Effect of metal modifiers on the characteristics of resistive hydrogen sensors based on thin films of tin dioxide

A V Almaev¹, N K Maksimova², E Yu Sevastyanov¹,², E V Chernikov², T A Davydova², T E Smirnova¹
¹Department of Semiconductor Electronics, Tomsk State University, Tomsk 634050, Russia
²Laboratory of Physics of Semiconductor Devices, Kuznetsov Siberian Physical Technical Institute, Tomsk State University, Tomsk 634050, Russia
E-mail: almaev_alex@mail.ru

Abstract. This work presents the results of investigation of the effect of the complex modifiers of Ag + Y introduced into bulk of SnO₂ thin films on the properties of hydrogen sensors and the stability of the devices at long-term test. Two types of the films with different deposited on the surface dispersed catalysts Pt/Pd/SnO₂:Sb, Ag, Y and Ag/SnO₂:Sb, Ag, Y were studied. It is shown that additives of Ag, Y in the presence Pt/Pd on the surface provide the maximum values of the response to hydrogen at the temperature 670 K. In the case of the deposited catalytic Ag the response to hydrogen is considerably lower and the temperature of the maximum response > 713 K. A common feature of two types of the films is the high stability of their properties under the periodical influence of hydrogen in long-term tests.

1. Introduction
It is known that the gas-sensitive characteristics of the sensors based on metaloxide semiconductors can be controlled by introducing metal modifiers into the bulk and depositing catalytic layers on the surface. In our works [1-3] it was shown that the presence of a two layer Pt/Pd catalysts on the tin dioxide surface promotes an increase in the density of chemisorbed oxygen, the sensors are characterized by a high adsorption response to low concentrations (10⁻¹⁻¹⁻³ ppm) of reduction gases (CO, H₂). Further studies [3] have shown that in the process of long-term tests of sensors at periodic influence of hydrogen, the decrease in the conductivity in clean air and the increase in the response to H₂ sensors are observed. The most significant changes occur in the first month of testing, and then the sensor’s parameters are stabilized. Interestingly, the long-term exposure of other reducing gases, such as hydrogen sulphide and acetone [4], carbon monoxide [5], leads to drop in the sensitivity of the sensors. We suggested [3] that in addition to the interaction with chemisorbed oxygen atomic hydrogen interacts with lattice oxygen at the dissociative adsorption of H₂ molecules. As a result, during testing the number of excess tin atoms and hence the density of the sites of oxygen adsorption increase, there is a growth of the density of chemisorbed oxygen on the surface of tin dioxide and of the response to H₂.

In this work the purpose of the investigation is the establishment of the effect the metal modifiers of Ag and Y introduced into the bulk of SnO₂ thin films on the electrical and gas-sensitive properties of hydrogen sensors and the stability of sensors at long-term test. Two types of the films with different deposited on the surface dispersed catalysts Pt/Pd/SnO₂:Sb, Ag, Y (series 1) and Ag/SnO₂:Sb, Ag, Y
(series 2) were studied. It should be noted that such materials as hydrogen sensors investigated for the first time.

2. Experiment

The sensitive material of sensor obtained by magnetron sputtering of tin – antimony alloy target (0.5 at.% of Sb) at the direct current. The antimony acts as shallow donor impurity and it’s presence in the bulk of the films leads to the decrease of the working resistance of the sensitive semiconductor layer. Ultra dispersed layers of metals (palladium, platinum and silver) were deposited on the surface of tin dioxide by magnetron sputtering. The fabrication process of sensors is described in detail in [1,3].

Ultra dispersed layers of metals (palladium, platinum and silver) were deposited on the surface of tin dioxide by magnetron sputtering. The fabrication process of sensors is described in detail in [1,3].

