ВОДОРОДНАЯ ЭКОНОМИКА

HYDROGEN ECONOMY

ВОДОРОДНАЯ ЭКОНОМИКА

HYDROGEN ECONOMY

ГАЗОАНАЛИТИЧЕСКИЕ СИСТЕМЫ И СЕНСОРЫ ВОДОРОДА

GAS ANALYTICAL SYSTEMS AND HYDROGEN SENSORS

Статья поступила в редакцию 28.12.17. Ред. рег. № 2642 The article has entered in publishing office 28.12.17. Ed. reg. No. 2642

UDK 621.3

SEMICONDUCTOR GAS SENSORS FOR DETECTION OF CHEMICAL WARFARE AGENTS AND TOXIC INDUSTRIAL CHEMICALS*

V. M. Aroutiounian

Yerevan State University
1 Alex Manoogian St., Yerevan, 0025, Republic of Armenia
tel.: +374(10)55 52 40, e-mail: aroutiounv1@yahoo.com

doi: 10.15518/isjaee.2018.01-03.037-048

Referred 10 January 2018 Received in revised form 15 January 2018 Accepted 22 January 2018

The sensors for detection of toxic and chemical warfare agents (CWA) should be sensitive to low concentrations of gases – considerably lower than ones immediately dangerous to life or health concentrations. The paper shortly discusses classical CWAs and toxic industrial sensors; makes a comparison between nuclear weapons and chemical agents and a toxicity comparison between real gases and simulants. Moreover, the paper analyzes the simulants for testing the sensor devices and semiconductor gas sensor' technique; shows sensitivity change with dimethyl methylphosphonate (DMMP) gas concentration for sensor made of SnO_2.

The MoO_3, NiO, Al_2O_3, In_2O_3, Pt, ZnO and ZrO_2 additives are reported to exhibit enhanced sensitivity to dimethyl methylphosphonate (DMMP), and Al_2O_3, In_2O_3, ZrO_2 and ZnO additives – to exhibit enhanced sensitivity to dipropyleneglycol methylethylene (DPGME). SnO_2 devices with ZrO_2 and ZnO additives exhibit high sensitivity to acetonitrile.

The sensors made from Co-doped SnO_2 films demonstrate sensitivity to CWAs such as sarin and yperite. We performed the measurements at the operating temperature of 210 ºC, and found that the sensor exposed comparatively greater concentration of target gas (200 ppm sarin and 100 ppm yperite) and the SnO_2<Co> sensor was sensitive to yperite starting from 25 ppm. Furthermore, the sensitivities to 50 ppm and 12.5 ppm sarin were found.

The paper presents the results of our studies on tin oxide/ multiwall carbon nanotube film nanocomposite sensors of PG, dimethylformamide (DMF) and formaldehyde (FA) using hydrothermal synthesis and sol-gel methods. The investigations of response/recovery characteristics in the 50–300 °C operating temperature range reveal that the optimal operating temperature for the PG, DMF and FA vapor sensors, taking into account both high response and acceptable response and recovery times, was 200–220 ºC. A sensor response dependence on gas concentration in all cases was linear. We measured the minimal PG, DMF and FA gas concentrations at which the perceptible signal was registered.

Keywords: chemical sensor; toxic gas; chemical warfare agent; detection; simulants; metal oxide semiconductor; sarin; yperite; propylene glycol; dimethylformamide; formaldehyde.

Aroutiounian V.M. Semiconductor Gas Sensors for Detection of Chemical Warfare Agents and Toxic Industrial Chemicals // Международный научный журнал «Альтернативная энергетика и экология» (ISJAEE). 2018;(01-03):37-48.

ПОЛУПРОВОДНИКОВЫЕ ГАЗОВЫЕ СЕНСОРЫ ДЛЯ ДЕТЕКТИРОВАНИЯ ХИМИЧЕСКИХ АГЕНТОВ ВОЕННОГО НАЗНАЧЕНИЯ И ТОКСИЧНЫХ ИНДУСТРИАЛЬНЫХ ХИМИКАТОВ

В.М. Арутюнян

Ереванский государственный университет
д. 1 , ул. Алека Манукяна, Ереван, 0025, Республика Армения
тел.: +374(10)55-52-40; e-mail: aroutiounv1@yahoo.com

doi: 10.15518/isjaee.2018.01-03.037-048

Заключение совета рецензентов: 10.01.18 Заключение совета экспертов: 15.01.18 Принято к публикации: 22.01.18

Сенсоры для детектирования химических агентов военного назначения и токсичных индустриальных химикатов должны быть чувствительны к малым концентрациям детектируемых газов, значительно меньшим, чем опасные для жизни и здоровья концентрации.

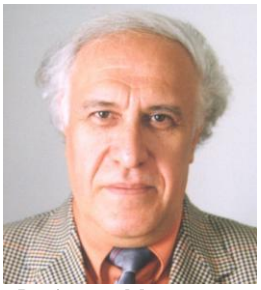
В статье кратко обсуждались классические военные и токсичные индустриальные сенсоры. Сравнивалось воздействие ядерных бомб и химических агентов и токсичность реальных и симулирующих газов. Проанализированы симулянты и методы для испытаний сенсоров. Показана зависимость чувствительности сенсора, изготовленного из SnO_2, от концентрации диметил метилфосфоната (ДММФ).

