
doi:

V.V. IL'CHENKO, O.M. KOSTIUKEVYCH, V.V. LENDIEL, V.I. RADKO,
N.S. GOLOBORODKO

Taras Shevchenko National University of Kyiv
(64, Volodymyrs'ka Str., Kyiv 01033, Ukraine; e-mail: mirror@ukr.net)

**EFFECT OF GAS ENVIRONMENT
ON ELECTROPHYSICAL PARAMETERS
OF HETEROJUNCTIONS ON THE BASIS
OF SCHOTTKY BARRIER WITH NANO-STRUCTURED
(95% In₂O₃ + 5% SnO₂) OXIDE FILMS**

PACS 07.07.Df

Electrophysical characteristics of gas-sensitive Ni – (95% In₂O₃ + 5% SnO₂) – p-Si heterojunctions have been studied experimentally. The analysis of their current-voltage characteristics (CVCs) registered in various gas environments reveals a significant increase of the reverse current through specimens in the atmosphere of ethanol or isopropyl vapor. Various mechanisms of current flow through the heterojunction are considered to explain this phenomenon. Variations in the potential barrier height under the action of image forces are demonstrated to play a significant role in shifts of the reverse CVC branches of examined specimens. The image force changes are explained by the influence of the adsorbate on the dielectric permittivity of oxide films.

Keywords: gas sensors, adsorption, dielectric permittivity, image forces, Schottky barrier.

1. Introduction

The qualitative and quantitative analyses of the gaseous medium composition become an urgent issue for scientists and physicians in connection with a necessity to solve a number of problems relevant to various domains in industry and agriculture. Semiconductor sensors, which are based on various operational principles and contain various transducers – acoustic, micro-calorimetric, optical, luminescent, resistive, capacitive, *etc.* – have been intensively developed in the last years [1]. A broad class of semiconductor materials is used in the form of pressed powders, single crystals, thin films, and porous formations [2]. A considerable attention is paid to the research of

nano-crystalline oxide materials, which are characterized by unique properties and demonstrate wide opportunities of their application. Highly effective sensors for detecting H₂S, CO, H₂, NO₂, hydrocarmonic compounds, alcohols, and so forth were created on the basis of ZnO, SnO₂, TiO₂, In₂O₃, WO_x, AgVO₃, CdO, MoO₃, CuO, and Fe₂O₃ substances [3–9].

The most developed are the sensors on the basis of metal oxides, in which the resistive effect is used. At the same time, surface-barrier structures are known to be more efficient for the detection of low gas concentrations in the *ppm*-range, as well as when functioning at temperatures of a gas-sensitive element close to room one, which was evidently demonstrated for silicon heterostructures with a porous layer [10, 11]. In theoretical works [12–14], it was shown, e.g., that the molecular adsorption affects the height of a potential barrier and parameters of the

© V.V. IL'CHENKO, O.M. KOSTIUKEVYCH,
V.V. LENDIEL, V.I. RADKO,
N.S. GOLOBORODKO, 2016

intermediate layer (its dielectric permittivity and the surface state density) in those structures. As a result, their response to the gas environment changes.

However, despite all that, sensor structures on the basis of heterojunctions with the Schottky barrier still remain rather a new object for researches. The physical principles that are responsible for the formation of their functionally important parameters have not been studied enough.

Mixtures of indium, In_2O_3 , and tin, SnO_2 , oxides taken in various proportions are one of the major materials for the fabrication of intermediate layers in heterojunction structures. They revealed themselves well in this quality owing to their high adsorption sensitivity and well-elaborated deposition technologies. This work is aimed at finding the dominating mechanism of how the gas environment affects the processes of current flow through surface-barrier structures containing (95% In_2O_3 + 5% SnO_2) nano-sized interlayers.

2. Theoretical Part

In the general case, the current-voltage characteristic (CVC) of a metal–semiconductor contact is described by the following expression in both the diode and diffusion theories of rectification [15]:

$$I = I_s \left(\exp \left(\frac{eV_2}{kT} \right) - \exp \left(\frac{-eV_1}{kT} \right) \right), \quad (1)$$

where I_s is a generalized parameter, which can be written in various explicit forms depending on the prevailing mechanism of charge transfer through the contact, k the Boltzmann constant, T the temperature, V_1 the voltage drop across the intermediate layer, and V_2 the voltage drop across the space charge region in the semiconductor.

