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# Gas—sensing properties of $In_2O_3-Ga_2O_3$ alloy films

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The effect of the gaseous medium composition on the electrically conductive properties of $In_2O_3-Ga_2O_3$ films obtained by halide vapor phase epitaxy has been studied. In the temperature range of 100−550°C, the $In_2O_3-Ga_2O_3$ films exhibit high sensitivity to $H_2$, $NH_3$ and possess hyphen performance and low base resistance. A qualitative mechanism for the sensitivity of $In_2O_3-Ga_2O_3$ films to gases is proposed.

**Keywords:** $In_2O_3-Ga_2O_3$, halide vapor—phase epitaxy, gas sensitivity.

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Films of semiconductor metal oxides are widely used in gas sensors [1,2]. Conventionally, both *n*-type oxides ($SnO_2$, ZnO, $TiO_2$, $\alpha$-$Fe_2O_3$, $WO_3$) and *p*-type oxides (CuO, NiO, $Cr_2O_3$, $Co_3O_4$) are used. Earlier we have reported on gas sensors based on $Ga_2O_3$ [3,4]. Indium oxide $In_2O_3$ is also a promising material for gas sensors highly sensitive to low concentrations of CO, $O_3$, $NO_x$ [5,6].

One of the ways of improving the sensitivity and selectivity of semiconductor gas sensors is to use mixtures and alloys of various oxides. The possibility of varying electrophysical properties of a semiconductor by varying its composition offers opportunities for developing new functional materials for sensory systems [7]. Alloys of $In_2O_3-Ga_2O_3$ are of interest in view of their application in gas sensors because it is possible to control their band gap width, as well as chemical and electrophysical properties, by varying their component composition.

Paper [8] has shown that, other things being equal, $In_2O_3-Ga_2O_3$ nanowires exhibit higher responses to $C_2H_5OH$ and $NO_2$ than pure $In_2O_3$ nanowires. Work [9] was devoted to studying hyphen properties of oxide composites $In_2O_3-Ga_2O_3$ with the gallium oxide content of 1−8 wt.%. Sensors based on $In_2O_3-Ga_2O_3$ (1 wt.% $Ga_2O_3$) exhibited a higher response than sensors based on pure $In_2O_3$. Authors of [10] have studied hyphen properties of thin $Ga_2O_3-In_2O_3$ films obtained by magnetron sputtering of a target made of eutectic Ga−In alloy (76% Ga−24% In). As compared with the $Ga_2O_3$-based films, the $In_2O_3-Ga_2O_3$ ones exhibited similar characteristics under the action of $C_2H_5OH$, $C_3H_6O$ and $NH_3$, but their operating temperature $T$ was lower. It was also reported that sensors based on the 50% $In_2O_3$−50% $Ga_2O_3$ films are highly selective to $NH_3$ [11]. Gas sensors based on $In_2O_3-Ga_2O_3$ films (96 : 4 wt.%) on hyphen substrates demonstrated a high sensitivity to $C_3H_8-C_4H_{10}$ and $C_4H_{10}$ at $T = 250°C$ [12].

This paper is devoted to investigation of sensitivity of the $In_2O_3-Ga_2O_3$ films electrical resistance to various gases in temperature range $T = 30-550°C$.

The $In_2O_3-Ga_2O_3$ films 0.5 $\mu$m thick were obtained by halide epitaxy (HVPE) on sapphire substrates [13,14]. Substances $InCl_3$, GaCl and $O_2$ were used as precursors. The film growth temperature was 625°C. Nominal Ga concentration under the given growth conditions was about 10 at.%. The film surface morphology was studied by scanning electron microscopy (SEM); chemical and phase compositions were analyzed by hyphen halide spectroscopy (EDS) and X−ray diffraction (XRD), respectively.

Analysis of XRD patterns of the $In_2O_3-Ga_2O_3$ films did not reveal peaks associable with $(In_xGa_{1-x})_2O_3$. However, reflexes from (222), (444), (004), (008) and (322) planes corresponding to cubic $c$-$In_2O_3$ were observed. The same feature of $In_2O_3-Ga_2O_3$ was noticed in [15] where composites with large contents of $Ga_2O_3$ were studied.