The additive content in the bulk of the tin dioxide films was estimated by the ratio of the areas of the sputtered target $S_{\text{Sn}}$ and metal pieces $S_{\text{m}}$ (m=Ag, Y). Based on special studies, the optimum ratios $S_{\text{m}}/S_{\text{Sn}}=3\times10^{-3}$ and $S_{\text{Y}}/S_{\text{Sn}}=3\times10^{-3}$. Manufacturing technology of the sensors includes a stabilizing annealing in air at 723 K for 24 h. In order to establish the equilibrium condition between the surface of sensors and gas mixture in the measuring camera before each measurement the samples were exposed to in the heating during 30 minutes at 673 K.

The principle of operation of gas sensors and methods of measurements of parameters of the devices are described in detail in works [1,2]. The resistance $R_0$ (conductance $G_0$) of films in pure air and similar parameters $R_i$ ($G_i$) at exposure to hydrogen were measured as functions of the operating temperature $T$ and the concentration of hydrogen $n$ in air. The ratio $G_i/G_0$ was taken as the adsorption response. The measurements were carried out at the same relative humidity $RH$ level of the gas mixture $RH = 30\div35 \%$.

3. Results and discussions

At first, microstructure of the film’s surface of series 1 and 2 was studied with atomic force microscopy. The thickness of films are about 120÷150 nm. There are two types of microcrystals with characteristic sizes $d_1 = 12\div14$ nm and $d_2 = 32\div35$ nm in the films and these microcrystals can form large agglomerates with characteristic size $d_3 = 150\div185$ nm.

The results in the present work are compared with the characteristics of the sensors Pt/Pd/SnO$_2$:Sb, Ag, Y (series 1) and Au/SnO$_2$:Sb, Au (series 4), which do not contain additives of silver and yttrium in the bulk and which have been studied by us earlier [1] (table 1). The introducing of silver and yttrium in the bulk of thin films of tin dioxide (series 1) leads to rise of resistance $R_0$ of the sensitive layer in compare with sensors of series 3. Magnitude of $R_0$ for films without deposited Pt/Pd dispersed layers on the surface (series 2, 4) is significantly lower.

| Type of sensor | $R_0$ ($T=300$ K), $\Omega$ | $\Delta E_1$, eV | $\Delta E_2$, eV | $T_{\text{max}}$, K | $G_i/G_0$ |
|---------------|-----------------|-----------------|-----------------|-----------------|----------|
| Pt/Pd/SnO$_2$:Sb, Ag, Y (series 1) | 26.4 | 0.23 | 0.69 | 670 | 30 |
| Ag/SnO$_2$:Sb, Ag, Y (series 2) | 0.23 | 0.22 | 0.47 | 750 | 6 |
| Pt/Pd/SnO$_2$:Sb (series 3) | 4.14 | 0.11 | 0.17 | 670 | 25.7 |
| Au/SnO$_2$:Sb, Au (series 4) | 0.25 | 0.03 | 0.08 | 780 | 5 |

The temperature dependence of the sensor resistance $R_0$ in pure air is defined by three independent values: the electron concentration and mobility in the film bulk and the negative charge density on the surface [1]. During heating from room temperature to $T = 470\div500$ K, the resistance of all samples decreases mostly due to the ionization of shallow and deep centres in the film bulk, and the dependencies $\ln R_0$ on $1000/T$ can be approximated by Arrhenius curves (Figure 1).
Arrhenius curves contain two linear portions from which the activation energies $\Delta E_1$ and $\Delta E_2$ were determined. The value of activation energy depends on the type of modifiers and the type of surface catalysts (table 1). It can be assumed that the introduction Ag and Y in the bulk of tin dioxide contributes to the formation of deep centers, characterized by the increased values of the activation energy in the samples from series 1, 2, and value of $\Delta E_1$ coincides.

The increase of the resistance of samples in the region of $T > 470$ K is caused by an increase in the negative surface charge due to water molecule desorption from the surface and the transition of chemisorbed oxygen from the molecular form $O_2^-$ to the atomic form $O^-$. As a result, the space charge region widens and the film resistance accordingly increases. The effects of a change in the surface charge come to an end at high temperatures (~700 K), and then $R_0$ decreases again. The type of modifiers in the bulk and the type of surface catalysts has a significant effect on the gas-sensitive properties of the sensors. The dependencies of the adsorption response on the operating temperature for the sensors of series 1 and 2 is shaped as curves with a maximum (Figure 2). The temperatures $T_{\text{max}}$ at which sensors have the maximal response at exposure to 100 ppm of hydrogen and the values of $G_1/G_0$ at this concentration of gas are presented in table 1.