In the framework of the diode theory of rectification, the parameter I_s is determined by the Richardson–Deshman formula, which describes the current of thermionic emission:

$$I_s = eP_nAT^2 \exp \left(\frac{-\varphi_b}{kT} \right), \quad (2)$$

where e is the electron charge, P_n the transmittance of a potential barrier, A the Richardson constant, $\varphi_b = \varphi_0 + \mu$, and μ is the Fermi level position. If the image forces are taken into account in the diode the-

ory approximation, expression (1) acquires the form

$$I = \frac{e\nu_n n_0}{4} P_n \exp \left(\frac{-\varphi_0}{kT} \right) \exp \left(\frac{\pm \Delta\varphi}{kT} \right) \times \left(\exp \left(\frac{eV_2}{kT} \right) - \exp \left(\frac{-eV_1}{kT} \right) \right), \quad (3)$$

where ν_n is the average velocity of charge carriers, n_0 the concentration of impurities in the semiconductor,

$$\Delta\varphi = \frac{2e^2}{\varepsilon_0\varepsilon_2} \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} Ln_0 \right)^{1/2}, \quad (4)$$

is a variation of the potential barrier height, ε_1 and ε_2 are the dielectric permittivities of the intermediate layer and the semiconductor, respectively, and

$$L = \sqrt{\frac{\varepsilon_0\varepsilon_2(\varphi_0 - eV_2)}{2\pi e^2 n_0}} \quad (5)$$

is the width of the space charge region in the semiconductor. The sign in front of $\Delta\varphi$ in Eq. (3) is positive if $\varepsilon_1 > \varepsilon_2$ and negative if $\varepsilon_1 < \varepsilon_2$.

From the viewpoint of explaining the regularities in the CVC behavior in the presence of a gas environment, the most interesting and important is the elucidation of the issue concerning the mechanism of charge transfer through the heterojunction. In rectifying contacts metal–semiconductor, the following ways of charge transfer take place [16]: emission of electrons over the barrier, tunneling through the barrier (the field and thermal-field mechanisms), transmission of charge carriers through the interface with the participation of surface electron states, tunnel-resonance mechanism of charge carrier transfer via a deep level located in the space charge region in the semiconductor, and generation-recombination mechanism. Each of them is characterized by specific features in the current-voltage characteristic and the behavior of the parameter I_s . This circumstance makes it possible, on the basis of their analysis, to draw conclusions about the dominance of one of the mechanisms mentioned above under those or other operational conditions, including the chemical composition of a sensor structure. As a quantitative measure of the current growth under a variation of the applied voltage, the following parameters of CVC non-ideality are used as a rule:

$$\alpha = \frac{d \ln I}{dV}, \quad (6)$$

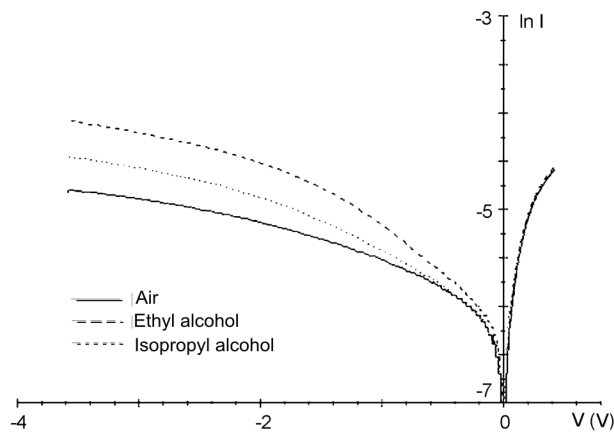


Fig. 1. Current-voltage characteristics for a specimen with a 12-nm oxide film obtained in various environments

$$\alpha^* = \frac{d \ln I^*}{dV}, \quad (7)$$

where I and I^* are the magnitudes of direct and reverse currents, respectively, and V is the applied voltage.

