

J. PAPPLER, N. BAHR, A. HÜLSE
Odessa I. I. Mechnikov National University
 Institute of Physical and Theoretical Chemistry, Center of Surface Analysis
 University of Jülich, Jülich

STATE OF THE ART OF GAS SENSORS — MOX SENSORS

AS A VARIOUS SOURCE TO ENHANCE THE PERFORMANCE AND EXPENSIVENESS OF GAS SENSORS

Sensor based on semiconducting materials has been developed for gas detection in various applications. The basic idea is to use a metal oxide semiconductor (MOS) sensor which consists of a thin film of metal oxide deposited on a substrate.

Introduction of a metal oxide into the sensor structure leads to a significant increase in its sensitivity and selectivity.



PHOTOELECTRONICS

INTER-UNIVERSITIES SCIENTIFIC ARTICLES

Found in 1986

P. Muster

State of the Art of MOX sensors Number 10

In previous two major generalities (1986, 1987) virgin or multi-layered structures of metal oxides have been established. Thick film technology is used to produce sensitive MOX layers with a thickness of few micrometers. Typical examples of thick film substrates are shown in figure 1.

On the other hand, the physical vapor deposition method is used to produce sensitive MOX on substrates which are fabricated in silicon technology, i.e. thick-filmed or thin-film technologies. Examples of MOX sensors in thin film technology in MOX layers with a thickness of few micrometers are shown in figure 2.

The major advantages of thick film sensors are good sensitivity and stability as it can be seen from the results of SnO₂ sensors and electro-chemical cells.

Typical results shown in figure 3 and 4. The electrical results shown in figure 3 and 4. The electrical characteristics of the sensors are measured at room temperature. The bars represent the measured average for a period of time. The error bars represent the standard deviation for a period of time. For low concentrations the 200°C sensor shows much higher resistance than the 300°C sensor.

Odessa
 «Astroprint»
 2001

The results of theoretical and experimental studies in problems of optoelectronics, solar power and semiconductor material science for photoconductive materials are adduced in this collection. The prospective directions for photoelectronics are observed.

For lecturers, scientists, post-graduates and students.

У збірнику наведені результати теоретичних і експериментальних досліджень з питань оптоелектроніки, сонячної енергетики і напівпровідникового матеріалознавства фотопровідних матеріалів. Розглянуто перспективні напрямки розвитку фотоелектроніки.

Для викладачів, наукових працівників, аспірантів, студентів.

Editorial board:

SMYNTYNA V. A. (editor-in-chief) — academician, Higher School Academy of Ukraine; **KUTALOVA M. I.** (executive secretary); **MAK V. T.** — Dr. Sci. (Physics and Mathematics); **LTOVCHENKO V. G.** — Associate Member of Ukrainian Academy of Sciences; **VIKULIN I. M.** — Dr. Sci. (Physics and Mathematics), Professor; **CHEMERESYUK G. G.** — Professor; **SHEINKMAN M. K.** — Associate Member of Ukrainian Academy of Sciences.

Address of editorial board:

Odessa I. I. Mechnikov National University 42, Pasteur str, Odessa, 65026, Ukraine

Здано у виробництво 13.03.2001. Підп. до друку 02.07.2001.
Формат 60×84/8. Папір офсетний. Гарнітура Літературна.
Друк офсетний. Ум. друк. арк. 13,25.
Тираж 100 прим. Зам. № 286.

Видавництво і друкарня «Астропрінт»
(Свідоцтво ДК № 132 від 28.07.2000 р.)
65026, м. Одеса, вул. Преображенська, 24.
Тел.: (0482) 26-98-82, 26-96-82, 68-77-33.
www.astropprint.odessa.ua

¹ Odessa I. I. Mechnikov National University, Odessa, Ukraine² Opole State University, Opole, Poland

PREPARATION OF THE $\text{Li}_x\text{Ni}_{1-x}\text{O}$ -SOLUTION FOR GAS SENSORS

The properties of metal-oxides, which are used as sensitive elements for gases are discussed. The systems of metals with variable valence have been got on the base of the given metals acetates and acetates of metal of 1A group are shown.

