Negative feedback phenomena in InP-based hydrogen detectors

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Properties of the hydrogen detectors on the basis of Pd/InP oxides/InP MOS structures are investigated, in particular the dependence between hydrogen pressure in the ambience and the coverage of the M/O interface by adsorbed H atoms. Presence of a negative feedback loop in the causal portrait of the hydrogen pressure – versus – M/O interface coverage by hydrogen atoms is established in the case when enthalpy of hydrogen adsorption diminishes with coverage, as supposed by the Temkin theory. The analysis is helpful in extracting model parameter values from empirical data and promoting better understanding of the modus operandi of the detectors.

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1. Introduction

Due to its direct bandgap, superior carrier mobility, elevated values of the index of refraction, as well as excellent technological properties, indium phosphide is the material of choice for various optoelectronic and high frequency applications. Building on previous experiences with InP-based metal-oxide semi-conductor (MOS) structures such as FET transistors, sensoric devices using this compound or its derivatives also emerged, in particular those detecting presence of the highly explosive hydrogen gas. There exists an urgent need for this functionality in the context of efforts to develop clean energy sources such as fuel cells [1].

Hydrogen-sensitive MOS structures are based on the phenomenon of dissociative adsorption of H_2 molecules on the surface of the catalytic metal (Pd or Pt); the H atoms then migrate through the thin metal layer to the M/O interface, where they become polarized due to difference in electron affinities between metal and oxide. Electrostatic potential of the dipole layer thus formed diminishes height of the Schottky-type barrier formed at the interface and in this way affords measurement of the hydrogen concentration in the ambient atmosphere [2]. Employment of InP instead of silicon in the role of semiconductor avoids the problem of Pd silicide formation and ensuing loss of sensitivity due to Fermi level pinning at the interface [3]. Some realizations of the sensors use more advanced microelectronic solutions such as high electron mobility transistors [4] or other III-V materials, like GaN [5].

This paper addresses the phenomenon of negative feedback influencing in important ways the operation of InP-based MOS hydrogen detectors. In section 2 existing models of the sensory function are briefly presented, in section 3 the causal diagrams analysis is applied to visualize the feedback pattern underlying the device operation. Sections 4 and 5 contain results of the numerical study and discussion.

2. Summary of the results related to the sensoric function

Analysis of the hydrogen diffusion/ adsorption phenomena in MOS structures was given by Lundström et al. [6] in the context of the Pd/SiO_2/Si material system. Hydrogen atoms that reached the M/O divide do not form an uninterrupted layer; this is expressed by the interface coverage Θ defined by the ratio n_i/N_i of the occupied versus total number of available adsorption sites at the interface. This is the quantity that immediately determines the Schottky barrier reduction (actually, the voltage change is proportional to it [7]) and hence the electrical signals carrying information about hydrogen pressure. Under steady-state conditions, Lundström et al. found that hydrogen pressure and interface coverage are bound by the relation $\Theta / (1 - \Theta) = k\,(p_{H2})^{1/2}$. The constant k is given by the kinetics of the adsorption processes and can depend on the presence of oxygen in the ambient gas.

This Langmuir-type relation is valid under the assumption that the enthalpy of adsorption of hydrogen atoms at the interface, ΔH_i, is independent of coverage. Various factors, most notably the electrostatic interaction between the adsorbed H atoms [8] may cause departure from this condition. Usually linear diminution is considered:

$$\Delta H_i = \Delta H_{i0}(1 - a\Theta). \qquad (1)$$

This yields the following expression for the Θ versus p_{H2} relation [9]:

$$\frac{\Theta}{1-\Theta} = F^{1/2}\,\exp\left(\frac{\Delta H_i}{2\mathrm{R}T}\right) p_{H_2}^{1/2}\,, \qquad (2)$$

with R the gas constant, T the temperature and the factor

$$F = \frac{2N_A\tau_0}{N_i\sqrt{2\pi MRT}} \qquad (3)$$

has the character of an equilibrium constant. (N_A is Avogadro number, $\tau_0 \approx 10^{-13}$ s [10] is related to the period of surface-atom vibration, and M is hydrogen molecular mass.) Equation (2) in conjunction with (1) yields in the vicinity of Θ = 1/2 logarithmic dependence of Θ on p_{H2} known as the Temkin isotherm.

