Inversion of NH\textsubscript{3} sensor signal and paramagnetic centers of nanocrystalline ZnO(Ga)

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Abstract

Inversion of nanocrystalline ZnO(Ga) sensor signal during ammonia detection is reported for the first time. In the middle temperature region (250-300°C) the presence of ammonia in air results in increase of resistance. Comparative EPR study and dc conductance measurements allows to attribute this effect to changes in donor and acceptor defect concentration.

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1. Introduction

Zinc oxide is a promising functional wide-gap semiconductor with unique optical and electrical properties. Materials based on zinc oxide are intensively investigated for using as optoelectronic transducers and transparent electrodes. Of particular interest is the possibility to create ZnO based materials for highly sensitive and selective gas sensors of resistive type. Currently, the most studied matter is doped zinc oxide, which provides an opportunity to regulate the electrical properties over a wide range: to manufacture the materials of \textit{p}-type conductivity by doping with acceptor impurities (N, P, As, Sb) or to increase the concentration of electrons by doping with donor impurities (Al, In, Ga). In this work we demonstrate for the first time the inversion of nanocrystalline ZnO(Ga) sensor signal during ammonia detection. The switching from \textit{n}- to \textit{p}- type response was reported for the different oxides: MoO\textsubscript{3}, In\textsubscript{2}O\textsubscript{3}, doped SnO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3} [1]. Authors [1] attribute this phenomenon to the oxygen adsorption and
formation of an inversion layer, which changes the type of mobile carrier at the surface. In present work we discuss this effect for nanocrystalline ZnO(Ga) during NH₃ detection in relation with donor and acceptor defect concentration.

2. Experimental

Nanocrystalline zinc oxide powders with different Ga content \([\text{Ga}] / ([\text{Ga}]+[\text{Zn}]) = 0 \div 10\ \text{at.}\%\) were synthesized by calcining (at 250, 500, 750°C) precursors prepared from Zn(NO₃)₂, Ga(NO₃)₃ and NH₄HCO₃ solutions by co-precipitation method. Gallium content was measured by ICP-MS and ICP-OES. Materials were characterized by means of XRD, TEM and BET. Electron paramagnetic resonance (EPR) spectra were recorded at 298 K using ELEXSYS-580 (Bruker) instrument (X-band, sensitivity is \(~10^{10}\text{spin/G}\)).

The sensor responses to NO₂, H₂S, NH₃ were assessed from in situ dc conductance measurements on thick films. The powders were deposited in the thick films form on microelectronic chips with interdigital Pt electrodes and Pt meander as heater. Sensor signals \(S\) were calculated as:

\[
S = \frac{(G_{\text{gas}} - G_{\text{air}})}{G_{\text{air}}} \quad \text{or} \quad S = \frac{(R_{\text{gas}} - R_{\text{air}})}{R_{\text{air}}},
\]

where \(G_{\text{gas}}\) – conductance of the sample in the presence of reducing gas (H₂S, NH₃), \(G_{\text{air}}\) – conductance in pure air, \(R_{\text{gas}}\) – resistance of the sample in the presence of NO₂, \(R_{\text{air}}\) – resistance in pure air.

3. Results and discussion

All samples annealed at 250°C consist of nanocrystalline ZnO (wurtzite) phase. The ZnGa₂O₄ secondary phase was detected only for the sample with the highest gallium content (7.5 at.%) and annealing temperature 750°C. The ZnO grain size decreases from 10-12 nm for pure ZnO to 5-7 nm for 9.5 at.% Ga-doped samples annealed at 250°C. The specific surface area of the synthesized materials increases with Ga content from 43 ± 5 to 93 ± 5 m²/g.

The sensor responses to NO₂ and H₂S are typical for \(n\)-type semiconductor. In the presence of H₂S (reducing gas) in air the resistance decreases. Temperature dependence of sensor signal in the range 100-450°C has maximum at 250-300°C (Fig. 1(a)). The increase of gallium content leads to the decrease of sensor signal towards H₂S. This effect we attribute to the increase of Lewis acidity of ZnO(Ga) surface causing the difficulties for heterolytic break of H – S bond in H₂S molecule [2].

