Effect of composition on properties of In$_2$O$_3$–Ga$_2$O$_3$ thin films

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Abstract. The In$_2$O$_3$–Ga$_2$O$_3$ mixed oxide polycrystalline thin films with various ratios of components were obtained by pulsed laser deposition. The effect of films composition on surface morphology, electrophysical and gas sensing properties and energies of adsorption and desorption of combustible gases was studied. The films with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition showed maximum gas response (~25 times) combined with minimum optimal working temperature (~530 °C) as compared with the other films. The optical transmittance of the films in visible range was investigated. For 50%In$_2$O$_3$–50%Ga$_2$O$_3$ films, the transmittance is higher in comparison with the other films. The explanation of the dependency of films behaviors on their composition was presented. The In$_2$O$_3$–Ga$_2$O$_3$ films were assumed to have perspectives as gas sensing material for semiconducting gas sensors.

1. Introduction

Oxides of transition metals have various applications. Some examples are semiconductor gas sensors and conductive transparent films. Semiconductor gas sensors, are actually one of the most investigated groups of gas sensors. They are low cost, have considerable long-term stability, provide a variety of detectable gases and able to operate in harsh environments [1]. All these advantages allow one to use semiconductor gas sensors in numerous fields [2].

An important trend in a field of semiconductor gas sensor research is the finding of novel gas sensing materials [3]. One of the achievements on that way is the use of mixed metal oxides. The main idea of that method is based on fundamental principle of the resistance variation of the sensing layer. It involves two important functions: the recognition and the transducer function. The recognition includes all the interactions between gas and solid. The transducer function is responsible for transformation of the chemical stimulus into an electrical signal.

The most accepted explanation of mixed oxide gas sensing performance is the separation of those functions between two parts of the compound system [3]. One part of multicomponent system may be responsible for recognition having very high reactivity to target gas while the second part takes over the transducer duties. This effective combination allows optimizing both functions simultaneously, which lead to a possibility of sensors sensitivity increase [4].

The production of multicomponent films requires a technique with a good control and reproducibility of parameters of resulting films [5]. The pulsed laser deposition (PLD) method used in the present study satisfies these requirements very well. The uniform distribution of components in prepared films and low growth rates (5–10 nm/min) allow achieving very high reproducibility of a sensing element. Another important advantage of the PLD is the stoichiometric transfer of material from sputtering target to substrate, which enables very precise control over the composition of the film [6].
A huge variety of mixed oxides are employed as sensing materials in semiconductor gas sensors [1, 4, 7]. Some well-known examples are In$_2$O$_3$–SnO$_2$ (ITO), In$_2$O$_3$–Ga$_2$O$_3$–ZnO (IGZO), ZnO–SnO$_2$, SnO$_2$–WO$_3$ and many others. The In$_2$O$_3$–Ga$_2$O$_3$ films among them are poorly investigated although they have good gas sensing properties [7, 8]. Most of the available data show possibility of their application as conductive transparent films [9–11]. In [8] there is a study on gas sensing properties of In$_2$O$_3$–Ga$_2$O$_3$ thin films made by magnetron sputtering from In-Ga eutectic alloy followed by annealing in air. Also there are results [12] on agglomerative single-electrode gas sensors with In$_2$O$_3$–Ga$_2$O$_3$ sensing layer, coated on a platinum spiral from In(OH)$_3$, Ga(OH)$_3$ sols. However, while perspectives of In$_2$O$_3$–Ga$_2$O$_3$ thin films in a field of gas sensing are clearly marked, there is insufficient information to date on the electrical and gas sensing properties and methods of their production.

The aim of this paper is the study of electrophysical, optical and gas-sensing properties of In$_2$O$_3$–Ga$_2$O$_3$ thin films (made by PLD) with different ratios of components. Gas induced resistance response was investigated for the following combustible gases: alcohol, acetone, ammonia and liquefied petroleum gas (LPG).

