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Effect of Humidity on the Properties of NO$_2$ Sensors Based on Thin WO$_3$ and SnO$_2$ Films Modified with Gold

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Abstract—The effect of humidity on the electrical and gas-sensitivity properties of NO$_2$ sensors based on thin (~100 nm) nanocrystalline films of tungsten trioxide and tin dioxide with additions of gold in the bulk and on the surface (Au/WO$_3$:Au, Au/SnO$_2$:Sb,Au) is investigated. It is found that the conductivity of these films in pure air increases only slightly as absolute humidity A rises from 2 to 16 g/m^3, the responses for nitrogen dioxide in the concentration range of 0.45–10 ppm do not depend on humidity, and the response time is shortened as A rises. Analysis of experimental data using a model based on the assumed microcrystal availability in WO$_3$ and SnO$_2$ thin films connected by conductivity bridges shows that the values of the heat of adsorption ΔE_N and activation energies of adsorption E_{aN} and desorption E_{dN} of ions NO$_2^-$ on the films surface modified gold, do not depend on the humidity.

Keywords: tungsten trioxide, tin dioxide, catalytic gold, gas sensors, nitrogen dioxide, humidity.

INTRODUCTION

It is known that one of the main reasons for parameter instability of gas sensors based on metal oxide semiconductors is their high sensitivity to changes in ambient humidity. The adsorption of water vapor on sensors of reducing gases based on tin dioxide was considered in great detail in [1–5]. We may assume that similar phenomena occur in the case of WO$_3$. However, the number of published works on the humidity effect on the properties of the oxidizing gas sensors (including NO$_2$) based on WO$_3$ and SnO$_2$ remains quite limited, and the results from different investigations are contradictory [6–9].

We showed in [10–12] that in order to develop sensors with high values of the responses to trace amounts of NO$_2$, it is worth using thin WO$_3$ and SnO$_2$ nanocrystalline films with additions of gold in the bulk and on the surface. In this work, we investigate the humidity effect on the electrical and gas-sensitive properties of such sensors. The experimental data are analyzed using the physical model of resistive sensors of oxidizing gases developed in [2, 11].

EXPERIMENTAL

WO$_3$:Au and SnO$_2$:Sb,Au films ~100 nm thick were prepared via HF magnetron sputtering (RFS) of a WO$_3$ oxide target, and with magnetron sputtering at direct current (DCS) of a target made from Sn + 0.5 at % Sb alloy, respectively. Mosaic targets with gold particles fixed on them were used with to introduce gold additives into the films volume. Sapphire plates thickness ~150 μm served as supports. Disperse layers of gold were deposited on the film surfaces by means of DCS. Manufacturing technology of sensors, collected in the body of the type TO-8, was presented in detail in [10–12]. We denote our samples as series i (Au/WO$_3$:Au) and series ii (Au/SnO$_2$:Sb:Au). The ratio G_0/G_1, where G_0 is a sample's conductivity in pure air and G_1 is its conductivity in a gas mixture was used as an adsorption response. The ratio $\Delta G/G_0$ with $\Delta G = G_0 - G_1$ was also estimated. The time in which conductivity reached 0.9 of the stationary G_1 value was considered as response time t_r. The procedure for measuring conductivity was similar to the one described in [10].

The samples were placed in a 1 L quartz chamber. Laboratory air was pumped through the chamber being purified using a sorption filter filled with CaA-type zeolite with pore sizes of 5 nm. Two air streams with regulated speeds were used to control humidity: air dried with zeolite and humidified with a bubbler. The humidity was controlled using an HIH-4000 capacitive sensor placed in the chamber. The gas sample was delivered via syringe, creating the required gas–air composition in the chamber. The chamber was pumped with pure air of the required humidity after measurements. The concentration dependences

Table 1. Typical values of parameters γ_0, t_r, G_0, G_0/G_1, and $\Delta G/G_0$ for the sensors of series i and ii at different operating temperatures