Отмечено, что добавки MoO_3, NiO, Al_2O_3, In_2O_3, Pt, ZnO и ZrO_2 повышают чувствительность к ДММФ, а добавки Al_2O_3, In_2O_3, ZrO_2 и ZnO – чувствительность материалов к дипропиленгликоль метилэтилену (ДПГМЭ). При этом SnO_2-сенсоры с ZrO_2 and ZnO добавками показывают высокую чувствительность к ацетонитрилу.

Сенсоры, изготовленные из пленок SnO_2, легированных кобальтом, продемонстрировали чувствительность к таким газам военного назначения, как зарин и иприт. Измерения были проведены при температуре нагрева подложки 210 ºС и экспозиции до сравнительно большой дозы газов (200 ppm зарина и 100 ppm иприта). Показано, что SnO_2<Co> сенсор проявлял чувствительность к иприту, начиная с 25 ppm. Установлены значения чувствительности такого сенсора при 50 ppm и 12,5 ppm.

Приведены результаты исследований сенсоров пропиленгликоля, диметилформамида и формальдегида, изготовленных из тонкопленочных нанокомпозитов на основе диоксида олова и многостенных углеродных нанотрубок путем гидротермального синтеза и золь-гель метода. Исследования характеристик отклика и восстановления сенсоров данных газов при рабочей температуре 50–300 °С позволили установить ее оптимальное значение в диапазоне 200–220 ºС. При этом зависимость чувствительности датчика от концентрации газа во всех случаях была линейной. Кроме того, были измерены минимальные концентрации газа PG, DMF и FA, при которых регистрируется воспринимаемый сигнал.

Ключевые слова: химический сенсор; токсичный газ; химический военный агент; симулянт; металооксидный полупроводник; зарин; пирит; пропилен гликоль; диметилформамид; формальдегид.



Владимир Михайлович Арутюнян
Vladimir Aroutiounian

Сведения об авторе: д-р физ.-мат. наук, академик НАН РА и Международной инженерной академии, заслуженный деятель науки Армении, зав. кафедрой «Физика полупроводников и микроэлектроника», Ереванский государственный университет.

Образование: Киевский политехнический институт (1964 г.).

Область научных интересов: полупроводниковые приборы; микро- и нанотехнологии; преобразователи солнечной энергии; сенсоры.

Публикации: 500.
h-index: 21
Research Gate: 17.70

Information about the author: D.Sc. in Physics and Mathematics, Academician of National Academy of Sciences and Intl. Engineering Acad., Honorary Scientist of Armenia, Head of Semiconductor and Microelectronics Department, Yerevan State University.

Education: Kiev Polytechnic Institute, Ukraine, 1964.

Research interests: semiconductor devices; micro- and nanotechnology; conversion of solar energy; sensors.

Publications: 500.

Introduction

Threat of military operations and terrorist acts with application of chemical agents is not only maintained, but also unfortunately rises in the modern world. Two sarin gas attacks in Japan (Matsumoto and Tokyo, 1994–1995) and recent military operations in Syria confirm this horrible reality. Therefore, the researchers continue to investigate possibilities of developing of sensors for detection of chemical agents.

Weapons of mass destruction are weapons which are capable of producing large scale destruction and/or of being used to kill or seriously injure a large number of people. Toxic chemicals are defined as any chemical which can cause death, temporary incapacitation, or permanent harm to humans or animals. Thus, chemical agent (CA) is the term used to signify the toxic component of a chemical weapon and can include CWAs and/or TICs. It is well known that chemical agents (CAs) have been used against military personnel during conventional warfare; however, due to the increasing threat of terrorist activities, the focus has now broadened to encompass the threat posed to civilians. A CA attack has the potential to create great panic in parties that are unprepared because when released, these agents are amorphous and not able to be evaded. Today there is no capability or simple devices available to detect and monitor these agents or even assume that there is no preparation for a potential attack, and therefore the first signs of exposure to an agent will be when symptoms begin to appear, that may be too late.

In a military setting, the threat of CAs can radically affect land and sea operations as well as the use of air assets. In the event of a CA release, any agent will need to be quickly detected and identified to allow such facilities to operate at their optimum level. Rapid detection will inform commanders and allow them to instruct troops to done protective equipment and plan appropriate courses of action. Electronic devices which will allow effective response in the event of exposure are necessary. If the military are well prepared for a potential attack, in that they have the ability to detect and therefore protect themselves, the likelihood of their operations being adversely affected will be significantly reduced. It will reduce panic and chaos and minimize potential casualties. Therefore, sensitive, accurate and easy to use detectors are necessary.

Technologies used today for manufacture of semiconductor sensors of chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) are shortly reported below. Such sensors should be sensitive to very low concentrations of agents – considerably lower than immediately dangerous to life or health concentrations. We reviewed papers reported in literature and carried out research with our colleagues in the UCT in Prague. This review is based on the open-source literature.