2. Experimental

The In$_2$O$_3$–Ga$_2$O$_3$ thin films were obtained in two consecutive steps: fabrication of bulk targets followed by pulsed laser deposition of the films. The targets were formed by pressing the mixture of In$_2$O$_3$ and Ga$_2$O$_3$ powders and Ga(NO$_3$)$_3$·8H$_2$O. The obtained targets were annealed in natural air at 820 °C for 10 minutes to prepare them for subsequent pulsed laser deposition, which requires sufficient durability of targets [13].

The pulsed laser deposition was carried out with Nd:YAG pulsed laser «Melaz» at 1.06 µm in residual air with pressure 10$^{-5}$ Pa. Pulse parameters: duration 16 ns, repetition rate 10 Hz, focal spot area 7.85 $10^{-5}$ cm$^2$, laser pulse energy density 637 J/cm$^2$. Substrate parameters: temperature 400 °C, material ST $50-1$ glass ceramics. The film thickness reaches 0.20–0.21 µm after 20 minutes of deposition. Compositions of the targets were 100%In$_2$O$_3$, 75%In$_2$O$_3$–25%Ga$_2$O$_3$, 50%In$_2$O$_3$–50%Ga$_2$O$_3$, 25%In$_2$O$_3$–75%Ga$_2$O$_3$, and 100%Ga$_2$O$_3$. Surface morphology of the obtained films was investigated by atomic force microscopy (NT-MDT AFM «Solver Pro»). Optical transmittance spectra were obtained using spectrophotometer «SF-56» in the wavelength range 200–1100 nm.

Study of electrophysical and gas-sensing properties of the films was conducted in the temperature range 150–750 °C on a special experimental setup (two-electrode method of resistance measurement) placed in a sealed chamber with natural air. The sample gas was injected into chamber in small portions by medical injector to achieve required concentration of that gas in the volume of the chamber. The resistance response $S$ was calculated as a ratio of $R_0$ to $R_g$, where $R_0$ and $R_g$ are resistances of the film in the natural air (base resistance) and in natural air with sample gas, respectively.

$$S = R_0 / R_g,$$  \hfill (1)

More details of the experiment may be found in [13, 14].

3. Results and discussion

3.1. Atomic force microscopy

Atomic-force microscopy (AFM) images of films surfaces allow calculating mean grain size, making assumptions of gas penetrability of films [15] and new phases formation. Results of AFM studies of films surfaces deposited from targets with 100%In$_2$O$_3$, 75%In$_2$O$_3$–25%Ga$_2$O$_3$, 50%In$_2$O$_3$–50%Ga$_2$O$_3$, 25%In$_2$O$_3$–75%Ga$_2$O$_3$ and 100%Ga$_2$O$_3$ compositions are presented in figure 1 and in table 1. Mean grain size was calculated using watershed method of image processing. All films have polycrystalline structure with a developed surface consisting of grains with diameters 0.10–0.13 µm. Films with 100%In$_2$O$_3$ composition have least mean grain size and least standard deviation of surface
profile. Films made of pure Ga$_2$O$_3$ demonstrate another minimum of grains parameters. Maximum of mean grain size and standard deviation of surface profile is achieved for films with 75%In$_2$O$_3$–25%Ga$_2$O$_3$ and 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition.

![AFM images of In$_2$O$_3$–Ga$_2$O$_3$ films.](image)

**Figure 1.** Examples of AFM images of In$_2$O$_3$–Ga$_2$O$_3$ films.

Observed increase in grain size may be a result of new phase formation. Indium oxide and gallium oxides have nearly equal melting points: 1910 °C and 1900 °C, respectively. They may form InGaO$_3$ alloy during deposition procedure under certain conditions, because it have lower melting point, than pure oxides. Formation of this alloy is the only explanation of relatively large droplet-like grains appeared on the surface of films with composition close to 50%In$_2$O$_3$–50%Ga$_2$O$_3$, which is not observed for films with 100%In$_2$O$_3$ and 100%Ga$_2$O$_3$ composition (see figure 1). The InGaO$_3$ phase formation in obtained films may be the cause of other effects discussed below.