Parameter	(i) Au/WO$_3$:Au			(ii) Au/SnO$_2$:Sb, Au		
T, K	463	493	573	463	493	573
t_r, s	117	63	15	52	37	18
G_0, μS	0.31	0.42	0.53	3.61	3.89	4.25
G_0/G_1	219	145	73	69	44	12
$\Delta G/G_0$	0.995	0.993	0.986	0.993	0.977	0.918
$\Delta G/G_0$ (0.45 ppm)	0.963	0.94	0.86	0.959	0.89	0.42
γ_0, m^3/g	–	0.02	0.04	–	0.11	0.12

Parameters t_r, G_0/G_1, and $\Delta G/G_0$ were measured at average humidity $A = 6.4$ g/m^3 and NO$_2$ concentration $n_{NO_2} = 7.2$ ppm.

were measured by way of multiple additions of the required amounts of gas. The sensor was heated at 773 K for 10 s prior to each measurement.

RESULTS AND DISCUSSION

According to the data obtained in [2, 11, 12], the electrical and gas-sensitive properties of NO$_2$ sensors based on films of tin dioxide and tungsten trioxide modified with gold can be explained using a physical model that assumes the availability of conductivity bridges between WO$_3$ and SnO$_2$ microcrystals. The maximum sensor responses for nitrogen dioxide are observed at operating temperatures of 460–490 K and they fall as T rises. The response times reach 100–120 s (series i) and 50–60 s (series ii) at low tempera-

Fig. 1. Dependence of conductivity in pure air for the sensors of series i (*1*, *2*) and ii (*3*, *4*) on absolute humidity at operating temperatures (*1*, *3*) 473 and (*2*, *4*) 573 K.

tures and then fall to 10–20 s at 570–600 K. All studies in this work were therefore conducted in the 460–600 K range of operating temperatures.

Basic parameters of typical sensors from series i and ii are presented in Table 1. Conductivity G_0 in pure air for i structures is one order of magnitude lower than for ii structures, due likely to the donor center concentration in the Au/SnO$_2$:Sb,Au films being considerably higher than in those with Au/WO$_3$:Au. Other works [10, 12] showed that the microstructure of tin dioxide films modified with gold is virtually the same as that of tungsten trioxide: crystallites 8–12 nm in size, partially aggregated into 160–230 nm agglomerates, were observed in atomic force microscopy images. We may assume that the width of the space charge region in the ii samples is narrower than in the i samples. As a result, the responses to nitrogen dioxide are weaker for the ii sensors. Estimates show that $\Delta G/G_0$ at $T = 463$ K and concentration $n_{NO_2} = 7.2$ ppm is close to 1; hence, conductivity G_1 is close to zero, and a complete overlap of conductivity channels is observed in sensors of both series. The $\Delta G/G_0$ ratio declines as the temperature grows and the n_{NO_2} concentration falls, with the channel overlap diminishing more strongly in the tin dioxide films (Table 1).

A linear increase in conductivity as the absolute humidity A rose was observed for all of the investigated sensors in the temperature range of 473 to 573 K (Fig. 1):

$$G_0(A) = G_0(0)(1 + \gamma_0 A), \qquad (1)$$

where $\gamma_0 = 0.02$–0.04 and 0.11–0.12 m^3/g for the samples from series i and ii, respectively (Table 1).

