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Effect of Pt Nanoparticles on the Plasmonic and Chemoresistive Gas Sensing Properties of ZnO:Ga Film †

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Abstract: In this paper, we used gallium doped zinc oxide (GZO) nanocrystals as novel plasmonic and chemoresistive sensors for the detection of hazardous gases including hydrogen (H_2) and nitrogen dioxide (NO_2). GZO nanocrystals with a tunable surface plasmon resonance in the near infrared are obtained using a colloidal heat-up synthesis. Thanks to the strong sensitivity of the plasmon resonances to chemical and electrical changes occurring at the surface of the nanocrystals, such optical features can be used to detect the presence of toxic gases. The same material can be used also as chemoresistive sensors. The effect of Pt nanoparticles (NPs), a well-known catalyst for H2 splitting, have been studied both for the optical and chemoresistive gas response. Both thermal and blue-light (λ = 430 nm) activation were investigated.

Keywords: transparent conductive oxides; gallium doped zinc oxide; optical gas sensors; surface plasmon resonance; chemoresistive gas sensors; light illumination

1. Introduction

In a previous study [1] we elucidated the role of Ga dopant on the sensing mechanism of GZO film combining the optical gas sensing data with electrical measurements and we show that Ga dopants within ZnO nanocrystals enhance the gas sensing response compared to undoped ZnO. Moreover, improved sub-ppm NO_2 gas sensitivity was achieved by activating the sensors response through combined purple-blue (λ = 430 nm) light irradiation and mild heating at 75 °C. In this paper, we study the effect of Pt NPs.

2. Experimental (Materials and Methods)

Doped and undoped ZnO NPs were synthetized through a non-aqueous heat up colloidal method, previously reported by Sturaro et al. [1]. Platinum NPs were synthetized using polyol method [2]. Tipically, 67 mg Chloroplatinic acid (H_2PtCl_6) and 18.7 mg Sodium chloride (NaCl) were dissolved in 3 mL ethylene glycol, degassed and manteined in nitrogen. In another flask, 150 mg of Sodium nitrate ($NaNO_3$) and 55 mg polyvinylpyrrolidone (PVP) were dissolved in 13 mL ethylene glycol, degassed, and heated to 160 °C in nitrogen. After ~20 min, the first solution was rapidly injected into the second one. Then temperature was kept at 160 °C in inert atmosphere for 30 min and

cooled down to room temperature. Particles were precipitated with excess acetone, centrifuged and finally redispersed in ethanol resulting in a 30 mM nominal concentration.

Thin films were produced by spin coating at 1000 rpm for 30 s using GZO dispersion in octane (~100–150 mg/mL). After spin coating, films were stabilized on a hot plate at 150 °C for 15 min. This procedure was repeated many times to obtain desired film thickness. Thin films were then treated at 450 °C following a procedure previously described by our group [1]. Pt NPs were added on some GZO film, in order to evaluate the Pt effect during gas sensing measurements. In particular, a 0.03 M solution of Pt NPs in ethanol, obtained with the previously described synthesis, was spin coated onto the GZO film at 2000 rpm for 30 s and then stabilized for 15 min at 150 °C.

Optical gas sensing tests were performed by making optical absorption measurements in the 350–2500 nm wavelength range on films deposited on SiO_2 substrates using a Harrick gas flow cell (with an optical path length of 5.5 cm) coupled with a Jasco V-570 spectrophotometer. The standard operating temperature (OT) was set between 80 and 200 °C and gases at concentrations of 1 vol% for CO and H_2 and of 1000 ppm for NO2 in dry air at a flow rate of 0.4 L/min were used. Details are reported in ref. [1].

Conductometric gas sensing tests were performed on films deposited onto a Si/Si_3N_4 supports, inserted in a chamber. Gases were mixed in a MKS147 multi gas mass controller to obtain final gas target concentrations in the ranges 100 ppb–400 ppb of NO_2 and 10–250 ppm of H_2. Details are reported in ref. [1]. In the analysis of the gas responses, the relative response (RR), is defined as the ratio between the electrical resistance to a target gas (Rg) and the electrical resistance in air (R_a) for NO_2. The recovery percentage (RP) is defined as the measure of the sensor ability to recover its baseline, calculated as the percentage ratio $(\Delta_D/\Delta_A) \times 100$, where ΔD and ΔA are the variations of the electrical resistance during gas desorption and absorption, respectively, calculated within the time scale of the sensing cycle. The adsorption/desorption time ($\tau_{ads/des}$) is defined as the time required to reach 90% of the full response at equilibrium, during both gas adsorption and desorption.

3. Results and Discussion

Figure 1 shows the optical gas sensing properties of GZO film with 5 and 10% Ga coated with Pt NPs. Due to the catalytic activity of Pt for hydrogen oxidation, the samples showed a strong enhancement of the response and a better dynamic response, for both Ga doping content with respect to pure GZO film. On the contrary, the Pt NPs have very little effect on NO_2 optical sensing.