Based on these studies it was found that the $T_{\text{max}} = 670$ K for the sensors of series 1 and series 3. $T_{\text{max}}$ is in the range from 713 K to 750 K for the sensors of series 2 and series 4. At the all investigated operation temperatures of the sensors the responses of series 1 and series 3 are higher than the responses of the devices of the series 2 and series 4. The introducing of silver and yttrium in the bulk of thin films with deposited Pt/Pd doesn’t lead to changes of the $T_{\text{max}}$ and the sensor response increases.

The characteristics of thin films of tin dioxide with deposited Ag dispersed layer on the surface (series 2) are similar to the characteristics of the thin films of Au/SnO$_2$:Sb, Au (series 4). These samples exhibit the low resistance and the low response at exposure to hydrogen. Value of $T_{\text{max}}$ is shifted at area of the higher operation temperature.

Figure 3 shows the concentration dependencies of responses to the hydrogen at $T = 673$ K for the films of series 1 and series 2. The response of sensor of series 1 rises as superlinear low and the response of sensors of series 2 increases as sublinear low with increasing of hydrogen concentration. The response of sensors of series 1 is larger than the response of the sensors of series 2 in all studied hydrogen concentration. The superlinear growth with increase of the hydrogen concentration was observed for sensors based on Pt/Pd/SnO$_2$:Sb (series 3), and the sublinear growth is observed for sensors based on Au/SnO$_2$:Sb, Au (series 4) [1]. In the work [6] it was shown that characteristics of
these samples are described by means of the over – barrier model of conductivity. It is assumed that the over – barrier model of conductivity is applicable to describe of the characteristics of the thin films of tin dioxide with modifiers of silver and yttrium.

Of most interest are the results of a study of the characteristics of the sensors of series 1 and series 2 depending on the duration of the test (table 2). Sensors of series 1 and series 2 demonstrate high temporal stability. The response on the hydrogen effect is virtually unchanged with increasing operating time of the sensor. It is important that during the 8 day daily the sensors was subjected to repeated (5 cycles) the impact of 1000 ppm hydrogen. Each cycle consisted of heating the sensors at the operating temperature $T_{\text{max}}$ for 30 minutes, filling into the chamber of hydrogen, the exposure to hydrogen for 25 minutes and pumping through the camera of clean air for 4 minutes. It can be seen that all the parameters has changed slightly. Therefore Ag and Y additives during tin dioxide deposition significantly improves the stability of characteristics of the hydrogen sensors.

![Figure 3](image)

**Figure 3.** The concentration dependencies of responses to hydrogen for sensors of series: 1 – 1, 2 – 2.

| Duration of test | Pt/Pd/SnO$_2$:Sb, Ag, Y (series 1) | Ag/SnO$_2$:Sb, Ag, Y (series 2) |
|-----------------|----------------------------------|---------------------------------|
|                 | $G_0 \times 10^7$, S | $G_1$, mS | $G_1/G_0$ | $G_0 \times 10^6$, S | $G_1$, mS | $G_1/G_0$ |
| 1               | 0.80                      | 0.046       | 579.5       | 6.05          | 0.076       | 12.6       |
| 29              | 1.30                      | 0.074       | 559.8       | 5.07          | 0.104       | 20.6       |
| 55              | 1.42                      | 0.078       | 545.8       | 4.52          | 0.087       | 19.3       |
| 85              | 1.32                      | 0.075       | 571.2       | 4.78          | 0.087       | 18.1       |

