Performance of alkali metal (Li/Na): ZnO thin films for NO2 gas sensing

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K. K. Jasmi; T. Anto Johny; V. S. Siril; K.N. Madhusoodanan

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Performance of Alkali Metal (Li/Na): ZnO Thin Films for NO_2 Gas Sensing

Jasmi K. K.[1, a)], Anto Johny T.[1], Siril V. S.[2], Madhusoodanan K. N.[2]

[1]*Department of physics, St. Thomas' college (autonomous), Thrissur-680001, India*
[2]*Department of Instrumentation, Cochin University of Science and Technology, Cochin-682022, India*

[a)] Corresponding author: *jasmifirdhouse@gmail.com*

Abstract. Metal Oxide Semiconducting (MOS) gas sensors based on ZnO are extensively explored due to their exceptional physicochemical properties. Here, prepared films were characterized through XRD, FESEM, and Hall measurements to verify the physical as well as electrical properties. NO_2 gas sensing performance of undoped and alkali-metal (Li/Na):ZnO films are evaluated. The operating temperature, sensitivity, and response/recovery time of prepared sensors towards nitrogen dioxide(NO_2) were conducted. Through a comparative analysis of NO_2 gas sensing activity of pure and 1 wt% of alkali metal (Li/Na) doped ZnO thin films. Lithium-doped ZnO sensors were found to exhibit higher sensitivity and rapid response/recovery time. Fabricated sensors detected NO2 test gas at 15 ppm, which is lower than the exposure limit (20 ppm). The gas sensing mechanism involving adsorption/desorption of the species on the surface of the sensor is also proposed.

INTRODUCTION

Air pollution caused mainly by rapid industrial development and urban migration. Gases emitted by industry byproducts and automobile exhaust have caused a major survival problem for all living things. Human activities and natural processes release around 48.8 terra grams of NO and NO_2 into the atmosphere every year[1]. Detection of NO_2 lower than the threshold exposure limit of 20 ppm is essential for developing gas sensors[2].

Zinc oxide (ZnO) is a favorable candidate in the field of semiconductors with excellent potential. ZnO is known to be an n-type semiconducting material with a large Exciton B.E(binding-energy) of 60 meV and broad band-gap of 3.2 eV at RT, chemical stability, biocompatibility, and good piezoelectric characteristics. Alkali metal doped Zinc oxide has found important applications in the Field of photodetector[3], photo catalytic, self-cleaning coatings[4], solar cell[5], light emitting diodes[6], gas sensors[7] etc. Alkali metal-doped ZnO thin film for NO_2 gas sensing application is rarely reported.

In this paper, pure and alkali metal-doped Li/Na:ZnO thin film gas sensors are synthesized by facile sol-gel spin-coating method. The crystal-structural and electrical properties are evaluated and correlated with the gas sensing mechanism of Li/Na:ZnO thin film gas sensors.

EXPERIMENTAL

In the presence of equimolar quantities of diethanolamine, zinc acetate dihydrate and lithium acetate dihydrate/sodium acetate trihydrate are dissolved in isopropyl alcohol to make a transparent solution. The prepared solution is spin-coated on a glass substrate. The substrate is thoroughly cleaned prior to coating to ensure the creation of high-quality films. The spin-coated substrate is dried at 150^0C for 20 minutes before being annealed in a tube furnace at 500^0 C for 30 minutes. All of the chemical reagents are of analytical quality and were acquired without further purification.

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RESULTS AND DISCUSSION

In the XRD spectra illustrated in Figure 1(a), no peak other than ZnO as per JCPDS card No 36-1451 are observed. Besides, the peak intensity of major diffraction peaks is reduced considerably by incorporating alkali metals (Li/Na). Reduction of crystallinity and intensity peaks recognized some distortion in ZnO lattice, which is higher in Na:ZO than ZLiO, due to the larger ionic radius of Na compared to that of Zn. Also, no significant shifts are observed in the peak position, as shown in Figure 1 (a)[7].

