Materials Science in Semiconductor Processing 49 (2016) 20–33

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Multifunctional device based on ZnO:Fe nanostructured films with enhanced UV and ultra-fast ethanol vapour sensing

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ARTICLE INFO

Article history:
Received 3 February 2016
Received in revised form
17 March 2016
Accepted 18 March 2016
Available online 24 March 2016

Keywords:
Nanocrystalline materials
ZnO:Fe
Ethanol sensor
UV photodetector
Fast sensor

ABSTRACT

Extensive application requests on high-performance gas sensors and photodetectors reveal the importance of controlling semiconducting oxide properties. Sensing properties of ZnO nano- and microstructures can be tuned and their functional performances can be enhanced more efficiently by metal-doping. Here, we report the synthesis of crystalline Fe-doped ZnO (ZnO:Fe) nanostructured films via a cost-effective and simple synthesis from chemical solutions (SCS) approach followed by rapid thermal annealing (RTA) with excellent potential for the development of multifunctional devices for UV and ethanol (C_2H_5OH) vapour sensing. The effects of two types of thermal annealing on the ZnO:Fe morphology, the crystallinity, the electronic and the vibrational properties, the UV radiation and the gas sensing properties are investigated. The experimental results indicate an increase in UV response ($I_{UV}/I_{DARK} \sim 10^7$) of as-grown ZnO nanostructured films by Fe-doping, as well as an essential improvement in rise and decay times due to RTA effects at 725 °C for 60 s. In comparison with un-doped samples, ZnO:Fe (0.24 at%) specimens showed a response to ethanol which is enhanced by a factor of two, $R_{air}/R_{gas} \sim 61$. It was demonstrated that by using Fe-doping of ZnO it is possible to reduce essentially the response τ_r and recovery times τ_d of the multifunctional device. The involved gas sensing mechanism is discussed in detail in this paper. The presented results could be of great importance for the application of RTA and doping effects for further enhancement of UV detection and gas sensing performances of the ZnO:Fe nanomaterial-based multifunctional device.

1. Introduction

High-performance photodetectors and sensors are critical devices for high-speed optoelectronics, optical communication and environmental-industrial network monitoring [1]. On the other hand, the increased concern over safety in industry and homeland indicate the demand of highly selective and sensitive gas sensors for fast leakage detection of poisoning, toxic, volatile organic compounds (VOCs) and flammable gases. Due to a wide direct band gap of ∼3.37 eV at room temperature, good selectivity towards infrared (IR) and visible light, ZnO nanostructures are excellent candidates for the fabrication of UV photodetectors and gas sensors [2–13]. Recent studies demonstrated remarkable progress in the development of UV and gas sensing applications based on ZnO nanostructures by controlling their chemical and physical properties [1–3,7,14]. In this context, multifunctional devices which are able to perform several different tasks get into the focus of many research groups due to the highly competitive global market for miniaturization of sensors and photodetectors on the same platform. Thus, it appears a necessity for the development of efficient methods to control semiconducting oxide properties. One of the most efficient and reliable approaches is the electronical and chemical sensitization by controlled doping of ZnO nanostructures, which demonstrates the capability to improve the sensors sensitivity and selectivity [4,6,8,10,15–22]. On the other side, the ethanol vapour sensor is one of the most popular devices for biomedical, chemical, pharmaceutical, domestic safety, breathe analysis, and food industry. In this context, the food industry is an important and complex field. The development of new cost-effective and simple concepts for control of food quality and technologies becomes an essential and important issue. Thus, reliable biosensors which are easily handled, offer high selectivity, short response and recovery times as well as low-cost are desirable for customers [23–25]. Since ethanol is one of the main products of alcoholic fermentation in winemaking processes [24], various

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http://dx.doi.org/10.1016/j.mssp.2016.03.024
1369-8001/

studies have been performed to develop cost-effective ethanol biosensors for continuous monitoring of the ethanol concentration during the wine production [23–25]. In this context, oxide semiconductors are most desirable candidates due to their low-cost methods of synthesis and controllable sensing parameters. Recent reports on gas detection performances of Fe-doped ZnO nano- and micro-structures demonstrated good perspectives for the elaboration of selective ethanol vapour sensors with high sensitivity [16,21]. Due to high catalytic properties of Fe_2O_3 nanoparticles adhered on the surface of ZnO nanostructures, which is beneficial for gas sensing. It is therefore possible to improve the adsorption of gas molecules on the oxide surface and accelerate the oxidizing process [16,19,21]. Extensive studies were performed on the development of ultra-fast responding and recovering gas sensors based on doped oxide semiconductors [2,3,14,26–30]. However, the high operating temperatures (400–450 °C) for such gas sensors limit their possibilities in some applications, since they require higher power consumption for the heating element.

The post-growth thermal annealing can serve as an excellent solution for the improvement of oxide semiconductor properties, e.g. UV and gas sensing. Numerous studies on different types of thermal annealing, such as conventional thermal annealing (TA) in a furnace, rapid thermal annealing (RTA), rapid photothermal processing (RPP), and hydrothermal treatment (HT) [4,6,8,31–33], revealed higher efficiencies of ZnO nanostructures and quality improvement for advanced optoelectronic devices and gas sensor applications. Thus, rapid thermal annealing is an attractive technique from an industrial point of view, since it may be easily scaled-up to industrial production of gas sensors without the need of complicated vacuum systems. Additionally, it allows the speed up of production processes when combined with a simple chemical synthesis (SCS) approach from solutions [34].

