sun on a daily basis [2]. The exposure to UV light originated from sun rays on human skin is known to have positive effects such as mental wellness and vitamin D synthesis, but high dosages are also known to have negative effects such as cataracts, melanoma, skin cancer, etc. [1,3]. The last one is the most important problem and many efforts to increase the public awareness are ongoing [2,3]. It is necessary to avoid excess exposure with UV rays, especially of UVB rays (λ = 280–315 nm) which can damage the DNA and can be a key factor in the initiation of the carcinogenic processes in skin [1]. Thus, in order to protect people from dangerous dosages from the sun, it is necessary to develop fast and reliable UV dosimeters/photodetectors, preferably in miniature, which also have applications in medicine, communications and defense [3,4]. Because industrial UV photodetectors typically possess high cost and low responsivity [4,5], it is necessary to develop cost-efficient methods for the fabrication of photodetectors with higher performances and lower dimensions for integration in portable devices, smartphones, etc. [6]. Regarding the material, ZnO is an ideal candidate for visible blind UV photodetectors [7], due to its wide band gap (E_g = 3.4 eV) and its low cost. Additionally, ZnO is available in a huge range of morphologies with high surface-to-volume ratios [8–11]. Among them, the 3-D ZnO

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tetrapods demonstrated very interesting sensing properties due to their specific detection mechanism [12]. Recently, the fast and simple methods for synthesis of interconnected free-standing 3-D ZnO-T networks with nanometric and micrometric sizes have been demonstrated, namely the crucible flame transport synthesis (FTS) and the burner flame transport synthesis (BTS) [12,13]. Due to the interconnections between the arms of tetrapods, the junction inside the tetrapods at the connection of four different arms and the high porosity of the ZnO-T networks, a high-sensitivity and an ultra-fast UV response can be obtained with ZnO-T networks [12,13], which was also demonstrated by other authors [14,15]. The effect of the junction inside the tetrapods on electrical transport between the legs of a tetrapod is less studied, especially in the case of sensing applications, and thus the sensing mechanism of the ZnO-T core is still not fully understood. However, Huh et al. measured the local resistances in the arms and the junction of individual ZnO-T using AC impedance spectroscopy, and observed that the resistance at the junction is greater compared to the resistance in the arms [16]. On the other hand, the height of potential barriers created at the junction between the arms of the tetrapods was found to be highly sensitive to a change in the charge carrier concentration (N_D). Upon UV illumination the photo-generated electrons lead to a fast decrease in height of the potential barrier, thus the influence of oxygen species is essentially reduced leading to a fast increase and decrease of photocurrent through the ZnO-T networks [7,12,13]. However, the response and recovery time of such networks is still higher compared to commercially available UV photodetectors. In this context, hybrid micro- and nano-structures of zinc oxides demonstrated a higher efficiency compared to pristine zinc oxide materials and give the possibility to improve the sensing properties [4,17,18]. For example, Gou et al., showed significantly improved UV sensing properties using ZnO nanoparticles active layer blended with semiconducting polymers compared to photodetectors typically made from single crystalline silicon or gallium nitride *p-n* junction [4]. Hatch et al. fabricated a self-powered UV photodetector based on a ZnO-nanorod/CuSCN structure with a fast rise (500 ns) and decay time (6.7 μs) and a UV-Vis rejection ratio of $\approx 10^2$ [19]. The main advantages of *p-n* heterostructures are the low applied field strengths and fast response due to the lack of oxygen dependencies [19]. Thus, material hybridization presents a high potential for UV detection applications with high performances. Recently, a novel method for hybridization of ZnO-T networks (synthesized by flame transport synthesis (FTS) approach [12]) with different types of Me_xO_y and $Zn_xMe_{1-x}O_y$ materials (Me = Sn, Fe, Bi, Cu or Al) has been demonstrated [12,17,18,20], and the excellent gas sensing performances of these hybrid ZnO-T networks have already been shown [17,18]. In addition, individual tetrapods or microwires were integrated into nanosensor devices working as efficient gas sensors and UV photodetectors [18,21]. Due to their low power consumptions and small sizes, the nanosensors are quite suitable for portable applications [6,22,23]. Different methods for improvement of UV sensing properties of individual ZnO structures such as doping, surface functionalization and formation of single and double Schottky contacts were reported. Recently, Lupan et al. fabricated a device based on a single Ag-doped ZnO microwire with a fast UV response [6]. Zhou et al. demonstrated the increase in UV response and decrease in response time for individual ZnO NW by the formation of a single Schottky contact and a surface coating with polymers by a layer-by-layer self-assembly method, excluding the influence of adsoprtion/photodesorption of oxygen molecules [24]. Netwon et al. fabricated an UV Schottky photodiode using a single ZnO-T with excellent sensing performances [25]. These promising results show that more investigations are desired and necessary to further improve the UV sensing properties of individual ZnO nanostructures, especially of ZnO-Ts, which have several advantages compared to nanowires and nanobelts: (i) the possibility to fabricate a multi-terminal nanodevice; (ii) transport properties tuned by the influence of arms (by UV light or electron beam [26], applied force [27], and possible the gaseous species (need investigations).

