

# Effect of Doping in $Zn_{1-x}Ag_xO_y$ Nanostructured Films on Hydrogen Gas Response

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**Abstract** — Nanostructured  $Zn_{1-x}Ag_xO_y$  films have been deposited using a chemical solution synthesis method. The as-deposited nanostructured films were subjected to thermal annealing in furnace and rapid thermal annealing, for different temperatures and durations of treatment. The morphological, structural, vibrational and chemical proprieties were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), micro-Raman spectroscopy and energy dispersive X-ray spectroscopy (EDS) techniques. Effect of silver doping in  $Zn_{1-x}Ag_xO_y$  nanostructured films on gas response was investigated. The influence of the thermal annealing, duration and operation temperature on selectivity of sensors was studied and found that annealing at 500 °C for 60 s forms most sensitive nanostructured films.

**Index Terms** — Chemical synthesis, Nanostructures, Sensor,  $Zn_{1-x}Ag_xO_y$ .

## I. INTRODUCTION

Present renewable sources of energy like solar energy, wind energy, geothermal energy and others, require static system of conversion without or reduced portability limiting certain applications. Hydrogen ( $H_2$ ) is expected to supplant hydrocarbons and becomes “the common fuel of the future” [1]. Hydrogen is high in energy, yet an engine that burns pure hydrogen produces almost no pollution. A fuel cell combines hydrogen and oxygen to produce electricity, heat and water. Fuel cells are often compared to batteries. Both convert the energy produced by a chemical reaction into usable electric power. However, the fuel cell will produce electricity as long as fuel (hydrogen) is supplied, never losing its charge. At standard temperature and pressure, hydrogen is a colorless, odorless, tasteless, non-toxic, nonmetallic gas that forms explosive mixtures with air if it is 4–74% concentrated. Thus, the detection of hydrogen gas becomes an essential step in industry, biomedical system, fuel system and others.

ZnO is one of the most interesting semiconducting oxide materials for  $H_2$  gas detection applications. It has the band gap energy of 3.37 eV at room temperature, a large free-exciton binding energy 60 meV [2] and sensibility to  $H_2$  gas. Un-doped ZnO films show *n*-type electrical conductivity and have poor stability in humid environment or corrosive medium and proprieties are altered by adsorption of  $O_2$ ,  $CO_2$  and water. The gas response of the ZnO bulk material is not sufficiently high, thus nanostructures are of major interest because of its larger surface area to volume ratio. Operating temperature is an important parameter to be considered in production of cost-effective gas sensors, because requires less electrical energy and devices are more stable during time.

In this work, we investigate the nanostructured films of ZnO and Ag-doped ZnO deposited using SCS method. Decrease in operating temperature and increase in response time to 100 ppm  $H_2$  was observed with doping in films after rapid thermal annealing (RTA).

## II. EXPERIMENTAL

### 1. Chemical solution synthesis of nanostructured films of Ag-doped ZnO

The glass substrate were cleaned in HCl solution for 10 min, rinsed in deionized (DI) water, cleaned in  $H_2SO_4$  solution for 10 min, rinsed in DI water, cleaned in  $HNO_3$  solution for 10 min, rinsed in DI water and dried in a stream of hot air. The aqueous zinc complex solution comprises a mixture of zinc sulfate ( $Zn(SO_4) \cdot 7H_2O$ ), silver nitrate ( $AgNO_3$ ) and sodium hydroxide (NaOH) mixed until complete dissolution. The concentration of the complex solution was diluted to obtain 0.05 – 0.15 M zinc concentration for deposition by adding respective quantities of deionized (DI) water [3].

The SCS technique is based on the adsorption and reaction of the zinc complex ions from the aqueous solution, which were kept at room temperature. The immersion of the wet substrate in the anions solution

kept at 95 – 98 °C during deposition. The as-deposited

nanostructured films were dried in air at 150 °C for 5 min.