In this work, we will focus on the growth of ZnO:Fe nanostructured films via a simple chemical synthesis SCS approach from aqueous solutions of zinc and iron ions. The UV and gas sensing investigations demonstrated an essential improvement of the response value, as well as of the ethanol vapour sensitivity, selectivity, response and recovery times by Fe-doping in ZnO samples after RTA. Effects of the rapid thermal annealing process on UV and gas sensing performances of the ZnO:Fe have been studied in detail and it was found, that RTA represents an efficient method for the development of ultra-fast ethanol vapour sensors with high sensitivity and selectivity.

2. Experimental details

2.1. Synthesis of un-doped and Fe-doped ZnO nanostructured films

The ZnO and ZnO:Fe nanostructured films were deposited on commercial microscope glass slides (76 mm × 25 mm × 1 mm) via a simple synthesis from chemical solutions (SCS) approach from aqueous baths. The glass substrates were cleaned before deposition by the method described in our previous work [8] and then sensitized with a $SnCl_2 \cdot 2H_2O/HCl$ solution [6]. Starting materials for the aqueous zinc-complex solution, that has been used as the cation precursor, were zinc sulfate $[Zn(SO_4) \cdot 7H_2O]$, sodium hydroxide and iron (III) sulfate heptahydrate. The concentration of the prepared complex solution was mixed with deionized (DI) water to obtain the required zinc concentration for the synthesis procedure. All chemicals were of analytical grade without further purification. The pH value of the complex solution amounted to 10. The doping level of the ZnO:Fe nanostructured films was achieved with 0.8 mM and 5.3 mM of $[Fe_2(SO_4)_3 \cdot 7H_2O]$ in the aqueous solution to reach a Fe content of 0.24 at% and 0.8 at%, respectively. More details on the developed synthesis from chemical solutions (SCS) approach can be found in previous works [8,35]. The SCS cycles were reproduced to obtain the required thickness of the nanostructured films on the glass substrates. After deposition, the samples were rinsed with DI and afterwards dried in a hot air flux (~150 °C) for 5 min. As-grown samples were split in several sets which were processed by two types of thermal annealing, the conventional thermal annealing (TA) at 450 °C and 650 °C, 30 min (noted as TA450 and TA650) and the rapid thermal annealing (RTA) at 575 °C and 725 °C for 60 s (noted as RTA575 and RTA725), respectively.

2.2. Morphological, structural and chemical investigations and spectral characterization of un-doped and ZnO:Fe-doped nanostructured films

The morphology and chemical composition microanalysis of the SCS synthesized ZnO and ZnO:Fe nanostructured films was measured by a Zeiss Ultraplus SEM at 7 kV, as well as with energy dispersive X-ray (EDX) spectroscopy at 15 kV. X-ray diffraction (XRD) patterns were measured with a 3000 PTS Seifert X-ray diffractometer as reported before [8,35]. A WITec alpha 300 RA system was used for micro-Raman spectroscopy, the set-up was calibrated with a silicon substrate and more details are reported before [8,35]. For the X-ray photoelectron spectroscopy (XPS) studies an Omicron Nano- technology GmbH instrument with Al anode (240 W) was used, details were reported before [8]. In order to remove the very top contamination layer, surface cleaning was performed prior to XPS measurements. An Argon ion beam (3 keV) was used for that purpose. The obtained data was charge-referenced by using the position of aliphatic carbon C1s at 285.0 eV.

Electro-optical characterization was performed with a self-built device consisting of a 500 W Xe-lamp, a monochromator from Newport and a Keithley 6487 pico-ammeter with a built in DC voltage source. The leakage currents in the electrical setup were as low as 5×10^{-9} A. The whole setup was computer controlled by LabView software and allowed automatic illumination as well as continuous electrical measurements.

2.3. ZnO and ZnO:Fe nanostructured film based multifunctional devices

For investigations of UV and gas sensing performances, gold contacts (~170 nm) were deposited onto the ZnO and ZnO:Fe nanostructured films aided by an Al mask with meander configuration (width was 1 mm). The photocurrent measurements were performed with a Keithley 2400 as described in our previous works [2,3]. The Au/ZnO:Fe/Au structure demonstrated a linear behavior (Ohmic contacts at Au and oxide semiconductor interface, see Fig. S1). The Au/ZnO contact is known to demonstrate Schottky properties [36–38], however in our case a linear behavior can be explained by bombardment of the ZnO nanostructured films with Au atoms during the DC magnetron sputtering [39]. This leads to the accumulation of oxygen vacancies in the near surface region of undoped and Fe-doped ZnO [40], which acts as donor and results in heavily doped layers near the surface region. As a result, the height of the Schottky barrier is lowered [39,41]. Another important factor for the formation of Ohmic contacts could the presence of carbon, hydrocarbons and OH impurities onto the surface of ZnO and ZnO:Fe films due to exposure in ambient air before deposition of contacts (which will be further demonstrated in this work by XPS studies) [42], which can considerably decrease the rectifying properties of the Au/ZnO contact [42–44].

Photodetection investigations of the fabricated multifunctional devices to UV radiation ($\lambda = 365$ nm) have been carried out according to previous work [2,3]. The UV light power intensity was