| Composition of film | Mean grain size, nm | Standard deviation of surface profile, nm |
|---------------------|---------------------|------------------------------------------|
| 100%In$_2$O$_3$     | 93                  | 43                                       |
| 75%In$_2$O$_3$–25%Ga$_2$O$_3$ | 269               | 228                                      |
| 50%In$_2$O$_3$–50%Ga$_2$O$_3$ | 305               | 240                                      |
| 25%In$_2$O$_3$–75%Ga$_2$O$_3$ | 266               | 154                                      |
| 100%Ga$_2$O$_3$     | 231                 | 138                                      |

**Table 1.** Mean grain size and standard deviation of surface profile for In$_2$O$_3$–Ga$_2$O$_3$ films.

3.2. Temperature dependencies of resistance

Temperature dependencies of resistance for all films are shown in figure 2. The resistance of films with 100%Ga$_2$O$_3$ composition in chosen temperature range (150–750 °C) exceeded 10 MΩ. That was the reason to exclude those films from further research. Among other films, the highest resistance in all temperature range is observed for films with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ and 75%In$_2$O$_3$–25%Ga$_2$O$_3$ composition (see table 2). In a field of semiconductor gas sensors it is well known that high base resistance usually leads to high gas response [1]. Results of gas-induced resistance response study (discussed below) confirm that trend.
One of important characteristics of films for semiconductor gas sensors is relative change of resistance per °C, because of usual problem with temperature-caused baseline instability [1, 16–18]. Relative change of resistance per °C in temperature range 530–550 °C (range of maximum gas-induced resistance response) have values 1.0–1.5 % for films with different compositions. There is a peculiarity on all the temperature dependencies of resistance in the temperature range 270–400 °C – a region of positive temperature coefficient of resistivity. This behavior of resistance is well-known for oxides of transition metals. It is explained by the change in the oxygen adsorption mechanism [13, 19, 20]. The transition from preferential adsorption of molecular oxygen O₂⁻ to preferential adsorption of atomic oxygen O⁻ and O⁻⁻ occurs at these temperatures, which leads to increase in resistance.

Table 2. Maximum and minimum of resistance and corresponding temperature for In₂O₃–Ga₂O₃ films.

| Composition of film | Rₘᵢₘᵢₙ, kΩ | Rₘᵃₓ, kΩ | T(Rₘᵢₙ), °C | T(Rₘᵃₓ), °C |
|---------------------|-------------|-----------|--------------|--------------|
| 100%In₂O₃           | 21.9        | 77.8      | 221          | 403          |
| 75%In₂O₃–25%Ga₂O₃  | 28.9        | 345       | 210          | 441          |
| 50%In₂O₃–50%Ga₂O₃  | 122         | 1998      | 214          | 381          |
| 25%In₂O₃–75%Ga₂O₃  | -           | 9998      | -            | 280          |

3.3. Optical transmittance spectra
Optical transmittance spectra for all films are presented in figure 3. Films with 100% In₂O₃ composition have the highest transmittance in visible range (60%). In general, increase in Ga₂O₃ content reduces the film transmittance in visible range. The deviation from that trend is observed for films with 50% In₂O₃–50% Ga₂O₃ which have 20–25% transmittance in visible range composition. Optical transmittance of other films does not exceed 12%.

Figure 3. Optical transmittance spectra for In₂O₃–Ga₂O₃ films.  
1 - 100% In₂O₃, 2 - 75% In₂O₃–25% Ga₂O₃, 3 - 50% In₂O₃–50% Ga₂O₃, 4 - 25% In₂O₃–75% Ga₂O₃, 5 - 100% Ga₂O₃.

All films were obtained with identical deposition parameters, so the only explanation of the optical transmittance increase is the formation of new phase in films with 50% In₂O₃–50% Ga₂O₃ composition. It may be InGaO₃ phase, which is known for its good optical transmittance [10].