It was shown in [1] that similar behavior is observed for the Pt/SnO$_2$:Sb samples; however, $\gamma_0 = 0.94$ m^3/g at $T = 573$ K. It should be noted that these sensors with catalytic platinum deposited on their surfaces were characterized by a lack of sensitivity to the action of
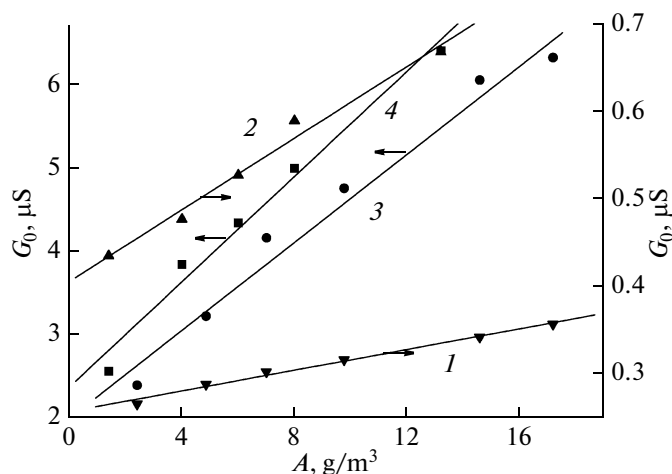
nitrogen dioxide [12]. Modifying SnO$_2$ films with gold obviously enhances their response to nitrogen dioxide and lowers the sensitivity of G_0 conductivity to humidity. A weaker dependence of G_0 on humidity ($\gamma_0 = 0.02-0.04$ m^3/g) is observed for Au/WO$_3$:Au films.

The following expressions for the adsorption response to nitrogen dioxide in a dry gas medium were obtained in [2, 11] using a model that includes conductivity bridges between the WO$_3$ grains:

$$G_0/G_1 = \eta n_{NO_2} + 1, \qquad (2)$$

where

$$\eta = (\alpha/\nu)\exp(\Delta E_N/kT). \qquad (3)$$

Here, α/ν is the ratio of NO$_2$ adsorption and desorption probabilities, $\Delta E_N = E_{dN} - E_{aN}$, E_{dN}, and E_{aN} are the heat of adsorption and the activation energies of the desorption and adsorption of NO$_2^-$ ions, respectively. The heat of adsorption is determined by the expression [2]

$$\Delta E_N = \Delta E_N^0 + (F - E_{tN}) - e\varphi_{sN}, \qquad (4)$$

where ΔE_N^0 is heat of adsorption of neutral NO$_2$ molecules; $(F - E_{tN})$ is the energy gap in the flat bands between Fermi level F and level E_{tN} created on the surface by an NO$_2$ molecule; and $e\varphi_{sN}$ is the energy band bending on a surface with adsorbed NO$_2^-$ ions.

It was shown in [2, 11] that modifying tungsten trioxide (and tin dioxide) films with gold helps reduce band bending $e\varphi_s$ on their surfaces, an increase in parameter η and binding energy ΔE_N between adsorbed NO$_2$ molecules and adsorption centers, and a reduction in desorption probability. As a result, the response to the action of the oxidizer (NO$_2$) is strengthened, while the response to the reducing gases (CO, H$_2$, CH$_4$, and others) becomes below.

Let us consider one possible dependence of the parameters of nitrogen dioxide sensors on absolute humidity A of a gas mixture. Water molecules chemisorb on SnO$_2$ and WO$_3$ surfaces, due likely to dissociation into hydroxyl groups OH$^-$ and protons H$^+$. The hydroxyl groups are localized on the surface atoms of the tin (tungsten) lattices, and protons are captured by O$^-$ ions, forming neutral OH-groups. Electrons are transferred to the SnO$_2$ (WO$_3$) conductivity bands following OH$^-$ group neutralization, and both hydroxyl groups can desorb. Hence, two hydroxyl groups are formed upon the adsorption of H$_2$O molecules on SnO$_2$ (WO$_3$) surfaces, the negative charge of O$^-$ ion disappears, and conductivity G_0 increases as a result.

According to this model, a rise in humidity must reduce chemisorbed oxygen density $N_i(A)$ and $e\varphi_{sN}(A)$:

$$e\varphi_{sN}(A) = e^2[N_i(A) + N_N(A)]^2/2\varepsilon_r\varepsilon_0 N_d, \qquad (5)$$

where $N_N = (N_c - N_i)\xi$ is the surface density of nitrogen dioxide ions; $\xi = \eta n_{NO_2}/(1 + \eta n_{NO_2})$; N_d is the concentration of donor admixture ions and oxygen vacancies in the semiconductor film; N_c is the density of the adsorption centers for oxygen particles; ε_r is the relative semiconductor permittivity; and ε_0 is a dielectric constant.