Now the complex materials of different metal-oxides are used as the primary sensitive elements to gases (CO , CH_4 , C_2H_2 , NO_x , NH_3). These materials used more often than pure ones because of their high sensitive qualities. The most effective materials are the solid solution of oxides of variable valence metals which have the general formula $\text{Me}_x^{\text{I}}\text{Me}_{1-x}^{\text{II}}\text{O}$, where Me_x^{I} — is the first group metal of the periodic system and the $\text{Me}_{1-x}^{\text{II}}\text{O}$ — is variable valence metal. These systems have stable electrophysical characteristics owing the oxygen balance establishment between volume, surface and gas phase at high temperatures. At the same time these systems are very sensitive to adsorption of small gas portions. This quality is their main trait.

We have got the systems on the base of metals with variable valence. The systems have been got on the base of given metals acetates and the acetates of metals of 1A group by decomposition in air during 5 hours by temperature 6000 °C. So we have got the oxides mixtures with the content of 1A group metals — 10, 20, 30, 40 and 50 per cent. These mixtures were the initial material for the obtained systems, by the treatment by different temperatures — 700, 800, 900, 1000 and 1200 °C.

We determined the number of «holes», corresponding to the quantity of inclusion metal of 1A group. The change of crystal lattice constant, electrical conductivity depends on the conditions to form of such systems. Fig. 1 shows the dependence of

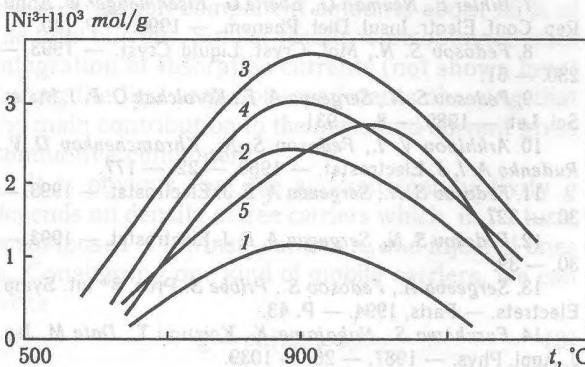


Fig. 1. Solid-solution concentration — temperature dependence. The content of 1A group metals:
1 — 10, 2 — 20, 3 — 30, 4 — 40, 5 — 50%

solid solution concentration on temperature of its formation. Fig. 2 shows the dependence of «hole»

$[\text{Ni}^{3+}] \cdot 10^3 \text{ mol/g}$

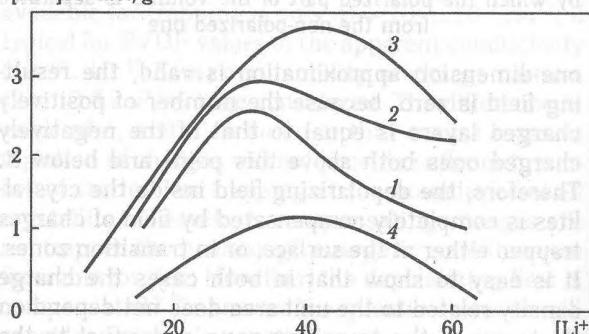


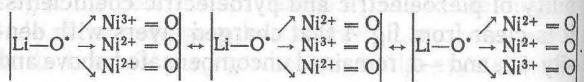
Fig. 2. «Hole» concentration — lithium concentration dependence. The temperature formation:
1 — 700, 2 — 800, 3 — 100, 4 — 1200 °C

concentration on the initial concentration of 1A group metal (lithium).

The quantitative determination of «holes» by chemical method in solid solution consists of determination of trivalent nickel in the system. When solid solution $\text{Li}_x\text{Ni}_{1-x}\text{O}$ is dissolving in the hydrochloric acid owing to oxidizing-reduction process between trivalent nickel and ion of chlorine, the uncombined chlorine is educating. The chlorine is determined by the iodometrical method. The quantity of lithium is increasing when the initial concentration is increasing.

This formula is right for all temperatures to form of solid solution. Fig. 2 shows that the curves go through the maximum (the initial concentration of lithium — at 30%) and then fall down. We have got the region where inclusion more lithium even by the way of another treatment of solid solution was impossible. The inclusion of lithium is desirable because sensor sensitivity depends on the quantity of «holes» in the system.

We can show the inner group of solid solution in mobile conduction as:



So, sensor sensitivity is the cause of the mobility. The possibility of getting the solution by the cheap well-known methods permits the possibility of gas primary making with the help of industry. The developing ideas about «hole complex» allow us to select sensors without using the method of «tests and mistakes». The goal of this work is to research the dependence of system sensitivity $\text{Me}-\text{MeO}$ ($\text{Me}-\text{Li}, \text{K}, \text{Na}, \text{Cs}; \text{MeO}-\text{NiO}$) on CO adsorption from atmosphere, draining air and nitrogen.