Finally, nanostructured films were subjected to thermal annealing in furnace (TA) and rapid thermal annealing (RTA) for different temperatures and durations. Nanostructured films with thicknesses of 1.5  $\mu m$  and 2.6  $\mu m$  were investigated in details.

### 2. Characterization

The samples of Ag-doped ZnO nanostructured films were analyzed by X-ray diffraction (XRD) using a Rigaky “DB/MAX” powder diffractometer with a nickel-filtered  $CuK\alpha$  radiation source ( $\lambda = 1.54178 \text{ \AA}$ ) and a scanning rate

of 0.02 °/s in the  $2\theta$  range from 10 to 80 °. The compositional analysis of Ag- doped ZnO nanostructured films was carried out using energy-dispersive X-ray spectroscopy (EDX), in combination with SEM. The different characterization techniques confirmed that the nanostructured films are crystalline material.

Information on vibrational modes in pure and Ag-doped ZnO nanostructured films was obtained from Raman backscattering experiments in a micro-Raman set Horiba Jobin Yvon LabRam IR spectrometer with a charge-coupled detector (CCD). Raman spectra were excited with photons from a Helium Neon laser ( $\lambda \sim 633$  nm). Gas sensing experiments were performed as reported before [1].

### III. RESULTS AND DISCUSSIONS

In this work were investigated structural, vibrational, gas response and selectivity to  $H_2$  of Ag-doped ZnO nanostructured films and compared effect of two types of treatments: thermal annealing (TA) and rapid thermal annealing (RTA) in air. Also were investigated response ( $\tau_r$ ) time and recovery ( $\tau_r$ ) time of the sensor structures.

#### 1. Morphological Characterization

To examine the surface morphology of nanostructured films, SEM has been used. The typical SEM image of  $Zn_{1-x}Ag_xO_y$  samples is represented in inset of Figure 1a. It was observed that nanocrystallites growth in agglomerations with different sizes, but with hexagonal shapes, which is typical Wurtzite structure. Radius value of nanocrystallites is estimated in the range 100 – 250 nm and dependent on Ag-doping concentration in ZnO.

#### 2. Chemical characterization

For chemical characterization were performed EDS measurements (not shown) from which the O:Zn ratio was found to be 50.72:49.28 atomic ratio in pure ZnO. Silver content in as-grown ZnO nanostructured films was found to be about 0.5Wt%Ag noted as concentration (1), about 0.95Wt%Ag noted as (2) and 1.3Wt%Ag noted as concentration (3).

#### 3. Structural analysis

Figure 1 shows the XRD diffractogram of pure and Ag-doped ZnO nanostructured films (doping concentrations (1), (2) and (3)) thermal annealed in furnace at 450 °C for 2 hours recorded in the range of 10-80° with scanning step of 0.02°. All diffraction peaks can be attributed to crystalline ZnO with the hexagonal wurtzite structure (space group:  $P6_3mc(186)$ ;  $a = 0.3249$  nm,  $c = 0.5206$  nm). The data are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS 036-1451). In Figure 1(a) the detected  $(hkl)$  peaks are at  $2\theta$  values correspond to lattice planes: (100), (002), (101), (102), (110), (103), (112) and (004), respectively.

To study effect of doping on the crystallinity of the  $Zn_{1-x}Ag_xO_y$  nanostructured films, the intensities of the (100), (002) and (101) diffraction peaks were monitored. For Ag-doped ZnO samples intensity of (002) diffraction peaks and full width at half-maximum (FWHM) was increased, while intensity and FWHM for (100) and (101)

diffraction peaks was decreased as compared with those of pure ZnO. From Figure 1b was observed a shift to a lower  $2\theta$  angle value of the XRD diffraction peaks for doped samples as compared with those of pure ZnO. Such lattice deformation might be result of  $Ag^{1+}$  atoms incorporation in lattice of ZnO, which have greater ion radius ( $r(Ag^{1+}) = 0.126$  nm) than that of  $Zn^{2+}$  ( $r(Zn^{2+}) = 0.074$  nm) [4].