It should be noted that NO$_2$ molecules can be adsorbed only on centers not occupied by oxygen ions by competing with the OH hydroxyl groups, provided the adsorption centers of oxygen and nitrogen dioxide have the same nature.

When $\eta n_{NO_2} \geq 1$, parameter ξ is close to (0.5−1) and its dependence on the ambient humidity can be disregarded. An increase in A must result in a drop in $N_i(A)$ and $e\varphi_{sN}(A)$, which should raise ΔE_N, η, and $\Delta G(A)/G_1(A)$. The effect the humidity of the gas mixture on the sensor response must decline with an increase in n_{NO_2} and ξ.

The following expression for the change in sensor conductivity over time after beginning of interaction with gas was obtained by solving the kinetic equation for adsorption in the nonstationary mode [2, 11]:

$$\Delta G(A, t) = \Delta G(A)[1 - \exp(-t/\tau_a)], \qquad (6)$$

where τ_a is time of the relaxation of adsorption of NO$_2^-$ ions:

$$\tau_a = \frac{\exp(E_{dN}/kT)}{\nu(1 + \eta n_{NO_2})}. \qquad (7)$$

Analysis of the experimental data obtained in this work showed that the concentration dependences of the sensor response to nitrogen dioxide and the η parameter were linear in logarithmic coordinates at different humidities (Fig. 2), since $\eta = \Delta G/(G_1 n_{NO_2}) \propto n_{NO_2}^{-l}$ and $\Delta G/G_1 \propto n_{NO_2}^m$. The G_0/G_1 and η values did not depend on A for all of the investigated films. Exponent $l = 0.25$ and 0.33, and $m = 0.75$ and 0.67 for series i and ii, respectively, also did not change with the humidity.

As was shown in [2, 11], analysis of the temperature dependences for the increase in conductivity and the adsorption time constant of nitrogen dioxide using the dependences $\ln[(\Delta G/G_1)/T^{1/2}]$ and $\ln[\tau_a(1 + \eta n_{NO_2})]$ on T^{-1} in the region of high temperatures when the conductivity channels overlap are not fully allowed us to estimate heat of adsorption ΔE_N and the activation energies of adsorption E_{aN} and desorption E_{dN} of NO$_2^-$
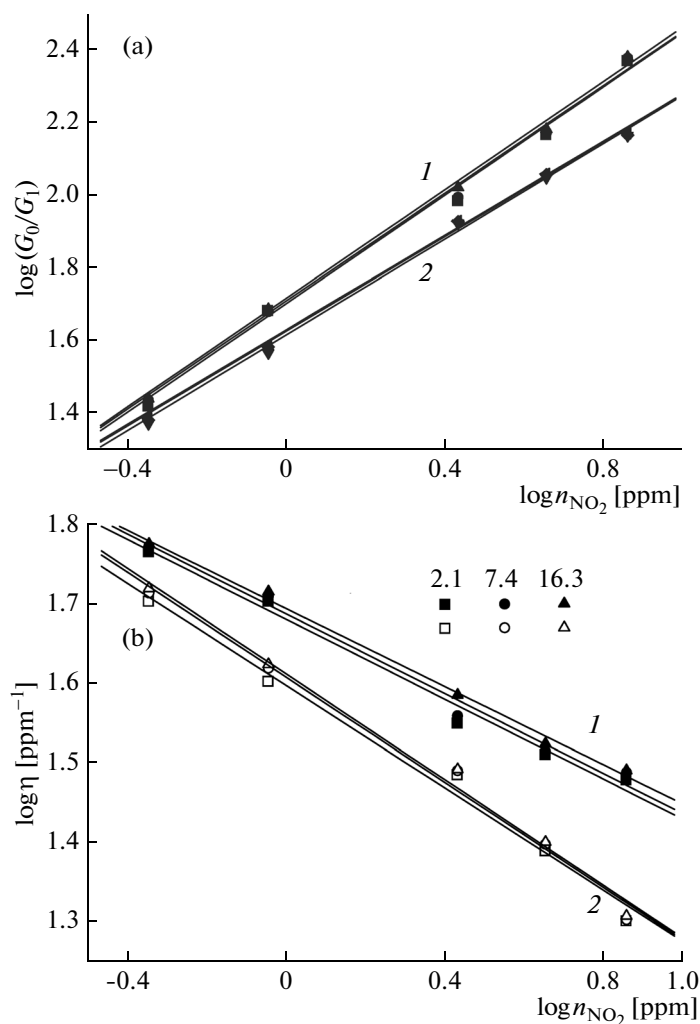
Fig. 2. Dependences in logarithmic coordinates of (a) the G_0/G_1 response and (b) parameter η on the NO_2 concentration for sensors i (set of curves *1*) and ii (set of curves *2*) at three levels of absolute humidity A, g/m^3: 2.1, 7.4, 16.3. Experimental points corresponding to different A are shown in the right upper corner of (b). Operating temperature $T = 493$ K.