The films of $\text{Me}^{\text{I}} \text{Me}^{\text{II}}_{1-x} \text{O}$ which is on quartz plate with platinum contacts were used as sensitive substrate. The research of these pellicles shows that there is no any charges in the process of marking of solid solutions. The crystals sizes ($3 \dots 10 \mu\text{m}$) are rather the same. We carried out the experiment in gas flow containing CO (2 volume percent, $T = 573 \text{ K}$). There is no any sharp increasing of electrical conductivity. This preparation brings to nearly full reversibility. We researched the kinetic curve of electrical conductivity $\Delta\sigma/\sigma_0 = f(t)$ and the de-

pendence of response upon the structure of solid solution and temperature of its preparation (fig. 3).

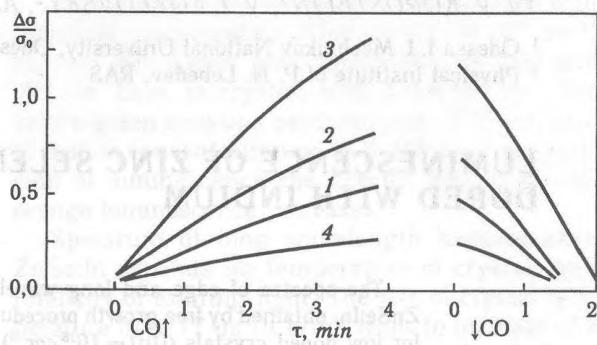
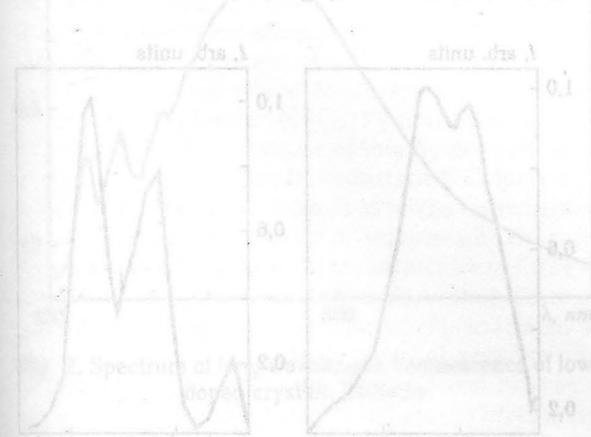


Fig. 3. Kinetic of electroconductivity. The temperature of preparation:

1 — 700, 2 — 800, 3 — 1000, 4 — 1200

The received facts are explained in terms of «hole complex».

present broad bands placed in the range 1600 cm^{-1} to 1800 cm^{-1} . The spectrum of luminescence of ZnS with low concentration of zinc ($\text{Zn}/\text{S} = 2 \dots 10^{-3}$) there is wide luminescence $\lambda_{\text{max}} = 526 \text{ nm}$. It is the consequence of another luminescence spectra were caused due to zinc lone-pair (ZLP) ions dispersed in the lattice. These detected $\lambda_{\text{max}} = 597.2 \text{ nm}$ and 608.2 nm .