SEM images have shown that the obtained $In_2O_3-Ga_2O_3$ films have a grain structure with developed surface. Grain diameter $D_g$ is comparable with the film thickness. Individial crystallites with triangular and square faceting are well distinguishable on the film surface; their lateral size is up to 1 $\mu$m, while height is comparable with the film thickness. EDS analysis revealed the presence of In, Ga and O in concentrations close to the nominal ones. In addition, EDS spectra demonstrated the presence of Al which is, evidently, originating from the sapphire substrate.

The experimental results, including the XRD diffraction pattern and SEM image of the surface, are described in detail in our earlier paper [13]; this paper also presents the data analysis.

On the film surfaces, Pt contacts were formed at $150\,\mu$m distance from each other. After that, the wafers were cut into chips of $1.2 \times 1.3$ mm in size. Volt–ampere (I–V) characteristics and time dependences of the sample resistance were measured under dark conditions in pure air or in a gas mixture of a target gas with pure air. The films sensetivity to $H_2$, $NH_3$, CO, $NO_2$ and $CH_4$ were studied. The equipment used to study the gas influence. Electrical conductive properties of the films was described in [3].

The studied structures exhibited purely resistive behavior; I–V characteristics measured in air remained linear in the voltage range $U = 0-5$ V and temperature range $T = 30-550°$C. The gas impacts led to variations in I–V characteristic slopes free of any peculiarities. In pure dry air, the $In_2O_3-Ga_2O_3$ films are characterized by low resistance $R_{air}$. Specific resistance of one of the samples in pure dry air decreases from $2.80 \cdot 10^{-5}$ to $1.02 \cdot 10^{-5}\,\Omega \cdot$cm with $T$ increasing from 30 to 300°C; after that, it increases up to $1.31 \cdot 10^{-5}\,\Omega \cdot$cm with further increase in $T$ to 550°C. Exposure to reducing gases ($H_2$, $NH_3$, CO and $CH_4$) resulted in reversible decrease in resistance $R$ of the $In_2O_3-Ga_2O_3$ films. Vice versa, the action of oxidizing gas ($NO_2$) caused reversible increase in resistance $R$. As the measure of response, we used the $(\Delta R/R_g) \cdot 100\%$ ratio, where $\Delta R = |R_{air} - R_g|$, $R_g$ is the film resistance in the mixture of the target gas with pure air. Values of $R_{air}$ and $R_g$ were derived from hyphen sections of time dependences of film resistances in pure dry air and gas the mixture of the target gas with pure air. Responses of the structures were measured at $U = 2$ V.

When $T$ increases, the response first increases up to its maximum at $T_{max}$, and then decreases (Fig. 1). The $T_{max}$ values under the influence of $H_2$, $NH_3$ and CO were 400°C; those upon exposure to $CH_4$ and $NO_2$ were 450 and 250°C, respectively. The highest responses were observed for $H_2$, $NH_3$ and CO; therefore, further investigation of hyphen

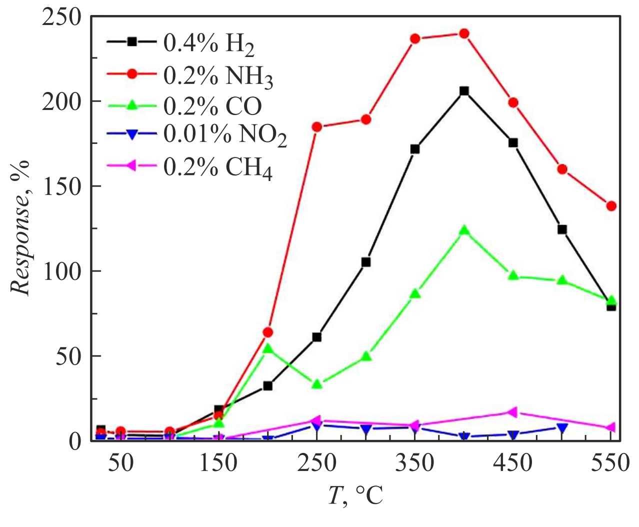


**Figure 1.** Temperature dependences of the $In_2O_3-Ga_2O_3$ film responses to different concentrations of $H_2$, $NH_3$, CO, $NO_2$ and $CH_4$.