Nomenclature	
Abbreviations	
CWA	Chemical Warfare Agents
CA	Chemical Agent
DMF	Dimethylformamide
DMMP	Dimethyl Methylphosphonate
DPGME	Di(Propyleneglycol) Methyl Ether
FA	Formaldehyde
IMS	Ion Mobility Spectrometer
MWCNTs	Multiwall Carbon Nanotubes
NP	Nanoparticle
PEMS	Piezoelectric Microcantilever Sensor
PG	Propylene Glycol
PMN-PT	Lead Magnesium Niobate-Lead Titanate
TICs	Toxic Industrial Chemicals

Chemical Agents

CAs can be delivered in artillery shells or missiles, by aerial bombing or spraying and can be dispersed in a variety of different forms, including solid, liquid, gas, vapour and aerosol. Thus, a CAs route of entry into the body is dependent on which form it is appears. A gas, vapour or aerosol can be inhaled and can also enter the body via the eyes, whereas entry via the skin usually occurs when the agent is in liquid form. A vapour can also be absorbed through the skin; nerve agents attack the central and peripheral nervous system and prevent them from functioning normally.

CAs refers to both the classical CWAs and TICs.

Classical Chemical Warfare Agents

Classical CWAs are listed in Table 1 and include nerve, blister, blood and choking agents. Incapacitating and riot control agents can also be included in this category. These agents are aptly named based on their mode of action (i.e. route of penetration and their effect on the body) and sometimes according to their intended use.

Table 1

List of Classical CWAs

Таблица 1

Список классических химических газов военного назначения

Agent Class	**Agent Name**	**Abbreviation**
Nerve	Tabun	HL
	Sarin	PD
	Soman	CX
	Ethyl Sarin	AC
	Cyclosarin	CK
	O-ethyl-S-diisopropyl amino methyl methylphosphonothiolate	VX
	S-(Diethyl amino)ethyl O-ethyl ethylphosphonothioate	VE
	Amiton or Tetram	VG
	Phosphonothioic acid,methyl-, S-(2-diethyl amino)ethyl) O-ethyl ester	VM
Vesicants	Sulfur Mustard	H, HD
	Nitrogen Mustard	HN-1, HN-2, HN-3
	Lewisite	L
	Mustard-lewisite	HL
	Phenilchloroarsine	PD
	Phosgene Oxime	CX
Blood	Hydrogen Cyanide	AC
	Cyanogen Chloride	CK
	Arsine	SA
Choking	Chlorine	Cl
	Phosgene	CG
	Diphosgene	DP
	Chloropicrin	PS

Nerve Agents

Nerve agents are a group of particularly toxic CWAs that belong to the chemical group of organophosphorus compounds. They are generally stable, easily dispersed and highly toxic. Nerve agents fall into two categories, the 'G' and the 'V' agents. The 'G' nerve agents include Tabun (GA), Sarin (GB), Soman (GD) and Cyclosarin (GF), which are fluorine (GB, GD, GF) or cyanide (GA) containing organophosphorus compounds. The 'V' agents are more toxic and persistent than the 'G' agents. The most common of these agents is VX1. In general, the persistency of nerve agents ranges from low for GB through to very high for VX2. The most characteristic symptoms include difficulties in breathing, tightness of the chest, constriction of the pupils, muscular twitching, drooling, excessive sweating, nausea, vomiting, and abdominal cramps. Due to the rapid action and high lethality of these agents, there are urgent demands for rapid and reliable methods for early detection and identification of nerve agents and their degradation products.

Vesicants (Blister Agents)

Vesicants, also known as blister agents, are primarily intended to injure rather than kill people; however, exposure in some cases can be fatal. The three types of blister agents, mustards, arsenicals and urticants(1), are relatively persistent. Vesicants are readily absorbed by all parts of the body, including the eyes, mucous membranes, lungs, skin and blood-forming organs. They cause inflammation, blisters and general destruction of tissue. The actions of some vesicants can be delayed anywhere between two and 24 hours before any pain or symptoms are produced by which time cell damage has already occurred.

Mustards include the agents sulfur mustard (HD) and the three nitrogen mustards, which are stable liquids with low volatility at room temperature. Mustards attack the skin, eyes, lungs and gastrointestinal tract and when absorbed through the skin or lungs, they are transported into the body where they can damage internal organs.

Symptoms of mustard exposure are influenced by the route of entry into the body. Entry by way of skin contact results in redness, itching and formation of blisters, whilst exposure to the eyes causes irritation, pain swelling and tearing. Inhalation of mustard results in symptoms which include a runny nose, sneezing, hoarseness, bloody nose, sinus pain, shortness of breath and coughing.

Arsenicals including lewisite (L), mustard-lewisite (HL) and phenyldichloroarsine (PD) have arsenic as a central atom in their chemical structure, and are more dangerous as liquids than vapours due to their lower volatility.

Urticants are blister agents that cause an immediate, severe burning sensation followed by intense pain and then a feeling of numbness.

Blood Agents

Blood Agents including hydrogen cyanide (AC), cyanogen chloride (CK) and arsine (SA) are highly

volatile and thus able to enter the body through the respiratory. Symptoms of blood agent exposure are related to dose. Low-dose exposure causes headache and uneasiness, higher-dose exposure causes chills, nausea, and vomiting and severe exposure damages blood cells, leading to anemia and eventual death.

Choking Agents

Choking Agents such as phosgene (CG) and diphosgene (DP) are lethal CWAs which target the respiratory tract and lungs and are designed to cause death to an exposed individual. Upon inhalation, these agents cause the respiratory tract to become irritated and the membranes to swell. This swelling triggers the secretion of copious amounts of fluid, which causes excessive coughing as the body tries to clear the airway.

