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Performance Degradations of MISFET-Based Hydrogen Sensors with Pd-Ta_2O_5-SiO_2-Si Structure at Long-Time Operation †

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Abstract: There are presented the generalized results of studies of performance degradation of hydrogen sensors based on MISFET with structure Pd-Ta_2O_5-SiO_2-Si. It was shown how responses' parameters change during long-term tests of sensors under repeated hydrogen impacts. There were found two stages of time-dependence response' instability, the degradation degree of which depends on operating conditions, hydrogen concentrations and time. To interpret results there were proposed the models, parameters of which were calculated using experimental data. These models can be used to predict performances of MISFET-based devices for long-time operation.

Keywords: hydrogen sensors; MISFET; Pd-Ta_2O_5-SiO_2-Si; responses' parameters; hydrogen concentrations; time-dependence response' instability

1. Introduction

The gas sensors based on the metal-insulator-semiconductor devices (MIS-capacitors and field-effect transistors called as MISFETs) have been studied by many investigators (e.g., [1–10]). A great contribution to the developments of gas-sensitive MIS devices has been made by the researchers at Linköping University [5]. MIS sensors with different gates' material (palladium, platinum and iridium), with dielectric films SiO_2, Si_3N4-SiO_2, TiO_2-SiO_2, Ta_2O_5-SiO_2 have been investigated. Semiconductors Si, GaAs [3] and SiC [7] were used in MIS gas sensors to detect the low concentrations of gases H_2 [2–4], NH_3 [5], H_2S [6] and CO [7]. The studies have shown that performances characteristics of MISFET-based hydrogen sensors depend on technological parameters [2], electrical modes [8], chip temperature [10] and external factors (other gases, irradiation [9]). The researchers at National Research Nuclear University MEPhI have developed and investigated the number of hydrogen sensors based on MIS-capacitors and MISFETs with structures Pd (or Pt)-SiO_2-Si, Pd/Ti-SiO_2-Si, Pd (or Pt)-Ta_2O_5-SiO_2-Si. The experiments have demonstrated, that among developed MIS-sensors the integrated cells, containing on single chip MISFET with Pd-Ta_2O_5-SiO_2-Si-structure, heater-resistor and temperature sensor, possess the best stability and reproducibility of characteristics [4].

Performances characteristics (sensitivity, stability and speed) are determined by sensor responses' parameters, the repeatability of which becomes an important characteristic at long-term operation of gas-analytical devices. The motivations of this paper are to generalize data on researches of responses' parameters changes of MISFET-based sensors on structure Pd-Ta_2O_5-SiO_2-Si at long-term operation and to propose models, taking in to account the performance degradations.

2. Materials and Methods

The testing *n*-channel MISFET element based on Pd-Ta_2O_5-SiO_2-Si structure was fabricated on single chip (2 × 2 mm^2) together with (*p*–*n*)-junction temperature sensor and heater-resistor by means of conventional *n*-MOS-technology using laser evaporation Pd-films. To measure the sensor's hydrogen responses there was used the special circuitry shown in Figure 1. The circuit provides the constant drain current I_D = 0.1 mA and source-drain voltage V_D = 1.0 V. In this circuitry the voltage V is equal to the gate voltage V_G. The constant chip temperature (T = 130 ± 2 °C) was supported by the temperature-stabilization circuitry with feedback loop using on-chip thermo-sensor and heater.

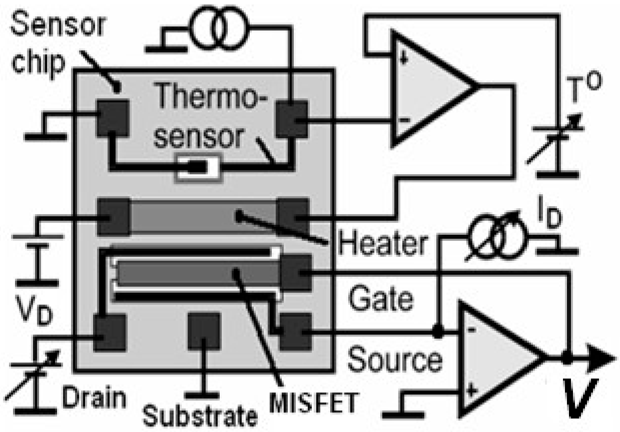

Figure 1. The simplified structure of the sensor characteristic measuring circuitry.