A processes causing instability of sensors at long-term test are described in the papers [4,5]. However the deciding factor determining the instability of the hydrogen sensors is the process of reduction of tin from oxide by hydrogen at high operating temperatures. A detailed discussion on the effect of modifiers of silver and yttrium on the stability of the sensor’s characteristics is difficult. Analysis of absorption spectra produced by UV-visible spectroscopy shows that after annealing of films silver in the structure of tin dioxide is presented in the form of a metal clusters Ag$_0$ with size 10 nm. To explain the role of Ag it is possible to use the data of x-ray photoemission spectroscopy (RFS) presented in paper [7]. The decrease of the bonding energy of Sn3d and O1s in SnO$_2$:Ag films by 0.5+0.7 eV compared to pure SnO$_2$ takes place. This process can facilitate the interaction of atomic hydrogen with lattice oxygen. By means of photoelectronic spectroscopy (XPS) [8] it was found that the bond length Y–O in SnO$_2$ does not correspond to the oxide Y$_2$O$_3$, i.e. the yttrium oxide is absent in the structure of tin dioxide, the ions Y$^{3+}$ are introduced into the lattice of SnO$_2$. By comparison of values of the bonding energy of Y–O and Sn–O, we can assume that in thin films of tin dioxide after annealing the yttrium segregates on the surface of the nanocrystals of SnO$_2$ and forms a strong bond

4
with lattice oxygen. In such condition increase the density of superstoichiometric tin atoms and consequently centers for adsorption of oxygen take place. In case of samples of series 1 and series 2 there are metal silver and yttrium ions $\text{Y}^{3+}$ in the film of tin dioxide. Due to the presence of metallic silver ions yttrium $\text{Y}^{3+}$ more actively form bond with lattice oxygen. As a result, hydrogen interacts only with chemisorbed oxygen on the surface of tin dioxide nanocrystals, recovery of tin dioxide to tin does not occur.

4. Conclusion

The introduction of modifiers Ag, Y in the bulk of tin dioxide thin films in the presence of Pt/Pd on the surface provides the maximum values of the response to hydrogen at $T_{\text{max}} = 670$ K. In the case of the deposited catalytic Ag the response to hydrogen is considerably lower and $T_{\text{max}} > 713$ K. A common feature of the films is the high stability of their properties under the periodical influence of hydrogen in long-term tests. In literature data on the stability properties of the sensors after long-term use are lacking. The complex modifiers of silver and yttrium interact with lattice atoms of tin and oxygen contribute to the emergence of deep centers in the semiconductor, and these additives prevent the process of reduction of tin dioxide at hydrogen adsorption and ensure the stability of the parameters of the sensors in operation.

Acknowledgments

This work was performed as part of the State Task of the Ministry of Education and Science of the Russian Federation (No 3.2068.2017/4.6).

References

[1] Sevastyanov E Y, Maksimova N K, Chernikov E V, Novikov V A, Rudov F V, Sergeychenko N V 2012 *Semiconductors* **46** 801
[2] Gaman V I, Almaev A V, Maksimova N K, Sergeychenko N V 2016 *Key Eng. Mat.* **683** 353
[3] Gaman V I, Almaev A V, Maksimova N K 2015 Proc. Int. Siberian Conf. on Control and Communications (Omsk) (IEEE conference publications), pp 1-4
[4] Lee Ingun, Choi Seon-Jin, Park Kwang-Min, Lee Sun Sook, Choi Sungho, Kim Il-Doo, Park C O 2014 *Sensor Actuat. B* **197** 300
[5] Vahdatifar Sahar, Khodadadi Abbas Ali, Mortazavi Yadollah 2014 *Sensor Actuat. B* **191** 421
[6] Almaev A V, Gaman V I 2017 *Russ. Phys. J.* **60** 1081
[7] Matsushima S, Teraoka Y, Miura N, Yamazoe N 1988 *Jpn. J. Appl. Phys.* **27** 1798
[8] Cheng L, Ma S Y, Li X B, Luo J, Li W Q, Li F M, Mao Y Z, Wang T T, Li Y F 2014 *Sensor Actuat. B* **200** 181