Toxic Industrial Chemicals

TICs are another class of CAs that are less deadly than conventional CWAs but pose a greater threat because they are more easily accessible in large quantities and are widely used in the manufacturing or primary material processing (mining and refining) industries. Whilst exposure to CWAs usually results in fatalities, exposure to TICs may not be life threatening, however multiple low level exposures can be extremely serious, causing ongoing effects on an individual's health.

Table 2

TICs and their hazard levels

Таблица 2

Токсичные индустриальные сенсоры и уровни их токсичности

High	**Medium**	**Low**
Ammonia	Acetone cyanohydrid	Allyl isothiocyanate
Arsine	Acrolein	Arsenic trichloride
Boron trichloride	Acrylonitrile	Bromine
Boron trifluoride	Allyl alcohol	Bromine chloride
Carbon disulfide	Allylamine	Bromine pentafluoride
Chlorine	Allyl cholorocarbonate	Bromine trifluoride
Diborane	Boron tribromide	Carbonyl fluoride
Ethylene oxide	Carbon monoxide	Chlorine pentafluoride
Fluorine	Carbonyl sulfide	Chlorine trifluoride
Formaldehyde	Chloroacetone	Chloroacetaldehyde
Hydrogen bromide	Chloroacetonitrile	Chloroacetal chloride
Hydrogen chlorine	Chlorosulfonic acid	Crotonaldehyde
Hydrogen cyanide	Dicetene	Cyanogen chloride
Hydrogen fluoride	1,2-Dimethylhydrazine	Dimethyl sulfate
Hydrogen sulfide	Ethylene dibromide	Diphenylmethane-4,4'-diisocyanate
Nitric acid, fuming	Hydrogen selenide	Ethyl chloroformate
Phosgene	Methanesulfonyl chloride	Ethyl chlorothioformate
Phosphorus trichloride	Methyl bromide	Ethyl phosphonothioic dichloride
Sulfur dioxide	Methyl chloroformate	Ethyl phosphonic dichloride
Sulfuric acid	Methyl chlorosilane	Ethyleneimine
Tungsten hexafluoride	Methyl hydrazine	Hexachlorocyclopentadiene
	Methyl isocyanate	Hydrogen iodide
	Methyl mercaptan	Iron pentacarbonyl
	Nitrogen dioxide	Isobutyl chloroformate
	Phosphine	Isopropyl chloroformate
	Phosphorus oxychloride	Isopropyl isocyanate
	Phosphorus pentafluoride	n-Butyl chloroformate
	Selenium hexafluoride	n-Butyl isocyanate
	Silicon tetrafluoride	Nitric oxide
	Stibine	n-Propyl chloroformate
	Sulfur trioxide	Parathion
	Sulfuryl chloride	Perchloromethyl mercaptan
	Sulfuryl fluoride	sec-Butyl chloroformate
	Tellurium hexafluoride	tert-Butyl isocyanate
	n-Octyl mercaptan	Tetraethyl lead
	Titanium tetrachloride	Tetraethyl pyrophosphate
	Trichloroacetyl chloride	Toluene 2,4-diisocyanate
	Trifluoroacetyl chloride	Toluene 2,6-diisocyanate

A comprehensive list of TICs and their hazard levels is shown in Table 2. High-hazard TICs are widely produced, stored and/or transported, have high toxicities and are easily vaporized. This group contains mainly inorganic chemicals excluding formaldehyde and ethylene oxide.

Although TICs are not as lethal as the highly toxic nerve agents, they can still have a significant impact on a targeted population. However, this is assumed to be more related to the amount of a chemical which can be employed and less related to its lethality. Therefore, larger doses of TICs may kill or harm more people than CWAs.

Chemical warfare agents (CWAs) are known to be highly dangerous for human health because of their fatal toxicity colorlessness and toxicity. Therefore, fast and selective detection of CWAs is essential to protect human beings and animals.

Table 3 shows a comparison between nuclear weapons and chemical agents. As shown here, the cost ($/ton) of chemical agents is about one tenth of that of nuclear weapons.

Table 3

Indicators of nuclear weapon and chemical agents [1]

Таблица 3

Показатели ядерного оружия и химических веществ [1]

Contents	**Nuclear weapon**	**Chemical weapon**
Direct offset angle (km^2)	190–260	260
Remaining effect period	6 months	3–36 hrs
Casualties	98% (death)	30% (injured or death)
Direct efficiency period	few seconds	7 sec – 30 min
Cost ($/ton)	1,000,000	10,000
Cost ($/ton)	1,000,000	10,000
Detection method	simple	complex

Table 4 shows a comparison of toxicity between real and simulant gases.