In this work, the UV sensing properties of 3-D ZnO-T–Me_xO_y and ZnO-T–$Zn_xMe_{1-x}O_y$ hybrid networks (Me = Sn, Fe, Bi, Cu or Al)

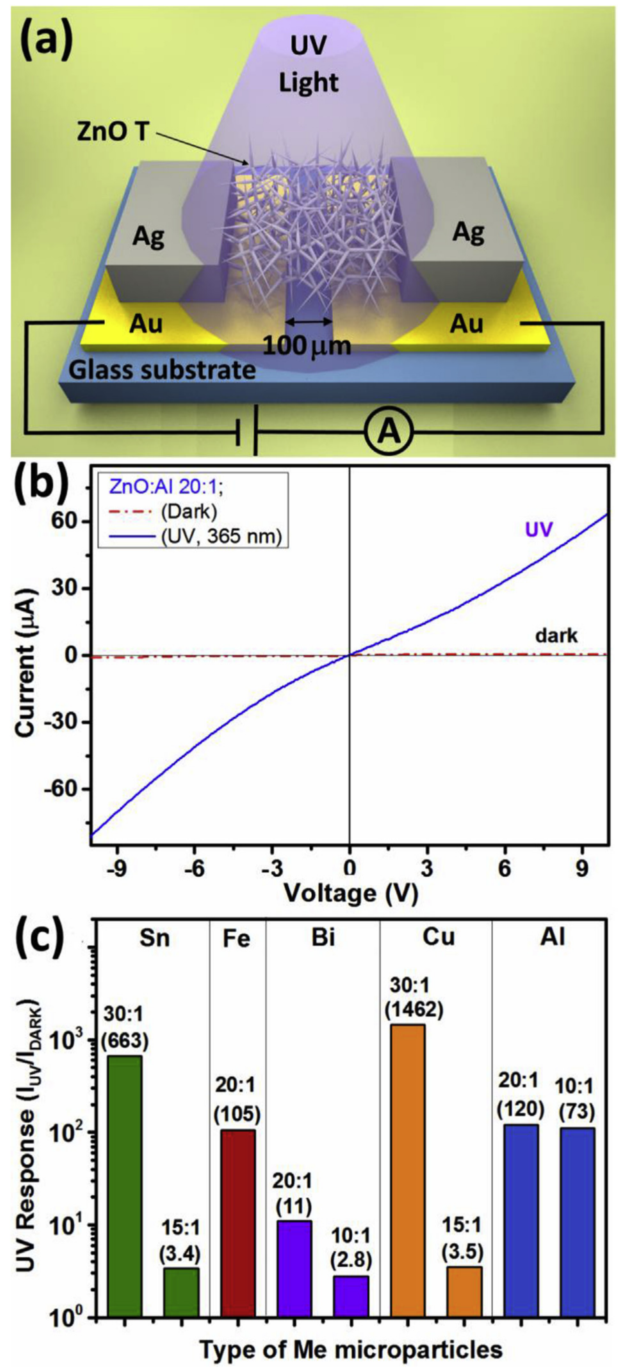

Fig. 1. (a) Schematic illustration of the photodetector structure based on Me_xO_y and $Zn_xMe_{1-x}O_y$ alloyed ZnO-T hybrid networks; (b) The current-voltage characteristic of the sensor based on ZnO-T–$ZnAl_2O_4$ hybrid networks in air at room temperature in the dark and under UV illumination; (c) The UV response (λ = 365 nm) of the devices based on pristine ZnO-T [12], ZnO-T–Me_xO_y and ZnO-T–$Zn_xMe_{1-x}O_y$ hybrid networks (Me = Sn, Fe, Bi, Cu or Al).

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