In the presence of NO₂ in air the resistance increases. The optimal temperature is 250°C for all samples (Fig. 1(b)). The dependence of the ZnO(Ga) sensor signal on the gallium content has non-monotinous character. The increase of Ga concentration up to 1.2 at.% is accompanied by the sensor signal growth. This may be due to the increase in the concentration of electrons that can be captured by a molecule of nitrogen dioxide during adsorption on the surface of nanocrystalline materials. The reducing of sensor signal at higher gallium concentration correlates with the change of resistance of the samples in air: the largest signal is observed for the samples with the lowest resistance in air. This indicates the role of electronic factor in sensor sensitivity.

In the case of NH₃ detection the direction of resistance change of ZnO(Ga) depends on operating temperature (Fig. 2(a)). At low (80-150°C) and high (400-450°C) temperatures it correlates with \(n\)-type behavior but at 250-300°C the presence of NH₃ in air results in the increase of the resistance. So the temperature dependence of sensor response calculated using eq. (1) has an area of “negative” values corresponding to \(p\)-type sensor behavior (Fig. 2(b)). This phenomenon is seen for all undoped and doped ZnO samples. The absolute value of sensor signal \(S\) increases with ammonia concentration for all temperatures (Fig. 3).
Fig. 1. Sensor response of ZnO(Ga) materials annealed at 250°C to 2 ppm H₂S (a) and 2 ppm NO₂ (b) as a function of operating temperature and gallium content.

Fig. 2. (a) The resistance response of 1.2 at.% Ga-doped ZnO (annealed at 250°C) at various operating temperatures (18 ppm NH₃); (b) The temperature dependence of sensor response S to 18 ppm NH₃ calculated using eq. (1): (1) – undoped ZnO annealed at 250°C; (2) – 0.5 at.% Ga-doped ZnO annealed at 250°C; (3) – 0.5 at.% Ga-doped ZnO annealed at 750°C.

The EPR study of ZnO(Ga) samples before and after NH₃ treatment at 100 and 300°C for 1 h was performed. In as-prepared sample two types of paramagnetic centers with $g = 1.96$ (I, $2.4 \times 10^{19}$ g⁻¹) and $g_1 = 2.022$, $g_2 = 2.013$, $g_3 = 2.0026$ (II, $1.6 \times 10^{16}$ g⁻¹) are observed (Fig. 4). The signals (I) and (II) can be attributed to single ionized oxygen vacancies [3] and $O_2^-$-radicals [4], respectively. Annealing in NH₃ at 100°C results in increase of oxygen vacancies concentration ($4.7 \times 10^{19}$ g⁻¹) which can be explained by oxidation of NH₃ by chemisorbed oxygen and decrease of oxygen concentration on surface. The signal from $O_2^-$-radicals is still observed. However NH₃ treatment at 300°C leads to decrease of oxygen vacancies concentration ($1.0 \times 10^{19}$ g⁻¹) and appearance of new signal ($g_1 = 2.0024$, $g_2 = 1.99$, $8 \times 10^{15}$ g⁻¹), attributed to $N_2^-$-radicals [5], instead of $O_2^-$-radicals. Formation of $N_2^-$-radicals can be indirect evidence of nitrogen presence in ZnO crystal structure. It is known that $N_2$ is considered to be a shallow $p$-type dopant for ZnO but N-acceptors are greatly compensated by N₂ molecules at oxygen sites [6]. The possibility to obtain the $p$-type N-doped ZnO during annealing in NH₃ was already demonstrated [7]. So the observed inverse sensor signal during ammonia detection may be connected with decrease of
concentration of intrinsic donor defects – oxygen vacancies and increase of quantity of generated $N_O$ acceptors in surface layer of zinc oxide.

Fig. 3. Sensor response of 0.5 at.% Ga-doped ZnO (annealed at 750°C) as a function of NH$_3$ concentration in air at different operating temperatures.

Fig. 4. EPR spectra of 0.5 at.% Ga-doped ZnO (annealed at 750°C) as-prepared (1) and after NH$_3$ treatment at 100°C (2) and 300°C (3) for 1 h.

4. Conclusions

Sensor properties of nanocrystalline ZnO(Ga) towards NO$_2$, H$_2$S and NH$_3$ were studied. The inversion of sensor signal during ammonia detection was observed for the first time. The EPR experiments allow attributing this effect to changes in donor $V'_O$ and acceptor $N_O$ defect concentration.

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References