Table 4

The toxicity of real gases and simulant gases [1]

Таблица 4

Токсичность реальных и имитационных газов [1]

Agents	**GA (Tabun)**	**Mustard**	**AC**	**CG(Phosgene)**
Type	Nerve	Vesicant	Blood	Choking
Chemical Formula	$C_5H1N_2O_2P$	$C_4H_8SCl_2$	HCN	$COCl_2$
Toxicity, mg/kg	0.6	0.7	1	3.2
(LD_{50}), ppm	83	99	830	724
Simulants	DMMP	DPGME	Acetonitrile	Acetonitrile
Chemical Formula	$C_3H_9O_3P$	$C1H1SO_3$	CH_3CN	CH_2Cl_2
Exposure, mg/m^3	10	600	70	175
Standard, ppm	2	100	40	50

Chemical warfare agent detecting techniques

Several techniques such as infrared spectrophotometry, Raman spectroscopy, Fourier transform, photoionization, colorimetric indicators, ion mobility spectrometer (IMS) and mass spectrometers combined with gas chromatography have been developed to detect the CWAs and toxic industrial chemicals (TICs). Various techniques have been developed for the detection of CWAs (see Table 5, which shows the most important detection techniques). Among the various detection techniques, the methods most highly recommended are: the use of an ion mobility spectrometer (IMS), semiconductors, and SAW-type devices.

Table 5

CWA detecting techniques [1]

Таблица 5

Методы обнаружения химических агентов военного назначения [1]

Techniques	**Advantages**	**Disadvantages**
Photoionization	Rapid response, sensitive to organics	Poor specificity
Paper tape	Very specific to certain	Require frequent compounds replacement
Fourier transform FT-IR	More sensitive than standard IR, rapid response	High cost
Gas chromatography	Applicable to a wide variety of gases, good sensitivity	Slow response, require frequent calibration
IMS	Very good sensitivity, very specific to certain	Slower than IR
Semiconductor	Low cost, fast response	Low selectivity
SAW type	Portability, high sensitivity, low cost	Sensitive to environmental factors

Ion mobility spectrometry allows realizing ion separation and recognition and analyzing the ion mobility difference of various materials. IMS is very sensitive to organic compounds. SAW type sensors are very sensitive to environmental factors and portability; the sensors are sensitive, selective, stable, etc. Photoionization rapid response is sensitive to organics, has poor specificity. Paper tape is very specific to certain compounds and needs in frequent replacement. FT-IR is more sensitive than standard IR, has rapid response, but high cost. Gas chromatography is applicable to a wide variety of gases, has good sensitivity, but slow response, and needs in frequent calibration. IMS has very good sensitivity to certain compounds.

Simulants for the testing of sensor devices

We have to note that handling of CWAs in laboratory, when testing the related sensor, is very dangerous because of their extremely high toxicity. Therefore, many researchers in place of CWAs usually utilize appropriate simulants for the testing of sensor devices. For example, dimethyl-methyl-phosphonate (DMMP) is often studied as a stimulant of nerve agents such as sarin and soman, 1.5-dichloropentane and di(propyleneglycol) methyl ether (DPGME) are considered as simulants of mustard gas (vesicants agents), acetonitrile known as a stimulant for cyanide agents.

Semiconducting device technique

One of the most recommended methods for the detection of CWA gases is semiconducting device. Several kind of semiconductor gas sensors have been developed based on different sensing materials and various transduction platforms. The main classes of gas-sensing materials include metal oxide semiconductors, metal-oxide/polymer composite, carbon nanotube, graphene and other novel materials. Now arrays of chemically sensitive micro resistors of above-mentioned gases produced from semiconductor metal oxide are considered as one of the most promising basic technologies for detection of chemical agents. These metal oxides based chemiresistive semiconducting sensors offer advantages such as their very low cost, high sensitivity, fast response and recovery times, easy in manufacturing, small size, simple electronic interface, low power consumption and portability [1].

Experimental results

SnO_2 is the most studied material and SnO_2-based gas sensors have been used to detect CWAs and TICs [2–8], but other semiconductor metal oxide such as ZnO, TiO_2, WO_3, CuO, In_2O_3 have also been considered [9–11].

Among such devices, there are several different types which can be differentiated according to the thickness and size. Although different, these types of sensor actually have similar aspects in terms of the arrangement of the sensing electrode. In addition, the thickness of micro-type sensors is, in general, almost the same as that of thin film devices.

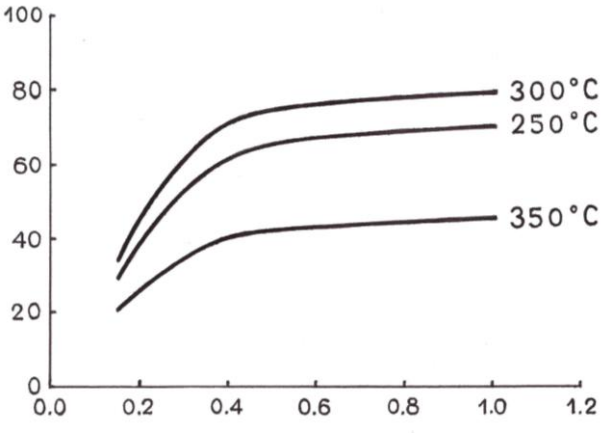


Fig. 1 – Sensitivity change with DMMP gas concentration for SnO_2
Рис. 1 – Изменения в чувствительности SnO_2 от концентрации ДММФ

Sensitivity change with DMMP gas concentration for SnO_2 was shown in Fig. 1 [1].