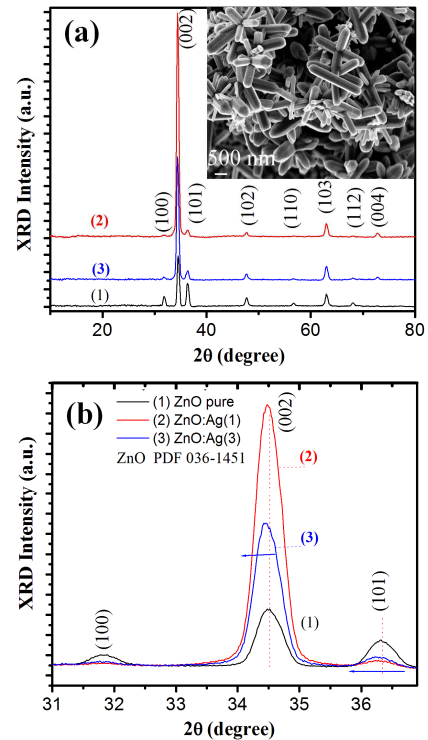


Fig. 1. XRD diffractograms of the ZnO and  $Zn_{1-x}Ag_xO_y$  nanostructured films: (a) Thermal annealed at 450 °C for 2 h and doping concentration (1) and (3); (b) Thermal annealed at 450 °C for 2 h and doping concentration 1 and 3 in the range 31-37 degrees.

#### 4. Micro-Raman studies

In order to investigate the influence of Ag-doping of ZnO films on the micro-Raman spectra, room temperature measurements of samples were performed. ZnO with a wurtzite structure belongs to the  $C_{6v}^4(P6_3mc)$  space group, and there are 12 degrees of freedom since there are 4 atoms per primitive cell. There are 9 optical phonon modes (LO) and six transverse-optical (TO) branches, one longitudinal-acoustic (LA), and two transvers-acoustic (TA) [4].

In Figure 2a are compared micro-Raman spectra of non-doped ZnO nanostructured films with  $Zn_{1-x}Ag_xO_y$  doped with concentration (1) after RTA treated at 500 °C for 60 s. Dominant peaks at 99 and 437  $cm^{-1}$  are attributed to the low- and high- $E_2$  modes ( $E_2^L$  and  $E_2^H$ ) of nonpolar optical phonons, peak at 330  $cm^{-1}$  is attributed to second order Raman processes involving acoustic phonons. It can be observed a LVM at value 416.5  $cm^{-1}$ .

Figure 2b shows Micro-Raman spectra of  $Zn_{1-x}Ag_xO_y$  samples annealed at 650 °C for 2 h. Besides the low- and high- $E_2$  mode ( $E_2^L$  and  $E_2^H$ ) and second order Raman processes involving acoustic phonons were detected peaks at 382  $cm^{-1}$  that is attributed to  $A_1$  (TO) mode. Peaks at 334  $cm^{-1}$  and 381  $cm^{-1}$  are attributed to  $A_1$  (TO) mode and to  $E_{2H}-E_{2L}$  (multi phonon). As well as was detected a LVM at 416.5  $cm^{-1}$ . LVM of doped ZnO are considered to be

induced by dopant species, and this is considered as an indication of dopant incorporation [4]. One of the possible mechanisms of the LVM is that the impurity centers break the translational symmetry of the crystal thus relaxing the

conservation of the wave vector. Therefore scattering by phonons in ZnO that have wave vectors far from the zone center [4] can occur.