If the current flow through a heterojunction is governed by the overbarrier mechanism of charge transfer, the adsorbed layer should affect the profiles of both direct and reverse CVC branches. As a rule, this occurs owing to a variation in the potential barrier height under the action of the electrostatic field created by adsorbed molecules. This influence can be caused, in particular, by the emergence of an additional electric field formed by the layer of polarized adsorbate atoms near the structure interface, as occurs in developed earlier gas-sensitive MOS-condensers [17], or by the charge variation at the surface levels localized at this interface, which was also studied by other authors [10].

3. Experimental Part

Experimental specimens were fabricated from silicon KDB-1 wafers $5 \times 5 \times 0.5 \text{ mm}^3$ in dimensions. Oxide films (95% $\text{In}_2\text{O}_3 + 5\% \text{SnO}_2$) 4, 6, 8, and 12 nm in thickness were sputtered onto the wafers. Nickel contacts 0.8 mm in diameter were deposited onto the oxide layer.

The deposition of the oxide layer was carried out on an industrial vacuum installation VUP-5. The method of reactive magnetron sputtering from a metal target with the corresponding ratio between

the indium and tin contents was applied. The process was carried out at a constant discharge current of 200 mA and a residual gas pressure at a level of $(3 \div 5) \times 10^{-5}$ Torr in a vacuum chamber. The working gas mixture consisted of argon and oxygen taken in a pressure ratio of 3:1. The total pressure of the gas mixture in the course of sputtering was equal to 6×10^{-3} Torr. The thickness of oxide films was controlled in the course of sputtering by the deposition time.

The metal contacts were created in the same vacuum installation by the magnetron sputtering from a metal target in the argon atmosphere.

The current-voltage characteristics of specimens were registered in the experimental chamber at gas concentrations corresponding to the saturation vapor pressures of corresponding substances. The measurements were executed with the help of an installation created on the basis of two digital multimeters connected to a computer.

4. Results and Their Discussion

In Fig. 1, the CVCs for a heterojunction fabricated on the basis of a thin 12-nm film measured in various environments are depicted. The current dependences for heterostructures with films of other thicknesses have a similar behavior.

The growth of the reverse current through the specimen with the applied voltage often testifies to a parasitic current leakage along the specimen lateral surface. However, with regard for the distance from the contact edges to the specimen edge (about several millimeters), as well as the small thickness of the film, we may assert that the leakage and the associated effects can hardly be a substantial factor that drives the behavior of reverse CVC branches.

In addition, those curves testify that the non-ideality parameter for the direct CVC branch, Eq. (6), remains independent of the atmosphere around the specimen in the whole interval of applied voltages. In the figure, this independence manifests itself as a coincidence of direct CVC branches measured in various environments.

On the contrary, the non-ideality parameter for the reverse CVC branch, Eq. (7), turned out substantially dependent on the heterostructure environment. One can see that the CVCs of the same specimen change if the vapors of different substances are consecutively

introduced into the measurement chamber of the experimental installation.

The values of a_{\max}^* and a_{\max} differ substantially from the values typical of contact structures if the influences of electron states at the interface and the intermediate layer are not taken into consideration ($a = e/kT$). Therefore, the further consideration of regularities in CVC variations requires that those factors have to be involved.

By applying an approach used in work [18] to those dependences and taking expressions (1) and (2) into account, one can try to clarify the dominating way of charge transfer in the experimental specimens and the mechanism of gas environment influence on the CVC behavior.

The estimation of the contribution made by the tunnel current to the formation of a gas sensitivity in the examined structures brings us at once to the conclusion that this contribution is not essential if we consider the charge carrier concentration in the substrate material. The tunnel-resonance mechanism of charge transfer via deep acceptor levels can also be excluded from consideration because of the absence of such levels in the substrate. Since the reverse current in the specimens is not described by the dependence $I \sim \sqrt{\varphi_0 + eV_2}$, it is evident that the generation-recombination mechanism of charge carrier transmission is insignificant as well.