ions. These dependences for the sensors of series i and ii, linearized in their respective coordinates, are presented in Fig. 3.

The results from processing the experimental data at three levels of humidity are presented in Table 2. The values are $\Delta E_N = 0.53-0.55$ and $0.46-0.47$ eV; $E_{dN} = 0.59-0.63$ and $0.52-0.56$ eV for the samples of the series i and ii, respectively.

Using the expression $\Delta E_N = E_{dN} - E_{aN}$, we can calculate $E_{aN}^0 = 0.06-0.10$ eV, which is ≤ 0.10 eV, independent of the film type. The energy of bonds between adsorbed ions and adsorption centers ΔE_N, along with the activation energies of NO_2^- desorption E_{dN} and adsorption E_{aN} obviously do not depend on humidity.

Our estimates showed (Table 2) that conditions $\eta n_{NO_2} > 1$ and $\eta n_{NO_2} \gg 1$ are valid for all of the sensors over the range of nitrogen dioxide concentrations.

According to Eq. (5), the effect the humidity of the gas mixture on $e\varphi_{sN}(A)$, ΔE_N, η, and the sensor response must in this case fall until it disappears completely.

The time dependence of the conductivity of the sensors investigated in this work includes two phases: the first is due to the adsorption of NO_2 molecules on their surfaces; the second is related to the diffusional penetration of the molecules into the film volume. The response times of the investigated sensors shorten as the humidity rises (Fig. 4, Table 2). Similar dependences were observed for sensors based on thick [13] and thin [7] WO_3 films prepared using the sol–gel method. Adsorption time constant τ_a (see Eq. (7)) is determined by E_{dN} and η, which do not depend on A. We may assume that water molecules fill pores in films with increased humidity and lower the probability of
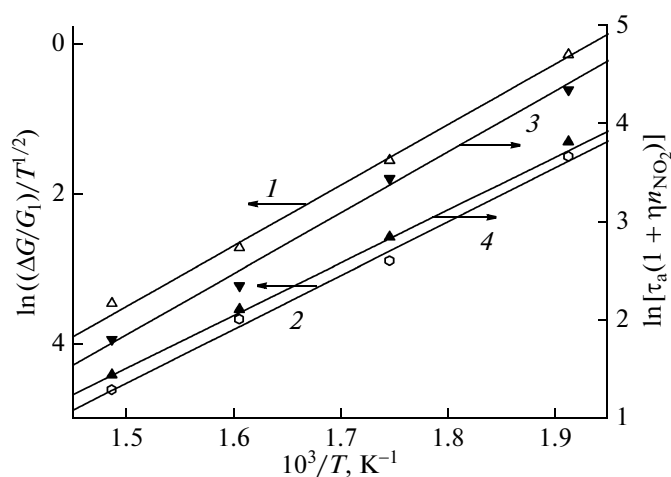
Fig. 3. Dependences of $\ln[(\Delta G/G_1)/T^{1/2}]$ (*1*, *2*) and $\ln[\tau_a(1 + \eta n_{NO_2})]$ (*3*, *4*) on the reciprocal of the temperature for samples i (*1*, *3*) and ii (*2*, *4*) at $n_{NO_2} = 0.45$ ppm.