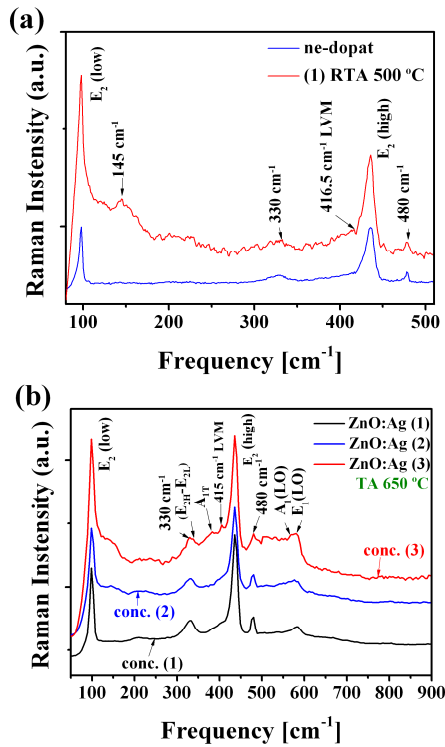
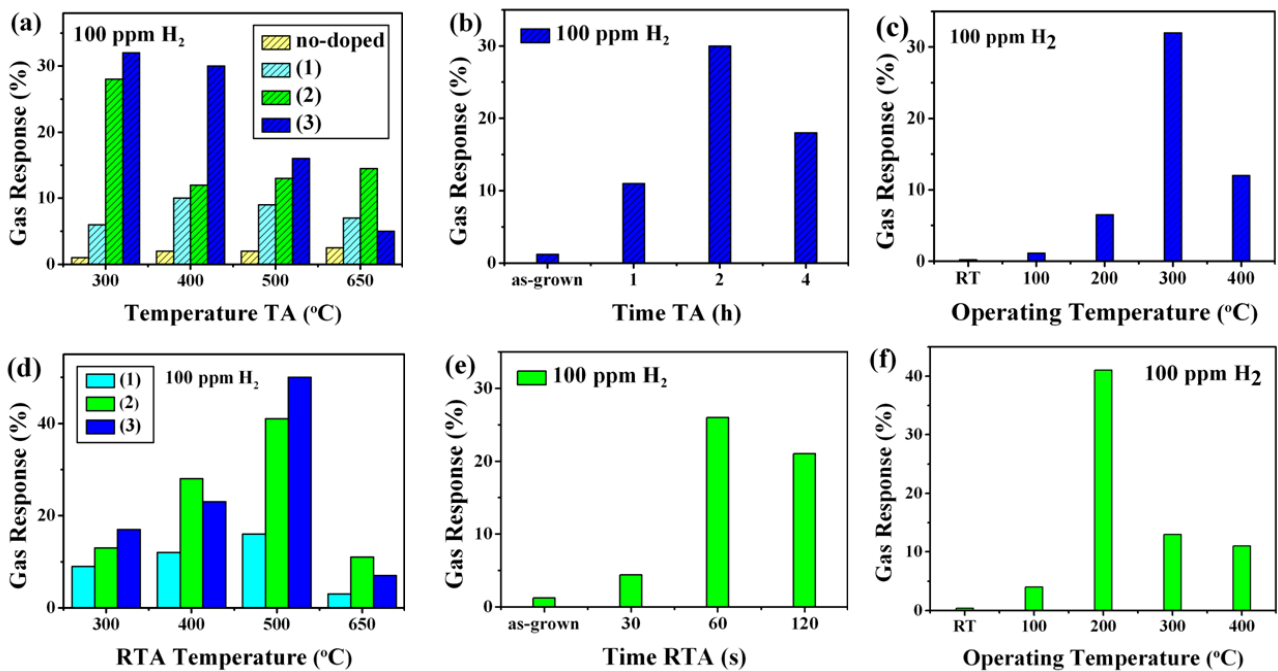


Fig. 2. Micro-Raman scattering spectra of the: (a) pure and doped with concentration (1) zinc oxide nanostructured films treated RTA at 500 °C for 60 s; (b) Thermal annealed at 650 °C samples with doped concentration of (1), (2) and (3).

### 5. Gas Response



Gas response of  $Zn_{1-x}Ag_xO_y$  nanostructured films were investigated in dependence of type of thermal treatment (TA and RTA), temperature, duration of annealing and operating temperature. Detailed experimental results are

summarized in form of diagrams in Figure 3. To test the selectivity to  $H_2$  gas of structures, the response to ethanol and  $CH_4$  has been investigated. The gas response of the sensors is given by the resistance ratio  $\Delta R/R$  [1]. In Figure 3a are shown dependences of gas responses to 100 ppm  $H_2$  of  $Zn_{1-x}Ag_xO_y$  nanostructured films with thickness 1.5  $\mu m$  versus different temperatures of thermal annealing for 2 h. As well as, in Figure 3a are compared different doping

concentrations at operating temperature (OPT) of 300 °C.