3.4. Temperature dependencies of gas-induced resistance response
Studies of temperature dependencies of gas-induced resistance response are essential for development of semiconductor gas sensors. Examples of that dependencies obtained for films with 100% In₂O₃, 75% In₂O₃–25% Ga₂O₃, 50% In₂O₃–50% Ga₂O₃ and 25% In₂O₃–75% Ga₂O₃ composition are shown in figure 4 (a case of response on 25 ppm of acetone after 10 min.). The dependencies for other combustible gases have a similar bell-shaped form. Experimental error for temperature measurements did not exceed 5%, for resistance measurements – 3%.

Figure 4. Temperature dependencies of resistance response on acetone:
1 – 50%In$_2$O$_3$–50%Ga$_2$O$_3$; 2 – 75%In$_2$O$_3$–25%Ga$_2$O$_3$; 3 – 100%In$_2$O$_3$; 4 – 25%In$_2$O$_3$–75%Ga$_2$O$_3$.

Temperature dependencies of gas response on the aforementioned combustible gases diluted in natural air have a maximum at a certain temperature, which is typical for semiconducting gas sensors. Amplitude of response on acetone and ethanol for all investigated films in temperature range 500–600 °C exceeds 3–4 times amplitude of their response on ammonia and LPG. Table 3 represents data on amplitude of resistance response on acetone for all films and data on temperature of maximum response on that gas. Data for other gases are similar. The temperature of maximum response was determined by approximation of experimental results with Gauss function. The obtained results show that temperature of maximum response for all films differs no more than 7%. The temperature of maximum resistance response on ethanol and acetone for films with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition is lower than that temperature for other films. Moreover, their amplitude of resistance response on those gases is significantly higher.

| Composition of film | Temperature of maximum response, °C | Maximum resistance response |
|---------------------|--------------------------------------|-----------------------------|
| 100%In$_2$O$_3$     | 566                                  | 2.8                         |
| 75%In$_2$O$_3$–25%Ga$_2$O$_3$ | 579                       | 6.0                         |
| 50%In$_2$O$_3$–50%Ga$_2$O$_3$ | 528          | 21.0                        |
| 25%In$_2$O$_3$–75%Ga$_2$O$_3$ | 609          | 2.6                         |

3.5. Temperature dependencies of resistance response in coordinates ln(S)=f(1/kT)

The temperature dependencies of gas response on combustible gases in coordinates ln(S)=f(1/kT) have two linear regions (see figure 5 for cases of acetone and ethanol). Slope angles for those regions are proportional to activation energies of resistance response, $\Delta E$. Table 4 represents obtained values of $\Delta E$ for all investigated films.

| Composition of film | $\Delta E_{LT}$, eV | $\Delta E_{HT}$, eV |
|---------------------|----------------------|---------------------|
| 100%In$_2$O$_3$     | 566                   | 2.8                 |
| 75%In$_2$O$_3$–25%Ga$_2$O$_3$ | 579            | 6.0                 |
| 50%In$_2$O$_3$–50%Ga$_2$O$_3$ | 528          | 21.0                |
| 25%In$_2$O$_3$–75%Ga$_2$O$_3$ | 609          | 2.6                 |
According to [1, 21] the main factor, influencing amplitude of resistance response in low temperature region ($\Delta E_{LT}$), is difference between energy of combustible gas adsorption ($E_R$) and energy of oxygen adsorption ($E_O$):

$$\Delta E_{LT} = E_R - E_O. \quad (2)$$

The activation energy of resistance response in low temperature region ($\Delta E_{HT}$) is determined by the difference between energy of combustible gas desorption ($q_R$) and energy of its oxidation products desorption ($q_{RO}$) [1, 21].

$$\Delta E_{HT} = q_R - q_{RO}. \quad (3)$$

Figure 5 represents two of obtained dependencies. Maximum of amplitude of resistance response is observed for films with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition. Films with 75%In$_2$O$_3$–25%Ga$_2$O$_3$ composition have 3.5 times lower amplitude of response. Amplitudes of response for other films are even lower.