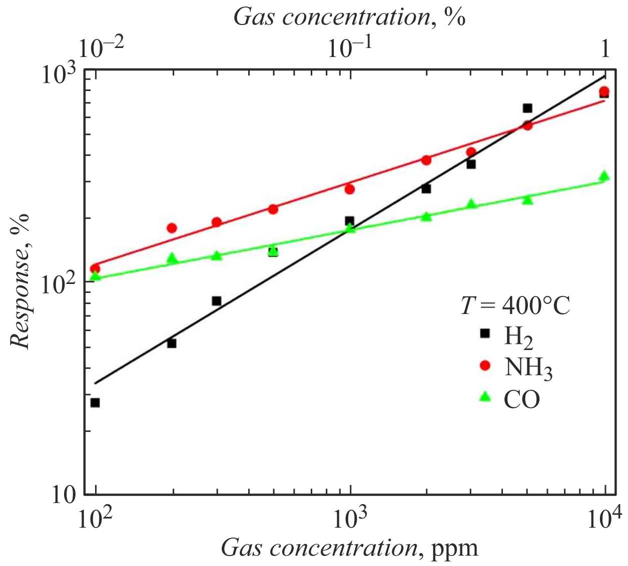


**Figure 2.** Dependences of the $In_2O_3-Ga_2O_3$ film responses at $T = 400°$C on the $H_2$, $NH_3$ and CO concentrations.

properties of the $In_2O_3-Ga_2O_3$ films was performed under the action of just those gases. The gas concentration dependences of the responses are describable by power functions and become linear when plotted in log-log scales (Fig. 2). Exponents for $H_2$, $NH_3$ and CO at $T = 400°$C are $0.72 \pm 0.03$, $0.38 \pm 0.02$ and $0.21 \pm 0.01$, respectively. Fig. 3 presents time dependences of the $In_2O_3-Ga_2O_3$ film resistance at $T = 400°$C for the case of cyclic six-time exposure to $H_2$, $NH_3$ and CO. The $R_{air}$ and $R_g$ deviations from mean values did not exceed 1.5, 0.2 and 6% under the action of $H_2$, $NH_3$ and CO, respectively. In hyphen testing at the same $T$ and gas concentrations, when the samples were stored in airtight packing and measurements were performed during two weeks with intervals of 1–2 days, there was observed an increase in responses by 1.7, 1.5 and 1.35 times upon exposure to $H_2$, $NH_3$ and CO, respectively; the main reason for this was a decrease in $R_g$. The most significant increase in $R_g$ and response took place during the first five days of testing. The response time $t_{res}$ was measured as a time interval between the onset of the respective gas mixture impact upon the film and the moment of resistance drop to $1.1R_g$. Recovery time $t_{rec}$ was measured as a time interval between the moment of starting purging the test chamber with pure air and moment of the resistance growth up to $0.9R_{air}$. The table presents the $t_{res}$ and $t_{rec}$ values at $T = 400°$C and fixed gas concentrations. Being exposed to $NH_3$ and CO, the films are characterized by short response times $t_{res}$ and long recovery times $t_{rec}$. The highest performance speed was observed with exposure to $H_2$. It is worth noting that $t_{res}$ and $t_{rec}$ include the time necessary to achieve the stationary state of the test chamber atmosphere.

The drop and rise sections of the time dependences of resistance (Fig. 3) may be approximated by two power