In Figure 3b is shown effect of thermal annealing durations on gas response to hydrogen. It can be observed that gas response to  $H_2$  was improved after doping nanostructured films of ZnO with Ag impurities. Also, it was observed that

after 300 °C TA treatment of samples doped with

concentration (3) the gas response is highest one. However, it was found that by further increasing temperature of TA treatment, the gas response to  $H_2$  is decreasing. From

Figure 3a-c can be concluded that optimal time for TA treatment is 2 h and optimal operating temperature to obtain highest gas response of Ag-doped ZnO samples to

Fig. 3. Dependence of gas response to 100 ppm  $H_2$  for  $Zn_{1-x}Ag_xO_y$  nanostructured films versus: (a) thermal annealing TA temperature for 2 h and doping concentration at 300 °C operating temperature; (b) time for thermal annealed TA samples treated at 400 °C with concentration (3) at 300 °C

H<sub>2</sub> is 300 °C. According to results presented in Figure 3d 500 °C RTA for 60 s was decreased to 200 °C in comparison with the optimal regime of TA treated samples (300 °C for 2 h). For RTA treatment was

can be concluded that gas response for RTA treatment samples of Zn<sub>1-x</sub>Ag<sub>x</sub>O<sub>y</sub> nanostructured films is higher in comparison to TA treated samples. From Figure 3e can be observed that optimal time for RTA treatment is 60 s. Also from Figure 3f can be concluded that optimal operating temperature for 1.5 μm thick Zn<sub>1-x</sub>Ag<sub>x</sub>O<sub>y</sub> films exposed to

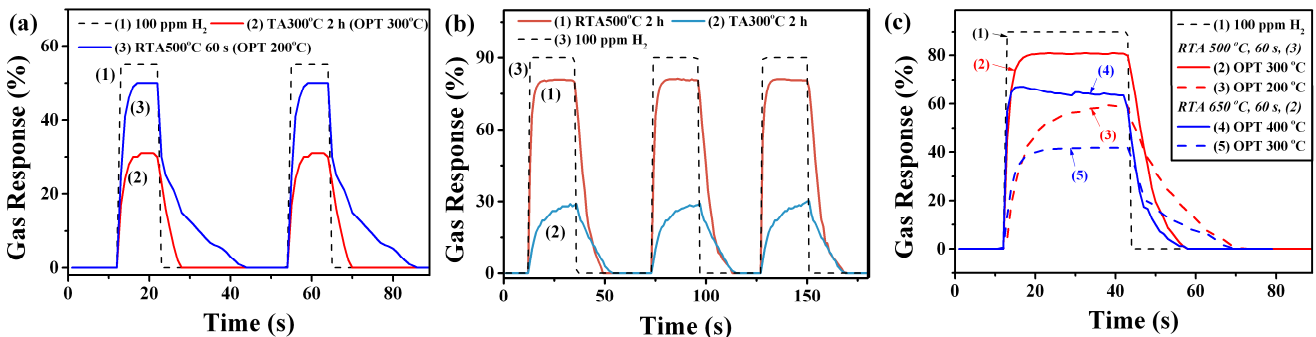


Fig. 4. Comparison of gas response to 100 ppm H<sub>2</sub> versus time for Zn<sub>1-x</sub>Ag<sub>x</sub>O<sub>y</sub> samples doped with concentration (3) grown with: (a) thickness of 1.5 μm and treated at optimal regimes: RTA 500 °C for 60 s at OPT 200 °C (#1) and TA 300 °C for 2 h at OPT 300 °C (#2); (b) thickness of 2.6 μm treated at