2. DPL determined [8]. No. 5 — 23.2 — 0.8. The reason (C₆₀) stipulate this spectra.

CONTENT

J. KAPPLER, N. BARSAN, U. WEIMAR. State of the Art of Gas Sensors — MOX sensors as a working example	3
V. GOLOVANOV, V. SMYNTYNA, V. BRINZARI, G. KOROTCENKOV. Cd _x S- and Sn _x WO _y -based gas sensors: the role of chemical composition in CO sensing	6
V. KOVALCHUK. Real nanodimensional silicon particles: cluster approximation	12
V. EVTEEV, M. MOISEENKO, E. ZHURAVEL, E. GLUSHKO. Two models of quantum bridges connected with semiconductors or metals	18
V. BORSHCHAK, N. ZATOVSKAYA, M. KUTALOVA, V. SMYNTYNA. Influence of photoexcitation on the parameters of surface potential barrier	25
V. ZAVADSKY, V. MOKRITSKY. CdHgTe grown by LPE for photoreceivers	29
A. NOSENKO, R. LESCHCHUK. Luminescence of Ca ₃ Ga ₂ Ge ₄ O ₁₄ single crystals and thin films doped with Tb ³⁺ and Eu ³⁺ ions	31
P. FEDCHUK, I. CHEMYR, O. FEDCHUK, M. HORNEY. Semiconductor and liquid crystalline sensors in the problem of artificial intellect	34
V. DROZDOV, V. POZHIVATENKO, M. DROZDOV, A. TOTSKAYA. The Peculiarities of the First-Principal Pseudopotential in Metals	43
A. LYASHKOV, A. TONKOSHKUR, V. MAKAROV. Dielectric properties of ZnO—Ag ₂ O gas sensitive ceramics	45
A. GLOT, R. BULPETT, A. NADZHAFZADE, I. SKURATOVSKY. Electrical properties of tin dioxide based ceramics in humid air atmosphere	47
I. VIKULIN, L. VIKULINA, Sh. KURMASHEV. Photodetectors with frequency output on the basis of unijunction and field-effect phototransistors	50
S. FEDOSOV, A. SERGEEVA, V. SOLOSHENKO, P. PISSIS. Correlation between polarization and space charge phenomena in corona poled ferroelectric polymers	52
Sh. KURMACHEV, A. SOFRONOV, A. GAVDZIK, S. GAYDA. Preparation of the Li _x Ni _{1-x} O-solution for gas sensors	56
Yu. VAKSMAN, Yu. NITSUK, Yu. PURTOV, S. IGNATENKO, Yu. KOROSTELIN, V. KOZLOVSKY, A. NASIBOV, P. SHAPKIN. Luminescence of zinc selenide single crystals doped with indium	58
E. NIKONYUK, V. SHLYAKHOVYI, M. KUCHMA, M. KOVALETS, Y. ZAKHARUK. The effect of self-purification in p—CdTe—Gd crystals	61
S. ZUBRITCKY, V. BEIZYM. Thermally stimulated luminescence of polycrystals ZnS	64
A. CHEBANENKO, V. GRINEVICH, L. PHYLEVSKAYA. The optimization methods for the electrooptic parameters of the ZnS transducers	66
A. PTASHCHENKO, F. PTASHCHENKO. Tunnel surface recombination in p—n junctions	69
V. TSMOTS, V. SHTYM. The Magnetic susceptibility of Si-Ni alloys rich on silicon: influence of phases distribution and their dispersity	72
Yu. VASHPANOV, V. SMYNTYNA. Study in degradation mechanism of adsorption sensitivity and increase of stability of oxygen microelectronic sensors	75
L. TERLETSKAYA, V. SKOBEEVA, V. GOLUBTSOV. Photosensors with Si—GaAs heterojunction as memory elements	78
V. GOLOVANOV, T. RANTALA, T. RANTALA, V. LANTTO. Rehybridization at (110) faces Of SnO ₂	80
V. BORSCH, V. IRKHA, G. MAKARENKO, V. GORBACHEV. Interaction of parameters in degradation of optoelectronic devices as interaction of parameters in composite system	84
V. DROZDOV, Yu. IVANOV, M. DROZDOV. To the investigation of the properties of cubic monocrystals	88
S. GEVELYUK, I. DOYCHO, M. KOVALENKO, D. LISHCHUK, V. MAK, L. PROKOPOVICH, V. CHISTYAKOV. Influence of g-irradiation on photoluminescence of porous germanium obtained by treatment in electric spark discharge	91
P. GORLEY, O. PARFENYUK, M. ILASHCHUK, K. ULYANYTSKY, V. BURACHEK. Electric and photoelectric properties of CdTe:V crystals	95
N. MALUSHIN, V. SKOBEEVA, V. SMYNTYNA, A. DALI. Residual photoconductivity effect in semi-insulator films ZnSe _x Te _{1-x}	98
A. GLUSHKOV, A. FEDCHOUK, I. KUKLINA. Stochastic dynamics of atomic systems in magnetic field. Zeemane effect for Wannier—Mott excitons	100
A. GLUSHKOV, S. AMBROSOV, V. IGNATENKO. Nonhydrogenic atoms and Wannier—Mott excitons in DC electric field: photoionization, stark effect, resonances in ionization continuum and stochasticity	103
I. SHPINAREVA. Selective photoionization of atoms and molecules in electric field: new models	107
A. LOBODA. Structure of ground state of superatom. Ionized superatom as single electrons counter	110
S. AMBROSOV. Selective photoionization of atoms by laser field: optimal scheme. Autoionization rydberg resonances in heavy atoms	112