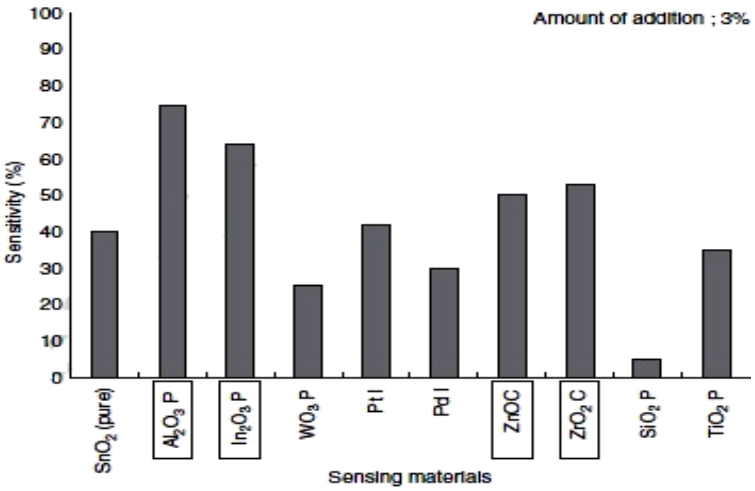
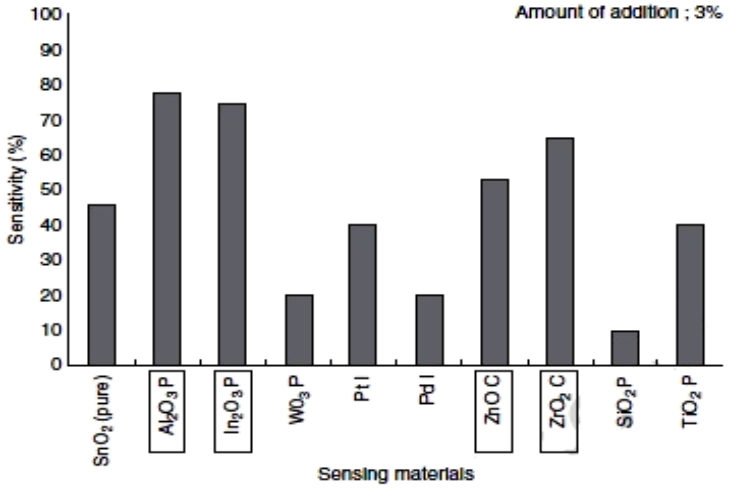


Fig. 2 – Sensing properties of various additives for DMMP [1]
Рис. 2 – Чувствительность различных материалов к ДММФ [1]

Figure 2 shows the sensing properties of various additives incorporated into the device. These results are for DMMP (ppb level). As shown here, the MoO_3, NiO, Al_2O_3 , In_2O_3, Pt, ZnO, and ZrO_2 additives exhibit enhanced sensitivity to DMMP. Figure 3 shows the sensitivities of materials with different additives to dipropylene glycol methyl ethylene, vesicant simulant. As in the case of DMMP, devices with Al_2O_3, In_2O_3, ZrO_2 and ZnO additives show high sensitivity to DPGME.

Fig. 3 – Sensing properties for DPGME [1]
Рис. 3 – Чувствительность различных материалов к ДФГМЭ [1]



As shown in Fig. 4, SnO_2 devices with ZrO_2 and ZnO additives exhibit high sensitivity to acetonitrile.

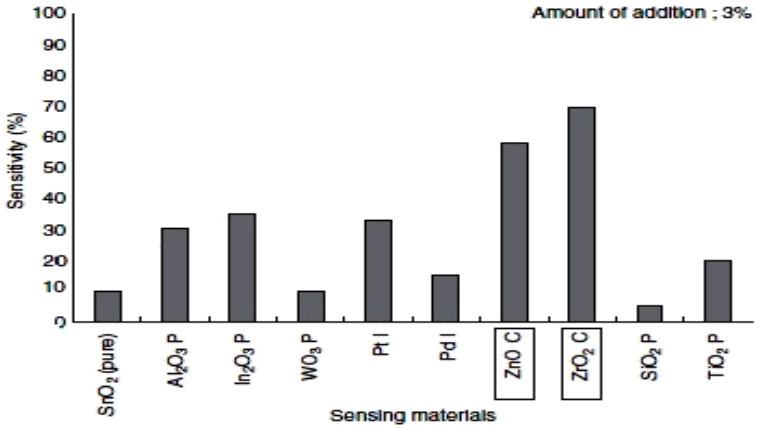


Fig. 4 – Sensing properties for CH_3Cn, simulant of blood agent [1]
Рис. 4 – Чувствительность CH_3Cn имитатора [1]

The detection of DMMP using lead magnesium niobate-lead titanate (PMN-PT) piezoelectric microcantilever sensor (PEMS) coated with various planar and particulate receptor coatings was examined in [2]. The

Young's modulus change in the PMN-PT layer was also shown to be induced by the surface stress generated by the binding of DMMP on a continuous receptor coating.

A DMMP gas sensor was fabricated in [4] using synthesized Al-doped ZnO NPs via a hydrothermal method. The average particle size of the Al-doped ZnO NPs was ~25 nm, and a single crystalline phase was confirmed through SEM and TEM observations. The variation in the response of the Al-doped ZnO NPs sensor within operating temperatures showed a rapid response of 2s and a relatively short recovery time of 96 s, compared with the un-doped ZnO NPs sensor, when exposed to 10 ppm DMMP at 350ºC. The sensitivity exhibited a linear increase of the response with an increase in DMMP concentration, and the selectivity for DMMP showed the fastest response among the gases. Such increased O2 vacancies and surface reactions with small nanocrystals in Al-doped ZnO NP sensors provide enhanced gas sensing performance for DMMP detection.