Fig. 4. Time dependences of the resistance of sensors from series i Au/WO₃:Au at nitrogen dioxide concentrations of 1.8 ppm and three levels of absolute humidity A: (*1*) 2.5, (*2*) 8, (*3*) 16 g/m³. Operating temperature $T = 573$ K. Arrows indicate times at which pure air was pumped through the chamber.

nitrogen dioxide molecule diffusion, which is responsible for the slow stage of reaching stationary conductivity.

CONCLUSIONS

Investigation of the effect humidity on the characteristics of NO₂ sensors based on thin tin dioxide and tungsten trioxide films modified with gold showed that conductivity in pure air G_0 increased only slightly (1.1–1.2 times for Au/WO₃:Au samples and 1.7–1.9 times for Au/SnO₂:Sb,Au samples) as the absolute humidity rose from 2 to 16 g/m³. Note for the sake of
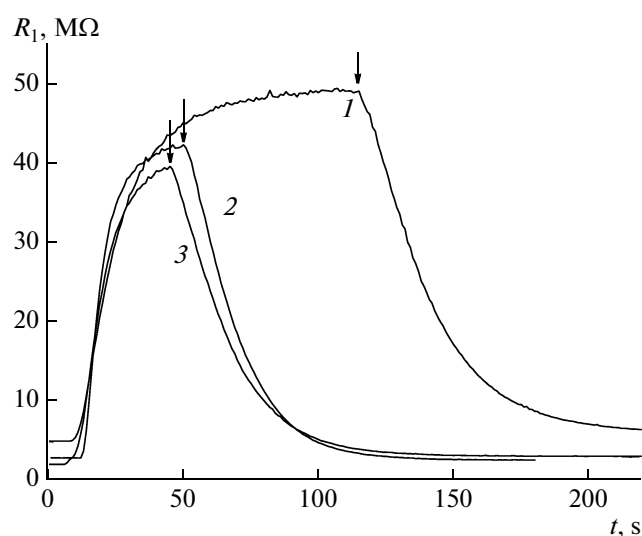
comparison that G_0 for Pt/SnO₂:Sb films grew 6–7 times in the same A range [1]. The concentration dependences of the sensor responses to the action of nitrogen dioxide were, along with the η parameter, linear in logarithmic coordinates at different humidities with G_0/G_1 and η being independent of A for all of the investigated films.

Analysis of temperature dependences of the conductivity increment and the nitrogen dioxide adsorption time constant allowed us to estimate heat of

Table 2. Typical values of response time t_r, parameter η, product ηn_{NO_2}, heat of adsorption ΔE_N, activation energies of NO_2^- ion adsorption and desorption E_{aN} and E_{dN} for sensors from series i and ii at different levels of absolute humidity

Parameter	(i) Au/WO₃:Au			(ii) Au/SnO₂:Sb, Au		
A, g/m³	2.1	8.5	16.3	2.1	8.5	16.3
RH, %	5	30	85	5	30	85
t_r, s	54	30	24	23	18	16
η, ppm⁻¹	10.6	12.1	11.3	4.9	4.6	4.6
ηn_{NO_2}	4.8	5.5	5.1	2.2	2.1	2.1
$\eta n_{NO_2}^*$	58.3	66.2	62.6	23.8	22.3	23.0
ΔE_N, eV	0.53	0.55	0.53	0.46	0.46	0.47
E_{aN}, eV	0.06	0.08	0.06	0.06	0.10	0.06
E_{dN}, eV	0.59	0.63	0.59	0.52	0.56	0.53

Values t_r and η were measured at $T = 573$ K and $n_{NO_2} = 0.45$ ppm. Values $\eta n_{NO_2}^*$ correspond to $n_{NO_2} = 7.2$ ppm.

adsorption ΔE_N along with the activation energies of NO_2^- ion adsorption E_{aN} and desorption E_{dN}. It was shown that the parameters did not depend on humidity.

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