![Figure 5](image)

**Figure 5.** The dependencies of logarithm of resistance response on inverse temperature for films exposed to acetone diluted in air. 1 - 50%In$_2$O$_3$–50%Ga$_2$O$_3$, 2 - 75%In$_2$O$_3$–25%Ga$_2$O$_3$.

The slope angles of high temperature linear regions of the dependencies in figure 5 are approximately equal. According to (2) it indicates that 50%In$_2$O$_3$–50%Ga$_2$O$_3$ and 75%In$_2$O$_3$–25%Ga$_2$O$_3$ films have approximately equal difference between energy of combustible gas desorption ($q_R$) and energy of its oxidation products desorption ($q_{RO}$). The slope angles of low temperature linear regions of those dependencies are significantly different. According to (3) this is possible in two cases. In the first case energy of combustible gas adsorption ($E_R$) for film with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition is higher, than energy of that gas adsorption for film with 75%In$_2$O$_3$–25%Ga$_2$O$_3$ composition. In the second case energy of oxygen adsorption ($E_O$) for film with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition is lower, than the same energy for film with 75%In$_2$O$_3$–25%Ga$_2$O$_3$ composition. The first case is not possible, because the energy of gas adsorption is connected with energy of its desorption. Those energies cannot be changed independently. However, energies of gas desorption for both films are approximately the same, based on previously made conclusion about slope angles of high temperature linear regions of the dependencies in figure 5. Therefore, the difference between slope angles of low temperature linear regions of dependencies for films with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ and 75%In$_2$O$_3$–25%Ga$_2$O$_3$ compositions is caused by the difference in their energies of oxygen adsorption.

3.6. Formation of InGaO$_3$ phase

Thus, films with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition have properties, which markedly differ from properties of films with other compositions. They have maximum of average grain size (table 1),
considerable local maximum of optical transmittance in visible range (figure 3), highest among other films amplitude of resistance response on combustible gases (figure 4, table 3) and lowest oxygen adsorption energy (table 4). A possible cause for all those properties may be a formation of some new objects in $\text{In}_2\text{O}_3$–$\text{Ga}_2\text{O}_3$ composite. There are several candidates for that role: $\text{InGaO}_3$ solid solution [8], rhombohedral $\text{In}_2\text{O}_3$ in the lattice of cubic $\text{In}_2\text{O}_3$ [12], area of heterojunction between the crystallites of $\text{In}_2\text{O}_3$ and $\text{Ga}_2\text{O}_3$ [3].

The most likely option is the formation of $\text{InGaO}_3$, because previously it was illustrated in [8] by the means of X-ray diffraction that $\text{In}_2\text{O}_3$–$\text{Ga}_2\text{O}_3$ films contain several phases: $\text{In}_2\text{O}_3$, $\text{Ga}_2\text{O}_3$ and $\text{InGaO}_3$. It is obvious, that the highest concentration of $\text{InGaO}_3$ phase should be in films with composition close to 50%$\text{In}_2\text{O}_3$–50%$\text{Ga}_2\text{O}_3$. It was confirmed in [8].

4. Conclusion

Presented results demonstrate, that $\text{In}_2\text{O}_3$–$\text{Ga}_2\text{O}_3$ thin films may be considered as promising materials for sensitive layers of semiconductor gas sensors and conductive transparent layers. Production of these films by pulsed laser deposition allows precise control of their composition and thickness. Considered films are sensitive to a number of flammable gases. The highest sensitivity of the films is observed for the case of acetone and ethanol vapors. Study of effect of films composition on their properties showed, that highest gas-induced resistance response have films with 50%$\text{In}_2\text{O}_3$–50%$\text{Ga}_2\text{O}_3$ composition. In addition, these films have least temperature of maximum resistance response as compared with films with other compositions. Also, their optical transmittance in visible range have noticeable local maximum. The reason for all those phenomena may be the formation of $\text{InGaO}_3$ solid solution in films with composition close to 50%$\text{In}_2\text{O}_3$–50%$\text{Ga}_2\text{O}_3$.

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