In order to elucidate the role of surface states in a change of the current through the heterojunction owing to a change of the gas environment, the dependences of the CVC non-ideality parameter a^* on the applied voltage were studied. The quantity a^* can be written in the form

$$\alpha^* = \frac{e}{kT} \left(\frac{\varepsilon_2 d}{\varepsilon_1 L} + \frac{eD}{\varepsilon_0 \varepsilon_1} \frac{dm_i}{dV} \right) \left(1 + \frac{\varepsilon_2 d}{\varepsilon_1 L} \right)^{-1}, \quad (8)$$

where $m_i = n_i / \left(1 + \exp \left(\frac{e_i - \mu - eV_1}{kT} \right) \right)$ is the degree of discrete level filling, and n_i is the concentration of surface states. The analysis of the behavior of n_i calculated from the values of non-ideality parameter a^* showed that the concentration of surface states decreases with the increase of the applied reverse voltage. Taking this circumstance into account, as well as the fact that the influence of the gas environment on the reverse current grows with the reverse voltage, we may draw conclusion that this growth is not stimulated by the currents via the surface levels. Moreover,

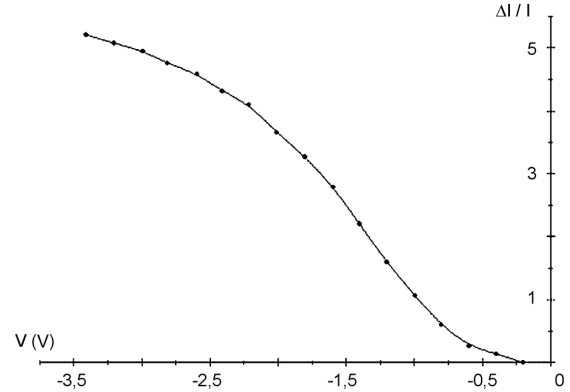


Fig. 2. Dependence $\frac{\Delta I}{I} = f(V)$ for a specimen with a 8-nm film obtained in isopropyl alcohol vapor

if the currents via the surface levels had played a considerable role, the variation of n_i at a change in the environment would have affected the parameter I_s . However, this is not observed in the relevant dependences, including those in Fig. 1.

Let us assume that the influence of the gas environment on the specimen CVC profiles is associated with a variation in the potential barrier height induced by the electric field generated by molecules adsorbed on the surface. In this case, on the basis of expressions (1) and (2), we obtain

$$I \sim \exp \left(\frac{\varphi_0}{kT} \right) \left(\exp \left(\frac{-(\varphi'_0 - \varphi_0)}{kT} \right) - 1 \right), \quad (9)$$

$$\frac{\Delta I}{I} = \exp \left(\frac{-(\varphi'_0 - \varphi_0)}{kT} \right) - 1, \quad (10)$$

where φ'_0 is the barrier height in the presence of a gas environment. From whence, one can see that this effect should be characterized by two important features:

- 1) since $\varphi'_0 - \varphi_0 = \text{const}$, the ratio $\frac{\Delta I}{I}$ should also be constant and independent of the applied voltage; and
- 2) the appearance of adsorbate molecules on the oxide film surface should affect both the direct and reverse branches of specimen CVCs.

Figure 1 demonstrates that the second feature is absent. To check the first one, the dependences $\frac{\Delta I}{I} = f(V)$ were plotted for all specimens. In Fig. 2, the CVC measured for a heterostructure with a 8-nm film in the presence of isopropyl alcohol vapor is shown. A similar behavior was also observed for other film thicknesses.

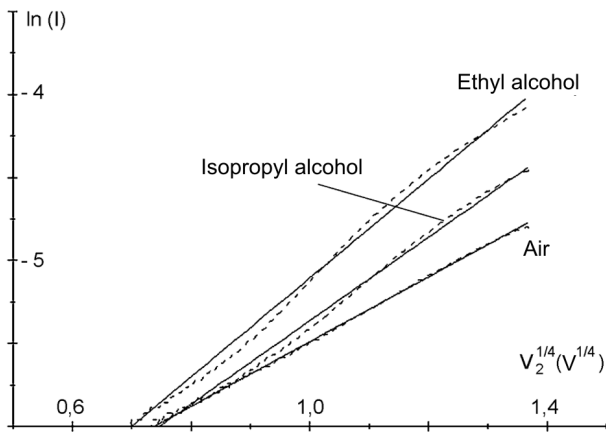


Fig. 3. Dependences $\ln I = f(V_2^{1/4})$ for a specimen with a 12-nm film obtained in various environments

