Pd-doped ZnO nanostructured films for multifunctional applications

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***Abstract* — In this work Pd-doped ZnO (ZnO:Pd) nanostructured films were deposited on pre-cleaned glass substrates via a synthesis from chemical solutions (SCS) approach from aqueous baths. The post-growth thermal annealing, namely thermal annealing (TA) and rapid thermal annealing (RTA) were applied in order to tune the sensing properties of such nanostructured films. The UV sensing investigations showed decreased performances compared to undoped films. However, the gas sensing measurements showed excellent H_2 response at near-room temperature for gas concentration of 1000 ppm.**

***Index Terms* — nanostructured films, gas sensor, ZnO, chemical synthesis, UV photodetector.**

I. INTRODUCTION

High-performance photodetectors and sensors are key devices for environmental-industrial network monitoring due to the increased concern about safety in industry and homeland [1]. In this context, ZnO micro- and nanostructures are widely used for various sensing applications, especially for UV and gas sensing due to their low-cost synthesis and a wide range of morphologies [2]. The multifunctional devices based on ZnO can be fabricated to perform several different tasks, preferable at the same operating conditions. However, because the gas sensors based on metal oxide are commonly working at elevated temperatures (> 200 °C) and UV sensing properties at these temperatures are considerably decreased, it is hard to fabricate the multifunctional devices able to detect at the same time UV light and specific gases (for example H_2 gas). In this work, we demonstrate that doping of ZnO with Pd can improve the near room temperature H_2 gas sensing. Therefore, these samples can be used as multifunctional devices able to detect UV light and H_2 gas at near room temperature, in perspective.

II. EXPERIMENTAL

The ZnO:Pd nanostructured films were synthesized via a simple synthesis from chemical solutions (SCS) approach from aqueous baths. As the substrate commercial microscope glass slides (76 mm × 25 mm × 1 mm) were used, which were pre-cleaned and then sensitized with a $SnCl_2 \cdot 2H_2O$/HCl solution [1]. For doping with Pd, a $PdCl_2$ aqueous solution was used. After growth, the two different types of thermal annealing were applied. First was thermal annealing in electrical furnace (TA) in an electrical furnace at 650 °C for 2 h (noted as TA650) and second was rapid thermal annealing (RTA) at 725 °C for 60 s (noted as RTA725). More details on the synthesis are presented in a previous work and in the references therein [1].

The sensor devices based on ZnO:Pd nanostructured films were fabricated as was reported previously [3]. The UV and gas sensing properties were investigated at room temperature and 50 °C as was described previously [1, 4]. The gas response was defined as ratio of the currents under exposure to H_2 gas (I_{gas}) and in air (I_{air}). The UV response was defined as the current ratio under UV illumination (I_{UV}) and the current in the dark (I_{dark}). The intensity of UV light was set to 15 – 20 mW/cm^2. The electrical measurements were performed using a computer controlled Keithley 2400 sourcemeter through the LabView software (National Instruments).

III. RESULTS AND DISCUSSIONS

Fig. 1(a-c) show SEM images of ZnO:Pd nanostructured films as-grown, TA at 650 °C and RTA at 725 °C. The thickness of films is ~ 1.1 μm (was measured in cross-section). The films are composed of closely packed and interconnected columnar grains with a rough surface, which is very important for sensing applications due to the higher surface-to-volume ratio. The grains completely cover the glass substrate. No agglomerations were observed, not even at larger surface area scans (not shown). The diameter of grains varies in a wide range from 200 – 300 nm, while neither the TA nor the RTA treatment show a significant influence on the morphology. The energy dispersive X-ray spectroscopy (EDX) measurements showed a Pd content of 0.17 at.%.

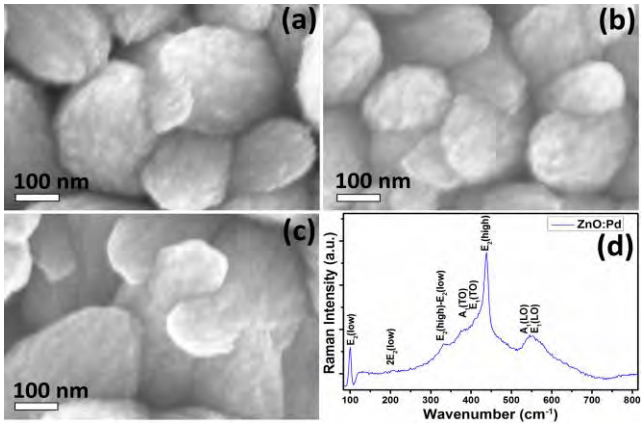

Fig. 1. SEM images of ZnO:Pd nanostructured films deposited on a glass substrate: (a) as-grown; (b) TA650; (c) RTA725. (d) Room temperature micro-Raman spectra of as-grown ZnO:Pd sample.