3. Results

We have tested the sensors for 5 or 8 weeks (5 days a week in a row with 2 day breaks) by 5 of repeated hydrogen *j*-impacts at values δV_{0j} and maximum response amplitudes δV_{CM} of vs. C for each *j*-cycle (Figure 4). In each *j*-impact sensors were consecutively exposed to hydrogen pulses of different concentrations C_i (Figure 2). The indexes *i*, *j*, *k* and *l* are serial numbers of responses, ordinary, day and weak cycles respectively. There were measured the parameters of each *i*-response (Figure 3). There were calculated the sums of residual characteristics, instability responses' parameters and its designations are presented in Table 1. Responses' and models' parameters changes are demonstrated in Figures 4–7 and in Table 2.

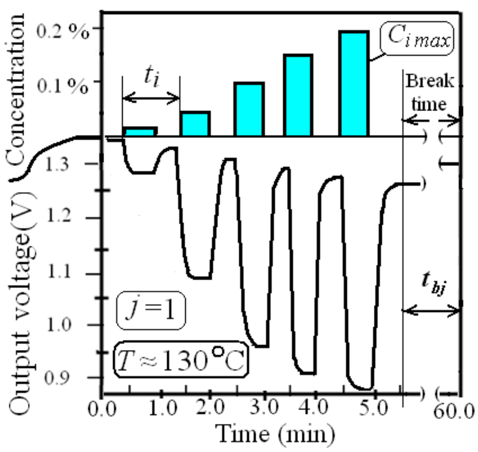

Figure 2. Time diagram of the typical *j*- ordinary cycle at different C_i.

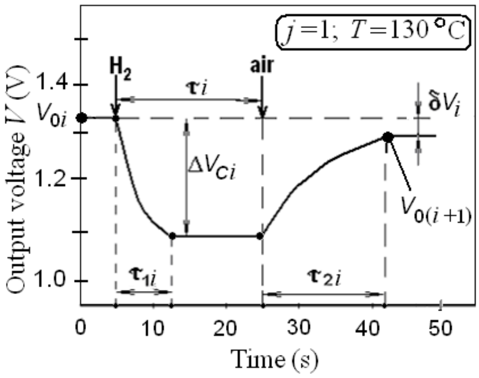

Figure 3. The typical *i*- hydrogen response and its parameters at C_i = 0.05% vol.

Table 1. Designations and n_{lkji}-responses' parameters (Y_{lkji}) for the characterization of instabilities and performance degradations' parameters of output voltage $V(C,t,t_C)$.

i-Response	*j*-Cycle	*k*-and *l*-Cycles	General Values
V_{00}—primary voltage	Maximum amplitude ΔV_{CM}	Amplitude' changes:	N—number of sensors
τ_i—H_2 pulse duration	Amplitude' changes:	$\delta V_{CM\,lk} = \Delta VCM - \Delta V_{CMlk}$	Y_0—primary value of Y
C_i—H_2 concentration	$\delta V_{CM\,j} = \Delta V_{CM} - \Delta V_{CMj}$	break times t_{bk} and t_{bl}	average of Y, variation indices, degradation degree:
V_{0i}—initial voltage	differential sensitivity:	cycle time $t_k = t_j \times j_{max} + t_{bk}$	$Y_a = \frac{1}{N} \cdot \sum_{n-1}^{N} \lvert Y_n \rvert$
ΔV_{Ci}—response amplitude	$S_{dj} = d(\Delta V_C)/dC$	cycle time $t_l = t_k \times kmax + t_{bl}$	
δV_{0i}—residual value	maximum sensitivity $S_{dM\,lk}$	summary ZLD (j = 1; k = 1)	$\rho_Y = \frac{1}{N} \cdot \sum_{n-1}^{N} \left\lvert \frac{Y_n - V_a}{V_a} \right\rvert \cdot 100\%$
τ_{1i}—response time	break time tbj	$\Delta V_{0Sk} = V_{0k} - V_{0(k+1)}$	
τ_{2i}—relaxation time	cycle time $t_j = t_{ji} \times i_{max} + t_{bj}$	$\Delta V_{0Sl} = V_{0l} - V_{0(l+1)}$;	
t_i—response period	ZLD $\Delta V_{0j} = V_{0j1} - V_{0j\,i\,\max}$	$\Delta V_{0S} = V_{0111} - V_{0(lkji)\max}$	
$S_i = \Delta V_{Ci}/C_i$ – sensitivity	summary SZLD (I = 1):	C-time factor $D = n_k \cdot n_l \cdot D_{jmax}$	$\delta Y_D = \left\{ \left[\int_0^t v_Y(t)\,dt \right] / Y_0 \right\} \cdot 100\%$
$D_i = (C_i \cdot \tau_i)$ is C_i-time factor	$\Delta V_{0Slkj} = V_{0lk1} - V_{0lk(j+1)}$	Degradation rate $v_Y = dY/dt$	