The character of the curve in Fig. 2 testifies that the ratio $\frac{\Delta I}{I}$ is not constant, so that the first feature is also absent. Therefore, we may assert that the gas sensitivity of examined specimens cannot be explained only by a variation of the potential barrier height induced by the field of molecules adsorbed on the oxide film surface.

It is known that the shape and the height of the potential barrier localized in the intermediate layer of metal–semiconductor junctions with superthin oxide layers, as well as in classical MOS structures, can depend, to some extent, on the applied voltage [19]. This phenomenon affects the electrophysical characteristics of those junctions and results in a substantial CVC non-ideality of diodes fabricated on their basis. Together with the influence of surface states, the effect of image forces is a major factor responsible for the instability of reverse currents in the case of overbarrier charge transfer mechanism, when the applied voltage is varied [16].

If the matter concerns heterostructures, in which the intermediate layer is thick enough or is formed from such wide-band gap substances as silicon dioxide, the influence of image forces is usually not essential against the dominating tunnel and other effects. However, in our case of superthin films, a reduction of the potential barrier height owing to the Schottky effect acquires a substantial value, and it cannot be neglected [19].

In order to elucidate the role of image forces in the mechanism governing a variation of the reverse current through the heterostructure, the dependence

$\ln I = f(V_2^{1/4})$ was studied. In particular, it was found that this dependence can be well approximated by straight lines for all specimens and for various gas environments in a wide range of reverse voltages. Figure 3 illustrates this fact on an example of a specimen with a 12-nm film. Therefore, we can assume that a variation of the barrier height in the film, which is stimulated by a change of image forces, plays a crucial role for the CVC profiles in the analyzed specimens.

In view of expression (4) for a variation of the barrier height and expression (5) for the width of the space charge region in the semiconductor, it is possible to write

$$\Delta\varphi \sim \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^{1/2} (\varphi_0 + eV_2)^{1/4}. \quad (11)$$

Here, the dielectric permittivity of the intermediate layer, ε_1 , is a control parameter for the reverse current through the heterojunction. We assume that it is this parameter that governs the influence of image forces on a variation of the potential barrier height in the film. In other words, the influence of the gas environment on the current created by minority charge carriers in heterojunctions is exerted indirectly, through changes in the dielectric permittivity of the intermediate layer. Those changes, in turn, are a result of the adsorption of molecules from the gas environment onto the oxide surface and their further diffusion into the film bulk.

5. Conclusions

Our research of the electrophysical parameters of gas-sensitive heterostructures on the basis of a rectifying Schottky junction with nano-sized (95% In_2O_3 + 5% SnO_2) intermediate layers has revealed a substantial growth of reverse currents through the heterostructures in the gas environment of ethyl or isopropyl alcohol. It is shown that the major mechanism of gas sensitivity in the examined specimens consists in a variation of the potential barrier height in the oxide film, which takes place owing to a change of the image force action on the minority charge carriers in the heterojunction. This variation is of crucial importance for the shape of heterojunction current-voltage characteristics and, in effect, is the major functional parameter governing the heterojunction response to the adsorption of ethyl or isopropyl alcohol molecules

in the researched sensor structures. The gas environment is demonstrated to affect the current of minority charge carriers in the considered heterostructures indirectly, by changing the dielectric permittivity of the intermediate layer. The latter phenomenon, in turn, can be a result of the adsorbate diffusion into the bulk of the oxide film.