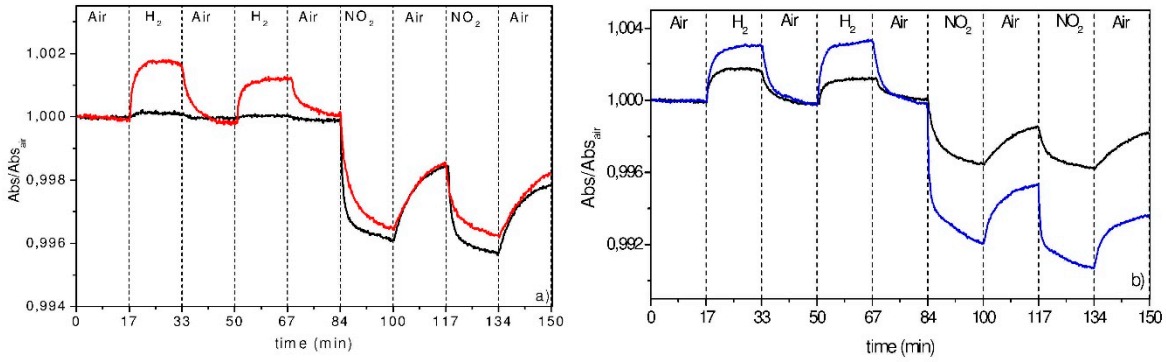

Figure 1. (**a**) Dynamic absorption change for two cycles Air/H_2 1% and two cycles Air/NO_2 1000 ppm at 2400 nm and at 150 °C OT for GZO film with 5% Ga uncoated (black line) and coated (red line) with Pt NPs. (**b**) Dynamic absorption change for two cycles Air/H_2 1% and two cycles Air/NO_2 1000ppm at 2400 nm and at 80 °C OT for GZO film with 5% (black line) and 10% (blue line) Ga.

The chemoresistive response of the Pt doped GZO films to sub ppm NO_2 gas concentration was also investigated and compared with optical gas sensing measurements. Changes of the electrical resistance of ZnO-based metal oxides to NO_2 have been extensively reported in the literature by activating the sensor response by thermal, [3] and visible light irradiation [4] in order to decrease the operating temperature toward mild (T < 100 °C) or even ambient (25 °C) conditions. In this study we

explored the effect of both temperature (in the OT range 25–100 °C) and visible light irradiation using purple–blue (PB) LED source (λ = 430 nm and 770 μW/cm² intensity) on the electrical gas sensing properties of Pt doped GZO films for the detection of NO_2 (400 ppb) gas. Figure 2 shows the normalized changes of the electrical resistance of Platinum doped GZO films to 400 ppb NO_2 gas concentration activated by thermal (Figure 2a–d) and purple-blue light irradiation (Figure 2e–h) modes in a temperature range from 25 °C to 100 °C.

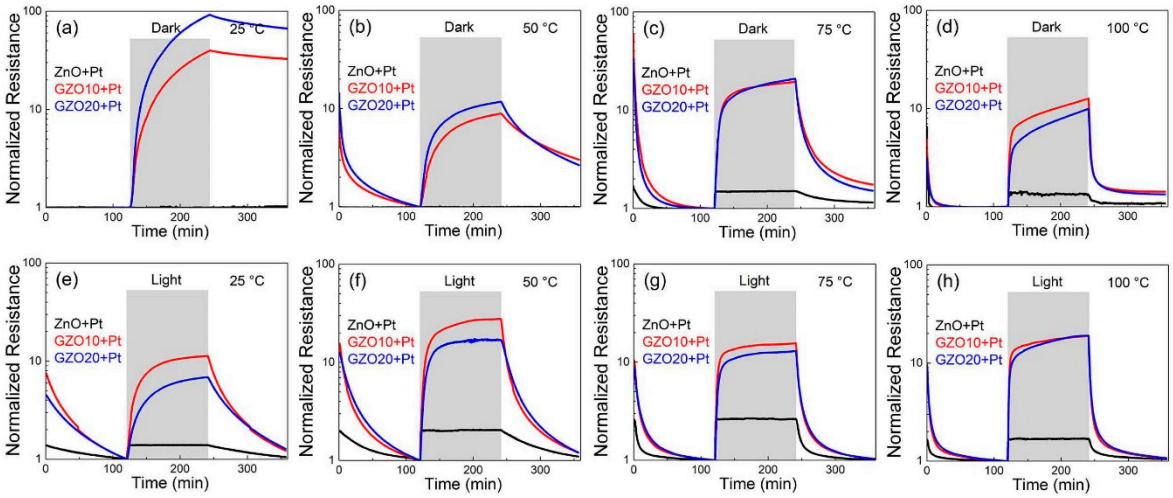

Figure 2. Chemoresistive gas sensing properties of ZnO and GZO film with 10 and 20% Ga doped with Pt NPs. Normalized resistance changes to 400 ppb NO_2 exposure (gray shaded box) at different operating temperatures (25 °C–100 °C) under dark (**a**–**d**) and purple–blue light irradiation (**e**–**h**) conditions.