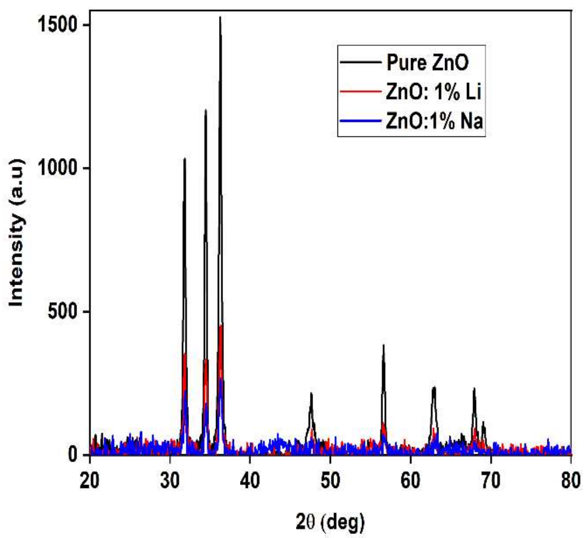

FIGURE 1. XRD pattern of Li/Na:ZnO thin films

The surface topographic study of Li/Na:ZnO thin films is characterized using the FESEM technique, depicted in Figure 2. FESEM analysis indicates the formation of spherical and irregular-shaped morphology having an average particle size in the range of 16.8 to 20.2 nm. FE-SEM image of 1%Li:ZnO sample consists of more porous and large number of voids are present compared with other prepared thin film samples, which act as an active site for test gas[8].

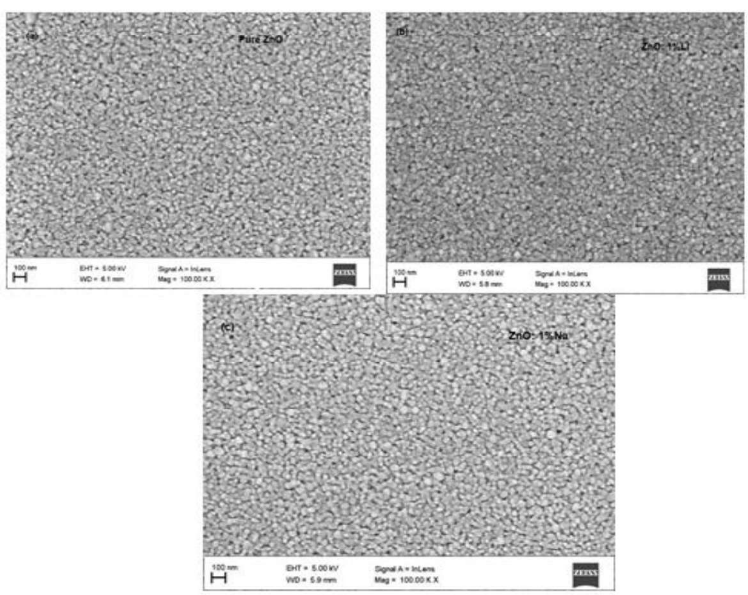

FIGURE 2. FE-SEM image of Li/Na:ZnO thin films

All the prepared thin film samples exhibit *n*-type conductivity. In Li/Na:ZnO, the dopant can enter into an interstitial site is the cause of showing n-type conductivity. 1%Li: ZnO show low resistivity, and high carrier density leads to good sensitivity towards the test gas. It is also correlated with structural studies.

TABLE 1. Gas-sensing and Electrical parameters of Li/Na:ZnO thin films

Thin Film	Carrier-Density(cm^{-3})	Mobility($cm^2V^{-1}s^{-1}$)	Resistivity (Ω-cm)	Type	Sensitivity (Rg/Ra)	Response/ Recovery time (Second)
(a) Pure ZnO	$2.25x10^{15}$	1.94	$1.42x10^{3}$	*n*	10.89	19/16
(b) ZnO: 1%Li	$5.13x10^{16}$	2.02	$6.02x10^{1}$	*n*	33.84	7/19
(c) ZnO: 1% Na	$1.51x10^{16}$	0.7	$5.88x10^{2}$	*n*	17.94	19/42

The prepared samples were subjected to the NO_2 gas of 15ppm concentration at 210^0C, the sensitivity-time plot, as shown in figure 3(a)[9]. Repeatability of the gas sensors are the major factor for the device applications. Repeatability of Li:ZnO thin film sample is illustrated in figure 3(b). Sensitivity and response/recovery time of the prepared samples are shown in Table1.