Investigations and measurements of the sensitivity of the prepared in YSU sensors made of Co-doped SnO_2 films to CWAs such as sarin and yperite were carried out at University of Defense (Vyshkov, Czech Republic). These measurements were performed at the operating temperature of 210 ºC (Figs. 5 and 6).

The measurements showed the sensor was exposed comparatively greater concentration of target gas (200 ppm sarin and 100 ppm yperite) at the beginning. Thus, the stabilization of the sensor parameters occurred. After that the SnO_2<Co> sensor was sensitive to yperite starting from 25 ppm. The sensitivities to 50 ppm and 12.5 ppm sarin were equal ~8 and ~15 accordingly at the operation temperature of 210 ºC.

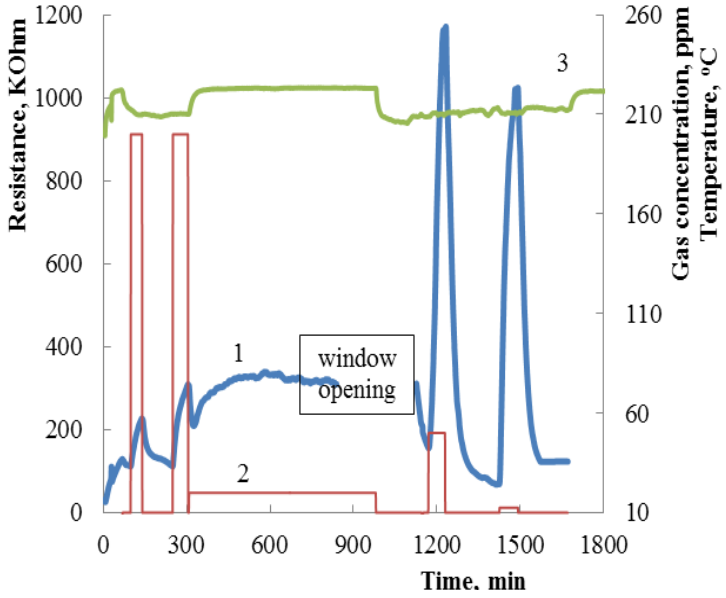


Fig. 5 – The resistance variation under influence of sarin for the Co-doped SnO_2 sensor [5].
Curves (2) and (3) – gas concentration and work body temperature accordingly
Рис. 5 – Изменения сопротивления легированного кобальтом SnO_2 -сенсора и влияние зарина [5]:
2 и *3* – концентрация газа и рабочая температура подложки соответственно

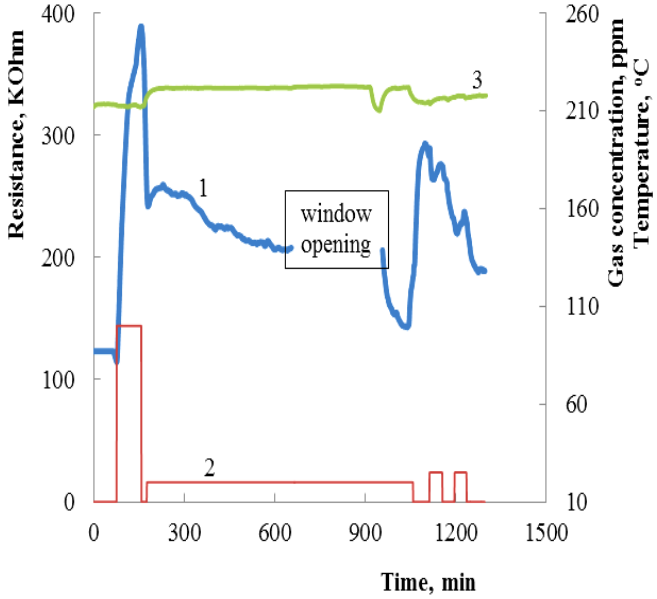


Fig. 6 – The resistance variation under influence of yperite for Co-doped SnO_2 sensor [5].
Curves (2) and (3) – gas concentration and work body temperature accordingly
Рис. 6 – Изменения сопротивления легированного кобальтом SnO_2-сенсора и влияние иприта [5]:
2 и *3* – концентрация газа и рабочая температура подложки соответственно

Propylene glycol (PG), dimethylformamide (DMF) and formaldehyde (FA) gases are toxic industrial chemicals (TICs), but DMF, PG and FA have also a huge impact on human organs (e.g. liver, skin, eyes and

kidneys [3, 6–9]). PG can cause nausea and vomiting, headache, dizziness and fainting. Moreover, it is known as a combustible liquid, which can explode in fire. FA gas can cause burning sensations of the eyes, nose, and throat, coughing, wheezing, nausea, skin irritation. Moreover, exposure to relatively high amounts of formaldehyde can increase the risk of leukemia and even cause to some types of cancer in humans. Due to the information noted above, PG, DMF and FA gas sensors have a huge application for detecting and continuous monitoring of these gases in the spheres where they are used.