3. Identification of feedback pattern in the model of hydrogen sensors

Mutual relationships among quantities bound by analytic conditions can be visualized with the help of causal diagrams [11]. The diagram in the upper part of Fig. 1 portrays the relation between differentials of quantities x and y, $\delta y = t_{xy}\delta x$. One may conceive the change δx as the cause of the change δy, the oriented line xy then represents the flow of causal influence. The quantity t_{xy}, or, sometimes t(xy), is called the transmission function of the diagram edge xy. One can, of course, envisage more complex diagrams; for the present purpose, the diagram in the lower part of Fig. 1 represents situation when there is a closed path – feedback loop – with transmission function t_{loop} attached to the output port of the rudimentary diagram, so that the transmission function is $t_{xy} = {}^0t_{xy}/(1 - t_{loop})$.

Returning to the sensor problem, we select quantities p_{H2}, Θ, and ΔH_i as the leading variables of the model, keeping other quantities fixed. Differentiating (1) and (2) (the latter squared on both sides) we obtain after some algebra

$$\delta\Delta H_i = -a\Delta H_{i0}\delta\Theta \qquad (4)$$

$$\delta\Theta = \frac{F}{2}\frac{(1-\Theta)^3}{\Theta}e^{\Delta H_i/RT}\delta p_{H_2} + \frac{\Theta(1-\Theta)}{2\mathrm{R}T}\delta H_i\,. \quad (5)$$

Introducing transmission functions

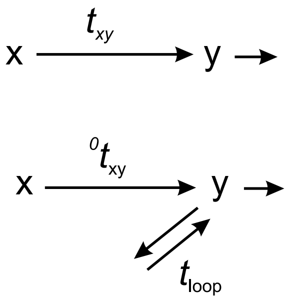

Fig. 1. Elements of the diagrammatic representation. Upper diagram represents relation $\delta y = t_{xy}\delta x$, with t_{xy} the transmission function of the oriented edge xy. *Lower diagram contains a feedback loop attached to the output vertex; its transmission function is $t_{xy} = {}^0t_{xy}/(1 - t_{loop})$.*

$$
\begin{aligned}
&{}^1t(\Theta\Delta \mathrm{H}_i) = -a\Delta H_{i0}\,, \quad {}^2t(\Delta H_i\Theta) = \frac{\Theta(1-\Theta)}{2\mathrm{R}T}\,,\\
&{}^0t(p_{H_2}\Theta) = \frac{F}{2}\frac{(1-\Theta)^3}{\Theta}e^{\Delta H_i/RT}\,, \qquad (6)\\
&t_{loop} = {}^1t(\Theta\Delta \mathrm{H}_i)\,{}^2t(\Delta H_i\Theta) = -\frac{a\Delta H_{i0}}{2\mathrm{R}T}\Theta(1-\Theta),
\end{aligned}
$$

one can set up the diagram (Fig. 2) depicting causal relationships implicit in the model of MOS hydrogen sensor as given by equations (1) and (2).

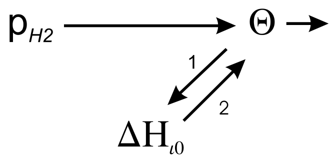

Fig. 2. Diagrammatic portrait of the Temkin model of interface adsorption phenomena in hydrogen detectors. (Symbols for diagram vertices, unlike the variables they represent, are not italicized.)

Differential form of the Θ versus p_{H2} isotherm is then

$$\frac{\mathrm{d}\Theta}{\mathrm{d}p_{H_2}} = \frac{{}^0t(p_{H_2}\Theta)}{1-t_{loop}}\,. \qquad (7)$$

4. Numerical study of the Pd/InP oxides/InP MOS detectors

We confront the derived analytical expressions with the Θ versus p_{H2} data in the paper of Liu et al. (Fig. 8 in [3]). These are two sets of experimental data obtained at 80 and 110°C, re-plotted in Fig. 3 as filled and open squares, respectively. In fitting these data (solid lines in the figure) following parameter values were found to yield the best least-squares approximation: N_i = 1.05x10^{16} M^{-2}, a = 0.08 for T = 353 K (80°C) and N_i = 1.54x10^{16} M^{-2}, a = 0.04 for T = 383 K (110°C). The value ΔH_{i0} = 40520 Jmol^{-1} = 0.42 eV/atom was found by Liu et al. [3]. Dependences of the feedback loop transmission function

t_{loop} on interface coverage Θ are shown in Fig. 4 for both temperatures.

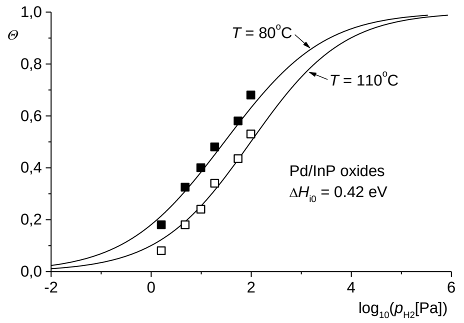

Fig. 3. Experimental surface coverage Θ versus hydrogen pressure p_{H2} data of Liu et al. [3] (discrete points) approximated by analytic expression (continuous curves) for two temperature values.