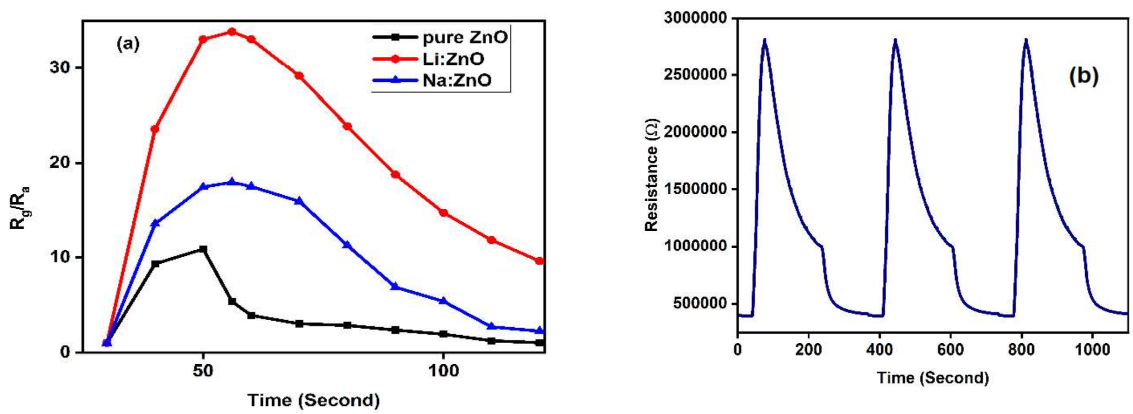

FIGURE 3. (a) Dynamic Response-time plot at 15 ppm for NO_2 gas of Li/Na:ZnO thin film gas sensors and (b) cyclic graph of Li:ZnO thin film sensor

The interaction between the surface of the sensor material and gas molecules describes the gas sensing mechanism[10]. The gas sensing method is affected by a number of elements, including, the operating temperature the number of oxygen species, the type of the test gas (oxidizing or reducing), and so on[11]. When thin film samples are exposed to air, oxygen molecules the rate of adsorption/desorption are adsorbed onto the surface of prepared thin film sensors, as a result, an adsorbed layer of oxygen anions forms. Adsorption occurs when electrons are extracted from the conduction band. This causes the depletion zone to appear on the surface prepared thin film samples, leads to an increase in electrical resistance. When oxidizing gas, like NO_2 gas, are exposed to the surface of Li/Na:ZnO additional NO_2 gas molecules are readily adsorbed on the surfaces of the prepared gas sensors. It is owing to the existence of voids and porous structure disclosed by FE-SEM and (ii) an adequate quantity of electrons revealed by the Hall measurement system for all manufactured samples. NO_2 is a powerful electrophile that takes electrons from the conduction band through the reaction (1) to (3).

$$NO_{2(gas)} \leftrightarrow NO_{2(ads)} \quad (1)$$

$$NO_{2(ads)} + e^- \leftrightarrow NO^-_{2(ads)} \quad (2)$$

$$NO_{2(ads)} + O^-_{2(ads)} + 2e^- \leftrightarrow NO^-_{2(ads)} + 2O^-_{(ads)} \quad (3)$$

Due to the porous structure and low resistance, ZLiO possesses the highest sensitivity and fastest response/recovery time of any prepared thin-film sensor. ZLiO gas sensors are a viable choice for building practical NO_2 gas detecting devices due to their shorter response/recovery durations and good sensing response at low optimum temperature.

CONCLUSION

We prepared pure and alkali metal-doped ZnO thin film gas sensors for NO2 detecting using a simple sol-gel spin coating process. Gas sensing investigations on NO2 were conducted for all fabricated gas sensors, and it was observed that the more porous, with a large number of voids, and low resistive Li doped ZnO based gas sensor displayed a response of 33.84 to 15 ppm NO2 gas at 210°C. Furthermore, it demonstrated a surprising swift response/recovery time at the same time. The increased gas sensing response was ascribed to the large surface area created by the development of nano-scale pores, as well as the presence of ZnO/ZMO thin film sensors.

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