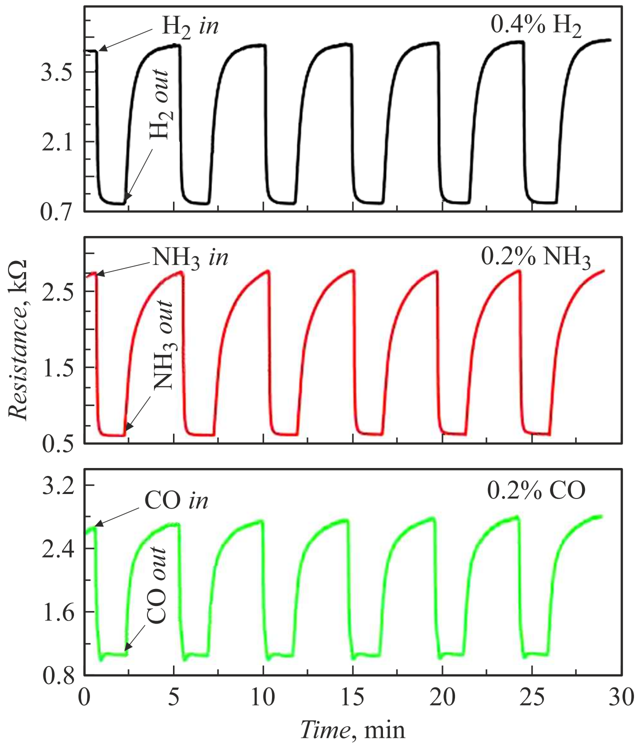


**Figure 3.** Time dependences of the $In_2O_3-Ga_2O_3$ film resistances under six-time exposure of $H_2$, $NH_3$ and CO. $T = 400°C$.

Response and recovery times the $In_2O_3-Ga_2O_3$ films upon exposure to $H_2$, $NH_3$ and CO ($T = 400°C$)

| Time | Gas | | |
|---|---|---|---|
| | $H_2$ (0.4%) | $NH_3$ (0.2%) | CO (0.2%) |
| $t_{res}$, s | 21 | 15.5 | 17 |
| $t_{rec}$, s | 58.8 | 90.0 | 90 |

functions with different time constants. The biexponential character of the time dependences of film resistance evidences for the existence of two processes occurring during the gas molecule adsorption on the $In_2O_3-Ga_2O_3$ surface. The first (fast) process is induced by chemisorption of gas molecules on the semiconductor surface, while the second one is, as per [7], caused by interaction between gas molecules and crystal lattice oxygen ($O^s_{lat}$) in the semiconductor near−surface near-surface region. When electron concentration in the $In_2O_3-Ga_2O_3$ films is $\sim 10^{18}\,cm^{-3}$ [16], the Debye length is significantly lower than $D_g$, which is characteristic of the hyphen conductivity mechanism. On the semiconductor grain boundaries there is a potential barrier $e\varphi_s$ for electrons, where $e$ is the electron charge, $\varphi_s$ is the surface potential. In air, oxygen gets chemisorbed on the surface of $n$-type semiconductors (to which $In_2O_3-Ga_2O_3$ belongs) with capturing electrons from the conduction band and forming near-surface region an hyphen region near the surface. Emergence of negatively charged oxygen ions on the $In_2O_3-Ga_2O_3$ surface causes upward band bending with $e\varphi_s \propto N_i^2$ [17,18]. At $T \geqslant 150°C$, the atomic form of chemisorbed oxygen $O^-_{(c)}$ prevails on the $In_2O_3$ surface [19]. It is reasonable to assume that this is valid also for the $In_2O_3-Ga_2O_3$ films. The film resistance is $R = R_0 \exp[e\varphi_s/(kT)]$ [17,18], where $R_0$ is the parameter defined by geometrical sizes of the semiconductor film and grains, as well as by the film electrophysical properties slightly depending on the surface electrical state; $k$ is the Boltzmann constant. The oxygen chemisorption leads to an increase in $e\varphi_s$ and $R$. The presence of the potential barrier on the grain boundaries should manifest istelf as a nonlinearity of I–V characteristic which is indeed observed at $U > 5$ V. It is noticed [20,21] that at $U = 0-5$ V I–V characteristics of low−resistance ITO (indium tin oxide) films and hyphen $SnO_2$ films are nonlinear and symmetric in case of the hyphen conductivity mechanism. We assume that the following reactions occur on the $In_2O_3-Ga_2O_3$ surface under the action of reducing gases [17,18]:

$$H_2 + O^-_{(c)} \rightarrow H_2O + e,$$

$$2NH_3 + 3O^-_{(c)} \rightarrow N_2 + 3H_2O + 3e,$$

$$CO + O^-_{(c)} \rightarrow CO_2 + e.$$

As a result of these reactions, $N_i$, $e\varphi_s$ and $R$ increase, electrons enter the $In_2O_3-Ga_2O_3$ film conduction band, and reaction products desorb from the surface as $H_2O$, $N_2$ and add space. For example, let us consider an interaction between $H_2$ and $O^s_{lat}$:

$$H_2 \leftrightarrow 2H,$$

$$H + S_a \rightarrow H^+ + S_a^-,$$

$$H^+ + O^s_{lat} \rightarrow OH + V_O^+,$$

where $S_a$ is the free adsorption center whose role may be played by hyphen metal atoms, $S_a^-$ is the adsorption center with an electron localized in it, $V_O^+$ is the oxygen vacancy. Reaction with $O^s_{lat}$ results in formation of a neutral OH-group that desorbs from the film surface, and in an increase in concentration of $V_O^+$ which, while diffusing into the semiconductor bulk, act as electron donors and cause a decrease in $R$. It is worth noting that processes associated with interaction between gas molecules and $O^s_{lat}$ followed by diffusion of $V_O^+$ may cause significant variations in the film $R$ and response in hyphen testing [22].

Earlier we have studied the gas sensitivity of 0.5 $\mu$m thick $\varepsilon(\kappa)$-$Ga_2O_3$ films obtained by the HVPE method [3]. As compared with those films, $In_2O_3-Ga_2O_3$ is characterized by higher responses to $H_2$, $NH_3$ and CO which are detected in a wider temperature range (beginning from 100°C). In addition, in contrast to other resistive sensors based on hyphen semiconductors, $In_2O_3-Ga_2O_3$ films possess low base resistance $R_{air}$, which is attractive in view of developing hyphen and reliable systems for acquiring and processing data from sensors fabricated based on this material. The high base resistance of the hyphen sensors is often associated with their high gas sensitivity. This prohibits integration of hyphen sensors with microcontrollers and other hyphen components fabricated using conventional microelectronic CMOS and MEMS techniques, mainly because of difficulties in measuring low currents and/or ensuring accuracy of these measurements [23–25].

The study has established high sensitivity of electrical resistance of HVPE $In_2O_3-Ga_2O_3$ films to $H_2$, $NH_3$ and CO gasses in a wide temperature range of 100 to 550°C. The maximal response to these gases is observed at 400°C. Among all the gases tested in this study, the films show the highest performance speeds when exposed to $H_2$ Resistances of the $In_2O_3-Ga_2O_3$ films in air and under the action of gases are characterized by a low drift in case of multiple exposure to gases. A mechanism for the film gas sensitivity has been suggested. The $H_2$, $NH_3$ and CO molecules are assumed to interact not only with hyphen oxygen but also with the hyphen oxygen on the semiconductor surface.

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### Conflict of interests

The authors declare that they have no conflict of interests.

## References

[1] M.V. Nikolic, V. Milovanovic, Z.Z. Vasiljevic, Z. Stamenkovic, Sensors, **20**, 6694 (2020). DOI: 10.3390/s20226694

[2] N. Vorobyeva, M. Rumyantseva, V. Platonov, D. Filatova, A. Chizhov, A. Marikutsa, I. Bozhev, A. Gaskov, Nanomaterials, **11**, 2938 (2021). DOI: 10.3390/nano11112938

[3] A. Almaev, V. Nikolaev, P. Butenko, S. Stepanov, A. Pechnikov, N. Yakovlev, I. Sinyugin, S. Shapenkov, M. Scheglov, Phys. Status Solidi B, **259**, 2100306 (2022). DOI: 10.1002/pssb.202100306

[4] A.V. Almaev, E.V. Chernikov, V.V. Novikov, B.O. Kushnarev, N.N. Yakovlev, E.V. Chuprakova, V.L. Oleinik, A.D. Lozinskaya, D.S. Gogova, J. Vac. Sci. Technol. A, **39**, 023405 (2021). DOI: 10.1116/6.0000723

[5] G. Neri, A. Bonavita, G. Micali, G. Rizzo, E. Callone, G. Carturan, Sensors Actuators B, **132**, 224 (2008). DOI: 10.1016/j.snb.2008.01.030

[6] H. Yamaura, K. Moriya, N. Miura, N. Yamazoe, Sensors Actuators B, **65**, 39 (2000). DOI: 10.1016/S0925-4005(99)00456-6

[7] M.C. Carotta, A. Fioravanti, S. Gherardi, C. Malagú, M. Sacerdoti, G. Ghiotti, S. Morandi, Sensors Actuators B, **194**, 195 (2014). DOI: 10.1016/j.snb.2013.12.021