Fig. 1(d) shows the room temperature micro-Raman spectra of ZnO:Pd nanostructured films. Peaks at 99.5 cm^{-1} and 438 cm^{-1} were assigned to E_2 (low) and E_2 (high) non-polar optical phonon modes. The peaks at 204, 333, 377, 575 and 582 cm^{-1} were assigned to E_2 (low) second order mode, E_2 (high)–E_2 (low) multi-phonon scattering, A_1 (TO), E_1 (TO), E_1 (LO) and A_1 (LO) modes, respectively. No additional peaks were observed.

Fig. 2(a) shows the current – voltage (I – V) characteristics of ZnO:Pd nanostructured films annealed by different methods with Au-contacts, as well as the as-grown sample. The results showed linear characteristics indicating the formation of ohmic contacts, i.e. at ZnO:Pd/Au interfaces. The main reason for the ohmic contact formation was explained in a previous work [1]. The calculated resistivity from I – V characteristics is presented in Fig. 2(b), showing a considerable decrease in resistivity after annealing, mainly due to the improvement of the ZnO crystallinity [1]. The dynamic UV response of the studied samples is presented in Fig. 2(c). The calculated UV response values (I_{UV}/I_{dark}), responsivity (R) and time constants of rising and decaying photocurrents (calculated fitting with a bi-exponential function [1]) are presented in Fig. 2(d), 2(e) and 2(f), respectively. The highest UV response of ~ 550 demonstrated the as-grown films, while samples treated with TA and RTA showed a response of ~ 5.5 and ~ 45, respectively. These values are lower compared to as-grown, Fe-doped or Sn-doped ZnO nanostructured films grown by the same method reported previously [1, 3]. The calculated responsivity values of ~ 0.035, ~ 0.057 and ~ 0.07 A/W (for as-gr, TA650 and RTA725) are also lower compared to as-grown and Sn-doped ZnO samples [3]. Thus, Pd-doped ZnO samples show a decrease in performance compared to the undoped ZnO nanostructured films. However, the same tendency of decreasing time constants after annealing of the films was remained (see Fig. 2(f)).

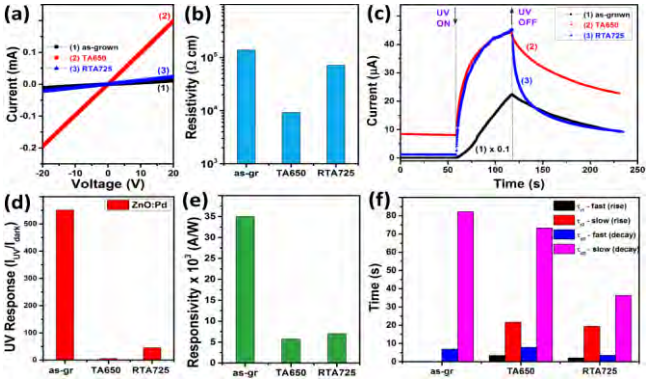

Fig. 2. (a) Current – voltage characteristics; (b) resistivity; (c) dynamic UV response; (d) calculated UV response; (e) responsivity; and (f) calculated time components of rising and decaying photocurrent of ZnO:Pd nanostructured films.

The gas sensing measurements showed a detectable gas response to 1000 ppm-hydrogen gas (H_2) at low-operating temperature of only 50 °C (see Fig. 3), which was not demonstrated for pristine or doped ZnO films before. The calculated gas response (R_{air}/R_{gas}) is ~ 1.5. The calculated response, defined as necessary time to reach 90% of full response is ~ 100 s. The recovery time at such low operating temperature is relatively big and even after 300 s the signal does not completely recover to the initial electrical baseline.

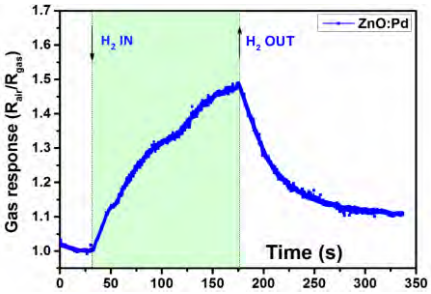

Fig. 3. The room temperature H_2 gas response of as-grown ZnO:Pd nanostructured films.

After the rapid thermal annealing (RTA) of ZnO:Pd samples at 725 °C for 60 s the gas response was slightly increased to ~ 1.7 (not shown). However, the response time was increased to ~ 170 s, while after evacuation of hydrogen gas from the chamber, the signal still not fully recover to the initial baseline.

IV. CONCLUSION

The obtained ZnO:Pd nanostructured films are promising candidates for multifunctional sensors able to work close to room temperature. The main advantage of nanostructured films compared to other nanostructures is the simple synthesis which excludes the need for an additional transfer step of the sensing material to the substrate for the fabrication of a gas sensor structure, as in the case of free-standing nanostructures.

ACKNOWLEDGMENTS

Professor Dr. Viana (CNRS, Paris, France) is acknowledged for the fruitful discussions and for his help with the PL experiments. This work was partially financially supported by the STCU-ASM under the Grant no. 6229.

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