1. D. Kohl, *J. Phys. D* **34**, R125 (2001).
2. G. Korotcenkov and B.K. Cho, *Crit. Rev. Solid State Mater. Sci.* **35**, 1 (2010).
3. G. Eranna, B.C. Joshi, D.P. Runthala, and R.P. Gupta, *Crit. Rev. Solid State Mater. Sci.* **29**, 111 (2004).
4. M.M. Arafat, B. Dinan, S.A. Akbar, and A.S.M.A. Haseeb, *Sensors* **12**, 7207 (2012).
5. V.A. Skryshevsky, O.V. Tretiak, V.A. Vikulov, V.M. Zinchuk, F. Koch, and Th. Dittrich, *Phys. Status Solidi A* **197**, 534 (2003).
6. G. Zhang and M. Liu, *Sensor. Actuat. B* **69**, 144 (2000).
7. S. Elouali, L.G. Bloor, R. Binions, I.P. Parkin, C.J. Carmalt, and J.A. Darr, *Langmuir* **28**, 1879 (2012).
8. H. Wang, K. Dou, W.Y. Teoh, Y. Zhan, T.F. Hung, F. Zhang, J. Xu, R. Zhang, and A.L. Rogach, *Adv. Funct. Mater.* **23**, 4847 (2013).
9. S.K. Gupta, A. Joshi, and M. Kaur, *J. Chem. Sci.* **122**, 57 (2010).
10. V.G. Litovchenko, T.I. Gorbanyuk, V.S. Solntsev, and A.A. Evtukh, *Appl. Surf. Sci.* **234**, 262 (2004).
11. V. Strikha, V.A. Skryshevsky, V. Polishchuk, E. Souteyrand, and J.-R. Martin, *J. Porous Mat.* **7**, 111 (2000).
12. D.B. Dimitrov, *Phys. Rev. B* **51**, 1562 (1995).
13. D. Stievenard and D. Deresmes, *J. Appl. Phys. Lett.* **67**, 1570 (1995).
14. V.A. Vikulov, V.I. Strikha, V.A. Skryshevsky, S.S. Kilchitskaya, E. Souteyrand, and J.-R. Martin, *J. Phys. D* **33**, 1957 (2000).
15. V.I. Strikha, *Contact Phenomena in Semiconductors* (Vyshcha Shkola, Kyiv, 1982) (in Russian).
16. E.H. Rhoderick, *Metal-Semiconductor Contacts* (Clarendon Press, Oxford, 1978).
17. V.S. Solntsev, V.G. Litovchenko, T.I. Gorbanyuk, and A.A. Evtukh, *SPQEO* **11**, 381 (2008).
18. O.Y. Bomk, L.G. Ilchenko, V.V. Ilchenko, G.V. Kuznetsov, V.M. Pinchuk, O.M. Pinchuk, and B.I. Strikha, *Ukr. Fiz. Zh.* **44**, 759 (1999).
19. Y. Hijikata, *Physics and Technology of Silicon Carbide Devices* (InTech, 2002).

Received 27.01.14.

Translated from Ukrainian by O.I. Voitenko

*В.В. Ільченко, О.М. Костюкевич,
В.В. Лендел, В.І. Радько, Н.С. Голобородько*

ПРО МЕХАНІЗМ ВПЛИВУ ГАЗОВОГО
СЕРЕДОВИЩА НА ЕЛЕКТРОФІЗИЧНІ ПАРАМЕТРИ
ГЕТЕРОСТРУКТУР НА ОСНОВІ БАР'ЄРА ШОТТКІ
З НАНОСТРУКТУРОВАНИМИ ПЛІВКАМИ
СКЛАДУ (95% In₂O₃ + 5% SnO₂)

Резюме

Проведено експериментальні дослідження електрофізичних властивостей газочутливих гетероструктур складу Ni – (95% In₂O₃ + 5% SnO₂) – p-Si. Аналіз їх вольт-амперних характеристик, отриманих у різних газових середовищах, виявив суттєве зростання зворотних струмів крізь зразки в присутності пари етилового та ізопропілового спиртів. Для пояснення цих змін розглянуті різні механізми протікання струму крізь гетероперехід. Було показано, що суттєву роль у зсувах зворотних гілок ВАХ даних зразків відіграють зміни висоти потенціального бар'єра гетеропереходу, спричинені зміною дії сил електростатичного зображення в інтерфейсі. А зміни дії сил електростатичного зображення, в свою чергу, зумовлені впливом адсорбату на діелектричну проникність оксидних плівок.