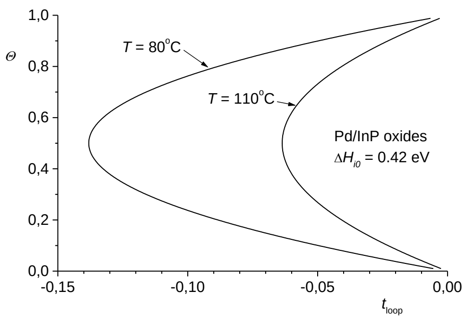

Fig. 4. Dependences of the transmission function of the feedback loop in the diagram in Fig. 2, t_{loop}, on surface coverage Θ. Companion curves to the two isotherms shown in Fig. 3.

5. Discussion and conclusions

Fitting procedure in Fig. 3 suggests that both the number of available adsorption sites at the interface N_i and the parameter a in (1) vary with temperature. As follows from (3), (6) and (7), the not inconsiderable increase of N_i with temperature causes, together with the factor $\exp(\Delta H_i/RT)$, the downward shift of the 110°C isotherm with respect to the one belonging to 80°C. As a matter of fact, a 47% increment in N_i due exclusively to a 30 K increase in temperature does not seem plausible. The quantity N_i apparently encompasses also interplay between diffusion and solubility phenomena in the catalytic metal (which have their own temperature dependence) and the adsorption proper at the metal/oxide interface. This is not explicitly expressed in the Langmuir or Temkin theory.

The sign of the feedback loop transmission function (Fig. 4) is negative, meaning that the feedback phenomenon tends, according to (7), to decrease the slope of the Θ versus p_{H2} isotherms. The diminution of the absolute value of t_{loop} with temperature is due to reduction in the value of a (caused by decreased interaction energy among the adsorbed H atoms) and to the thermal energy factor RT in the denominator of the expression for t_{loop} given in (6).

The oxide layer in InP-based MOS structures is formed by a mixture of In_2O_3 (about 70%) and P_2O_5 (about 30%) whose exact composition varies according to preparation conditions [12]. The values of the enthalpy of adsorption at the interface, ΔH_{i0}, can therefore differ from the one used by us.

The feedback phenomena, with their pronounced temperature dependence, play a more important part in the operation of InP-based hydrogen sensors than is the case for their Pd/SiO_2/Si counterparts. Due to its smaller bandgap, silicon cannot be used at elevated temperatures (above 200°C) tolerated by InP.

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References

[1] T. Hübert, L. Boon-Brett, G. Black, U. Banach, Sens. Actuators B: Chem. **157**, 329 (2011).
[2] K. W. Lin, H. I. Chen, H. M. Chuang, C. Y. Chen, C. T. Lu, C. C. Cheng, W. C. Liu, IEEE Sensors J. **4**, 72 (2004).
[3] W. C. Liu, H. J. Pan, H. I. Chen, K. W. Lin, S. Y. Cheng, K. H. Yu, IEEE Trans. Electron. Dev. **48**, 1938 (2001).
[4] T. H. Tsai, H. I. Chen, C. F. Chang, P. S. Chiu, Y. C. Liu, L. Y. Chen, T. P. Chen, W. C. Liu, Appl. Phys. Lett. **94**, 012102 (2009).
[5] J. R. Huang, W. C. Hsu, Y. J. Chen, T. B. Wang, G. I. Chen, V .C. Liu, IEEE Sensors J. **11**, 1194 (2011).
[6] I. Lundström, S. Shrivaram, C. Svensson, L. Lundkvist, Appl. Phys, Lett. **26**, 55 (1975).
[7] I, Lundström, L. G. Petersson, J. Vac. Sci. Technol. **A14**, 1539 (1996).
[8] M. Eriksson, I. Lundström, L. G. Ekedahi, J. Appl. Phys. **82**, 3143 (1997).
[9] L. G. Petersson, H. M. Dannetun, J. Folberg, I. Lundström, J. Appl. Phys. **58**, 404 (1985).
[10] G. A. Somorjai, Principles of Surface Chemistry, Prentice-Hall, Engelwood Cliffs (1972).
[11] F. Šrobár, Eur. J. Phys. **13**, 1 (1992).
[12] J. F. Wager, C. W. Wilmsen, J. Appl. Phys. **51**, 812 (1980).

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