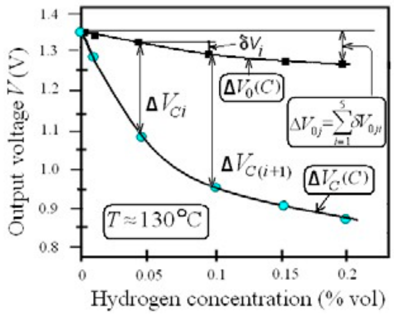

Figure 4. Experimental (symbols) and approximations (lines) of the responses' residual sum values ΔV_0 (ZLD) and amplitudes ΔV_Cvs. concentration C.

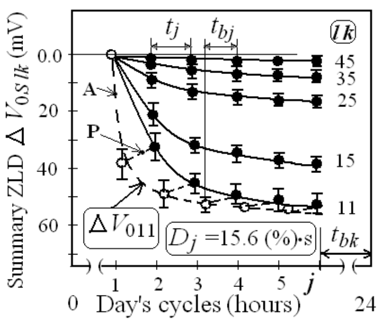

Figure 5. SZLD changes during the different day's *lk*-cycles. A and P are active and passive stages of ZLD.

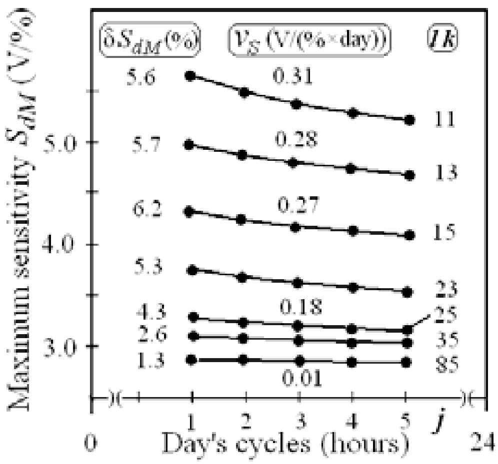

Figure 6. The changes of sensitivities S_{dM} during the different day's *lk*-cycles.

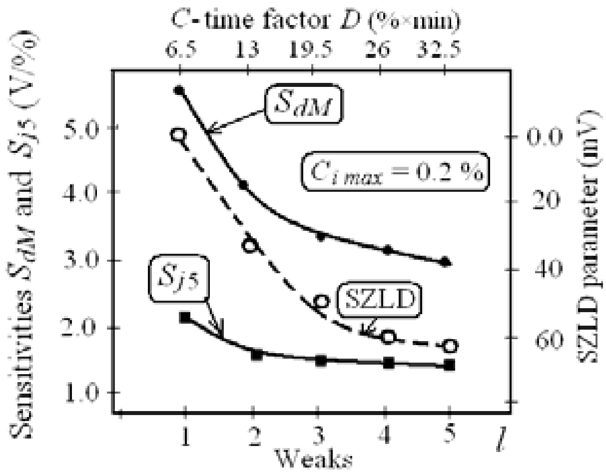

Figure 7. The changes of sensitivities S_{dM} during the weak *l*-cycles.