[8] E. López-Aymerich, G. Doménech-Gil, M. Moreno, P. Pellegrino, A. Romano-Rodriguez, Sensors, **21**, 3342 (2021). DOI: 10.3390/s21103342

[9] Yu.S. Gayduk, M.S. Okhmanyuk, A.A. Savitsky, I.A. Taratyn, Vestn. BGU. Ser. 2., № 3, 8 (2015). (in Russian) https://elib.bsu.by/handle/123456789/158895

[10] A.G. Kozlov, O.V. Krivozubov, E.A. Kurdukova, M.N. Lila, in *2012 28th Int. Conf. on Microelectronics Proceedings* (IEEE, 2012), p. 165. DOI: 10.1109/miel.2012.6222824

[11] I.E. Demin, A.G. Kozlov, AIP Conf. Proc., **2007**, 050004 (2018). DOI: 10.1063/1.5051948

[12] M.S. Aleksanyan, V.M. Arakelyan, V.M. Aroutiounian, G.E. Shahnazaryan, J. Contemp. Phys., **46**, 86 (2011). DOI: 10.3103/s1068337211020071

[13] S. Stepanov, V. Nikolaev, A. Pechnikov, M. Scheglov, A. Chikiryaka, A. Chernykh, M. Odnobludov, V. Andreeva, A.Y. Polyakov, Phys. Status Solidi A, **218**, 2000442 (2021). DOI: 10.1002/pssa.202000442

[14] V.I. Nikolaev, A.I. Pechnikov, L.I. Guzilova, A.V. Chikiryaka, M.P. Shcheglov, V.V. Nikolaev, S.I. Stepanov, A.A. Vasil'ev, I.V. Shchemerov, A.Ya. Polyakov, Tech. Phys. Lett., **46**, 228 (2020). DOI: 10.1134/S106378502003013X.

[15] G. Korotcenkov, Iu. Boris, V. Brinzari, S.H. Han, B.K. Cho, Yu.N. Lychkovsky, Ceram. Int., **41**, 7478 (2015). DOI: 10.1016/j.ceramint.2015.02.069

[16] A. Papadogianni, T. Nagata, O. Bierwagen, Jpn. J. Appl. Phys., **61**, 045502 (2022). DOI: 10.35848/1347-4065/ac4ec7

[17] N. Yamazoe, K. Shimanoe, J. Sensors, **2009**, 875704 (2009). DOI: 10.1155/2009/875704

[18] V.I. Gaman, Russ. Phys. J., **51**, 425 (2008). DOI: 10.1007/s11182-008-9065-7.

[19] M.N. Rumyantseva, E.A. Makeeva, S.M. Badalyan, A.A. Zhukova, A.M. Gaskov, Thin Solid Films, **518**, 1283 (2009). DOI: 10.1016/j.tsf.2009.07.201

[20] C.-W. Lin, H.-I. Chen, T.-Y. Chen, C.-C. Huang, C.-S. Hsu, R.-C. Liu, W.-C. Liu, Sensors Actuators B, **160**, 1481 (2011). DOI: 10.1016/j.snb.2011.07.041

[21] V.V. Simakov, O.V. Yakusheva, A.I. Grebennikov, V.V. Kisin, Tech. Phys. Lett., **31**, 339 (2005). DOI: 10.1134/1.1920390.

[22] G. Korotcenkov, B.K. Cho, Sensors Actuators B, **156**, 527 (2011). DOI: 10.1016/j.snb.2011.02.024

[23] J.L. Merino, S.A. Bota, R. Casanova, A. Dieguez, C. Cane, J. Samitier, IEEE Trans. Instr. Meas., **53**, 1173 (2004). DOI: 10.1109/TIM.2004.831459

[24] D. Barrettino, M. Graf, S. Taschini, S. Hafizovic, C. Hagleitner, A. Hierlemann, IEEE Sensors J., **6**, 276 (2006). DOI: 10.1109/JSEN.2006.870156

[25] A. Lombardi, M. Grassi, P. Malcovati, S. Capone, L. Francioso, P. Siciliano, A. Baschirotto, Sensors Actuators B, **142**, 82 (2009). DOI: 10.1016/j.snb.2009.07.030