optimal regimes: RTA 500 °C for 60 s at OPT 300 °C (#3) and TA 300 °C (#4) for 2 h at OPT 300 °C; (c) Comparison of gas response to 100 ppm H<sub>2</sub> versus time for 2 sets of Zn<sub>1-x</sub>Ag<sub>x</sub>O<sub>y</sub> samples with 2.6 μm thickness: (1) set – RTA 500 °C, 60s doped with concentration (3) at OPT 300 °C and 200 °C; (2) set - RTA 650 °C, 60s doped with concentration (2) at OPT 400 °C and 300 °C;

observed high selectivity of samples, because were not observed any gas response to ethanol and CH<sub>4</sub> at 200 °C

operating temperature. It indicates on good selectivity of developed sensor structures.

From our experimental results can be concluded that for RTA treatment was increased gas response and OPT at 200 °C to 300 °C. Also was observed that with increase in thickness of nanostructured films for TA treated probes was decreased selectivity at highest operating temperatures.

*Comparison of optimal TA and RTA treatment regimes*  
In Figure 4 is demonstrated comparison of gas response to 100 ppm H<sub>2</sub> versus time for Zn<sub>1-x</sub>Ag<sub>x</sub>O<sub>y</sub> samples doped with concentration (3) with thickness 1.5 μm treated at

optimal regimes: RTA 500 °C for 60 s at OPT 200 °C

(#01) and TA 300 °C for 2 h at OPT 300 °C (#02). It can

be observed that τ<sub>r</sub> are the same for both type of treatments, while τ<sub>f</sub> is higher for RTA treated sample.

In Figure 4b is demonstrated comparison of gas response to 100 ppm H<sub>2</sub> versus time for Zn<sub>1-x</sub>Ag<sub>x</sub>O<sub>y</sub> samples doped with concentration (3) and thickness 2.6 μm treated at

optimal regimes: RTA 500 °C for 60 s at OPT 300 °C

(#03) and TA 300 °C (#04) for 2 h at OPT 300 °C. It can

be observed that with increase in deposition cycles was increased response time  $\tau_r$  and recovery time  $\tau_f$  for TA treated sample. For RTA sample  $\tau_r$  remain the same, while  $\tau_f$  is comparable to  $\tau_f$  of TA sample.

#### *Comparison of OPT for RTA treatment*

In Figure 4c was compared gas response to H<sub>2</sub> versus time of two sets of samples RTA treated for 60 s: (1) set – samples treated at 500 °C at OPT 200 °C (#05) and 300 °C (#06); (2) set – samples treated at 650 °C at OPT 300 °C (#07) and 400 °C (#08). It's can be observed that with increase OPT is decrease  $\tau_r$  and  $\tau_f$  time and decrease gas response for both temperature of RTA treatment and both doping concentrations, namely (2) and (3).

## VI. CONCLUSION

In summary, Zn<sub>1-x</sub>Ag<sub>x</sub>O<sub>y</sub> nanostructured films with high crystallinity were grown on glass substrate using a SCS method. SEM, EDX, micro-Raman and X-ray diffraction has been used to characterize the morphology, chemical composition and structure of the samples. XRD measurements indicate that synthesized Zn<sub>1-x</sub>Ag<sub>x</sub>O<sub>y</sub> nanostructured films are in the hexagonal phase. From

XRD pattern was observed deformation in lattice of Zn<sub>1-x</sub>Ag<sub>x</sub>O<sub>y</sub> due to incorporation of Ag atoms.

Were fabricated sensors with rapid response time and 80 % gas response to 100 ppm H<sub>2</sub> based on 2.6 μm thickness 1.3wt% Ag doped ZnO nanostructured films RTA treated at 500 °C for 60 s and at OPT of 300 °C. For 1.5 μm thickness was obtained 50 % gas response to 100 ppm H<sub>2</sub> at OPT 200 °C.

For thermal annealed TA samples was obtained faster sensors but with lower gas response (32 % for 1.5 μm thick samples). With increase in thickness of nanostructured films was observed decrease of selectivity.

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