4. Discussion

It was found that all MISFET-sensors at long-term operation have the following degradations' features: (1) so-called "zero-line drift" (ZLD) – the changes of output voltage V at zero hydrogen concentration C; (2) reduction of hydrogen sensitivity S being equal $|dV/dC|$, if hydrogen exposition time t_C increases. The following 4-component model was used to interpret the results:

$$V(C, t, t_C) = V_{00} + \Delta V_{00}(t) - \Delta V_{0S}(C, t_C) - \Delta V_C(C, t_C) \quad (1)$$

$$\Delta V_{00}(t) = \Delta V_{0M}\cdot[1 - \exp(-t/\tau)];\ \Delta V_{0S}(C, t_C) = \Delta V_{0SM}(C, t_C)\cdot[1 - \exp(-D/D_0)];$$
$$\Delta V_C(C,t_C) = \Delta V_{CM}(C, t_C)\cdot[1 - \exp(-k_C\times C)];\ S_{dM} = k_C(C, t_C) \times \Delta V_{CM}(C, t_C), \quad (2)$$

where V_{00} is a primary voltage being about 1.4 V (at $T \approx 130$ °C). There are two sorts of ZLD: the initial time drift ΔV_{00} (t) and the drift $\Delta V_{0S}(C,t_C)$ associated with the total hydrogen dose $D = \int C(t)dt$ (C− time factor). The first one appears immediately after the turning the sensor in the operating mode (e.g., maximum changes of value $\Delta V_{00}(t)$ can be equal ΔV_{0M} in ranges from ±10 to ±50 mV during 1–5 min, and $\tau \approx 75$ s). The second sort of ZLD occurs due to operation of the sensor in a hydrogen environment. Summary ZLD (ΔV_{0Slkj}) increases, if hydrogen exposition time t_C is rising. These changes depend on time t_C, the primary operating conditions (preliminary temperature-hydrogen treatments), chip temperature and electrical modes. Maximum changes of responses' parameters are manifested in the first stages at values C-time factor D less than 25 (% vol.)×min, at D_0 being equal to about 8 (% vol.)×min.

Table 2. Average values of responses′ and model parameters of conversion function $\Delta V_C(C)$ for *lkj*-cycles.

↓parameters/*lkj*→	111	155	255	355	455	555	655	755	855	Total ΔY_D,%
ΔV_{CM}, V/ϱV_{CM}, %	0.46/4.3	0.41/3.7	0.39/3.8	0.38/3.9		0.37/4.0		0.36/4.2		21.7
k_C, 1/%/ϱk_{CM}, %	12/8.2	10/8.8	8.5/10.6	8.2/10.6		8.1/11.5		8.0/11.5		33.3
S_{dM}, V/%/ϱS_{dM}, %	5.52/12.5	4.1/12.5	3.32/14.4	3.12/14.5		2.96/15.5		2.88/15.7		47.8
v_S, V/(% × day)	-	0.28	0.16	0.024		0.016		0.08		-
S_{j5}, V/%/δS_{j5}, %	2.1/2.4	1.8/2.8	1.6/3.1	1.55/3.2		1.50/3.3		1.45/3.45		31.0
ΔV_{0Slkj}, mV	33	37	16	7		3				-
$v_{\Delta V0}$, mV/(day)	-	7.4	3.2	1.4		0.6				-
τ_{1i}, s/τ_{2i}, s (i = 2)	10/15	9/15	8/15	7/16		7/15				30/6.6
τ_{1i}, s/τ_{2i}, s (i = 5)	7/17	7/16	6/16	6/16		7/15				14.3/11.8
S_{dM}, V/%/ϱS_{dM}, % (for $C_{i\,max}$ = 1.0%)	5.5/8.7	3.9/9.2	3.65/9.8	3.5/10.2	3.4/9.5			-		38.2
D, % × min	0.26	6.5	13	19.5	26	32.5	39	45.5	52	-

5. Conclusions

This paper generalized data on researches of responses′ parameters changes of MISFET-based sensors on structure Pd-Ta_2O_5-SiO_2-Si at long-term operation and proposed models, taking into account the performance degradations. The all tested MISFET-sensors at long-term operation have degradations′ features: reduction of hydrogen sensitivity and "zero-line drift" (ZLD), which depend on operating conditions and accumulated hydrogen dose D (C-time factor). This can be explained by the effects of palladium aging (accumulation of Pd-H compounds and irreversible palladium swelling). Basic degradations′ parameters are manifested in the first stages at values D less than 25 (% vol.)×min. These effects for practical applications of hydrogen sensors were taken into account as the additive errors of "zero" (basic line drift).

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