From a previous study [1] we showed that Ga doping of ZnO films enhances the Relative Responses (RRs), improves the Recovery Percentages of the Baseline (RPs), and slightly increases the response times. By analyzing the electrical responses at different OT and under dark conditions (Figure 2a–d) we observed that addition of Pt to GZO improves the RRs with a maximum at GZO 20 + Pt at 75 °C operating temperature, see Table 1. RRs improvement of Pt doped films in Dark condition continues up to 75 °C and decreases at 100 °C. Also, addition of Pt improves the Recovery Percentages (RPs) over the operating temperature from 25 °C to 100 °C in Dark. It could be noted that under thermal activation mode in dark, addition of Ga and Pt increase both RRs and Recovery Percentages (RPs) indicating a synergistic effect with a maximum value obtained for GZO 20 + Pt at operating temperature not exceeding than 75 °C, see Figure 2a–d and Table 1.

Irradiation with PB light, as shown in Figure 2e–h, further enhances RRs in most of sensors and remarkably increases the RPs in all investigated sensors with respect to dark conditions. Given the positive effect of PB light irradiation, reasonable gas sensing features are maintained even at 50 °C OT, yielding for the GZO 10 + Pt. The best gas sensing response in terms of RR, RP and response time under combined thermal and light illumination condition was obtained for GZO10+Pt at 75 °C with values of 15.45, 99.38 and 41 respectively, see Table 1.

Regarding response time under combined thermal and blue light activation modes both Ga and Pt addition increases the adsorption and desorption times. Desorption times were always longer than adsorption times. Indeed, the adsorption/desorption times under LED illumination were much faster (given the same OT) with respect to the thermally activated samples. To this extend it is worth to notice that the light activation mode for most of the investigate films trigger the achievement of equilibrium conditions (i.e., most of the not detectable, n.d., conditions in Table 1 have been disappeared and substituted by the respective response time).

The chemoresistive H_2 response in the concentration range 10–250 ppm and 25–100 °C operating temperature reveals to be very poor for all the investigated films. This behavior is not related to differences in the H_2 concentration utilized in both chemoresistive and optical tests (i.e., 250 ppm vs.

10000 ppm), but more reasonably to the selected OT range (25–100 °C) which is too low to activate any chemoresistive response.

Table 1. Comparison of RR, RP, τ_{ads}, and τ_{des} to 400 ppb NO_2 in dark conditions and PB light (λ = 430 nm) illumination at different OT (25–100 °C).

OT (°C)	Sample	$RR = R_G/R_A$ [-]		$RP = [\Delta_D/\Delta_A] * 100$ [%]		τ_{ads} (min)		τ_{des} (min)	
		Dark	LED	Dark	LED	Dark	LED	Dark	LED
25	ZnO + Pt	1	1.36	0	77.13	n.d	4	n.d	110
	GZO 10 + Pt	39.09	11.01	18	95.95	110	71	n.d	115
	GZO 20 + Pt	93.82	6.72	26.68	90.28	108	87	n.d	120
50	ZnO + Pt	1	2.03	0	83.64	n.d	5	n.d	100
	GZO 10 + Pt	8.79	27.60	74.75	98.51	84	63	n.d	100
	GZO 20 + Pt	12.18	16.89	83.29	98.41	88	44	n.d	115
75	ZnO + Pt	1.49	2.63	69.40	98.59	6	5	79	29
	GZO 10 + Pt	19.20	15.45	95.85	99.38	72	41	117	100
	GZO 20 + Pt	20.70	12.72	97.43	99.32	74	45	117	96
100	ZnO + Pt	1.35	1.68	79.19	91.23	6	5	13	20
	GZO 10 + Pt	12.58	18.87	96.41	99.35	106	65	24	105
	GZO 20 + Pt	10.02	16.03	96.11	99.01	106	79	66	100

4. Conclusions

In conclusion, we have demonstrated plasmonic gas sensing using the infrared surface plasmon resonance peak of degenerately doped semiconductors, specifically Pt-doped GZO. We elucidated the role of Pt dopant, combining the optical gas sensing data with electrical measurements. Moreover, by exposing the GZO film to blue light during the sensing tests, we achieved room temperature sensitivity to sub-ppm NO_2 concentrations. These very thin Pt-GZO films are optically transparent in the visible range and can be used as electrical and optical sensors for the detection of hazardous gases at low operating temperatures, paving the way to the fabrication of highly efficient, multifunctional "invisible" sensors.

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