There are only resistive sensors of PG and DMF gases working in other principle (for example sensors working on modification of color of the substance), which is incompatible for contemporary technic, while, resistive gas sensors made from metal oxides have advantages such as electric signal, measurement of concentration, small sizes, low power consumption, high sensitivity, and long reliability [10–12].

As opposed to this case, there are many various types of FA gas sensors. For instance, FA gas sensors based on graphene or polymers are working at room temperature [13–14]. On the other hand, FA gas sensors based on metaloxide materials have advantages mentioned above. However pure metaloxide structures react on FA at higher operating temperatures (300–400°C).

The successful synthesis of a SnO_2–In_2O_3–CdO compound with good gas-sensing properties obtained by a simple solid state synthesis has been presented [15]. The fabricated sensor showed high sensitivity, high selectivity, quick response, and good recovery to FA gas at low operating temperature (133°C). The experimental results indicate the potentialities of using an In_2O_3–CdO doped nanocrystalline SnO_2 compound for sensing FA gas.

High sensitivity and good selectivity of ultralong MoO_3 nanobelts for trimethylamine gas was reported in [16]. Three-dimensional ordered SnO_2 inverse opals for superior FA gas-sensing performance was reported in [17]. Inverse opals, as a special kind of macroporous material with large surface to volume ratio and ordered layer structure, have great application potential in highly sensitive gas sensing area. Porous sizes were 140–400 nm. The response of the SnO_2 sensors increased gradually with the increase in porous size.

A selective room temperature FA gas sensor using TiO_2 nanotube arrays was reported in [18]. Results of studies of influence of structural properties and thickness of NiO thin films on FA detection were reported in [19].

We established earlier [20] that SnO_2 gas sensors containing carbon nanotubes (CNTs) have excellent responsive characteristics and low cost of mass production. Due to the covering of CNTs walls with metal-oxide nanoparticles, specific surface area of such gas sensitive nanocomposites increased. Moreover, nanochannels in the form of hollows of CNTs promote penetration of gas molecules deeper down in the nanocomposite sensitive layer [20]. Hence, it can be expected that application in gas sensors technology of nanocomposite structures composed of metal oxide functionalized with CNTs should enhance the gas sensor parameters, such as gas response.

Results of the study of tin oxide/ multiwall carbon nanotube film nanocomposite sensors of PG, DMF and FA are presented below (Figs. 7–10).

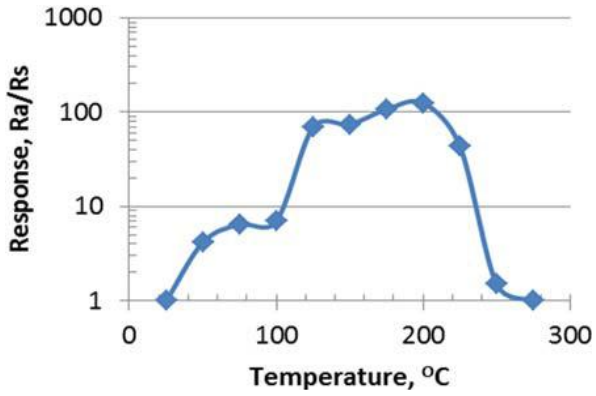


Fig. 7 – Response of SnO_2/MWCNTs thick-film PG sensors vs operating temperature
Рис. 7 – Отклик сенсора пропилен гликоля, изготовленного из тонкой пленки SnO_2/MWCNT

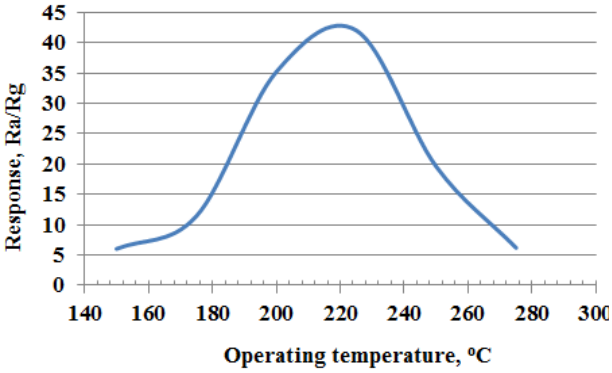


Fig. 8 – Response vs operating temperature at 500 ppm DMF vapor exposure
Рис. 8 – Отклик и рабочая температура сенсора в среде 500 ppm диметилформамида

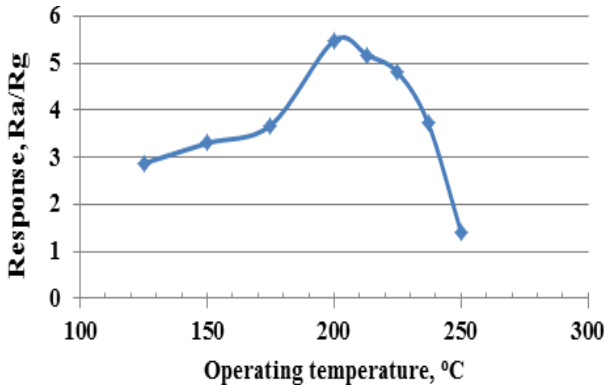


Fig. 9 – Response of SnO_2/MWCNTs thick-film FA sensors vs operating temperature
Рис. 9 – Отклик тонкопленочного SnO_2/MWCNT сенсора формальдегида в зависимости от рабочей температуры

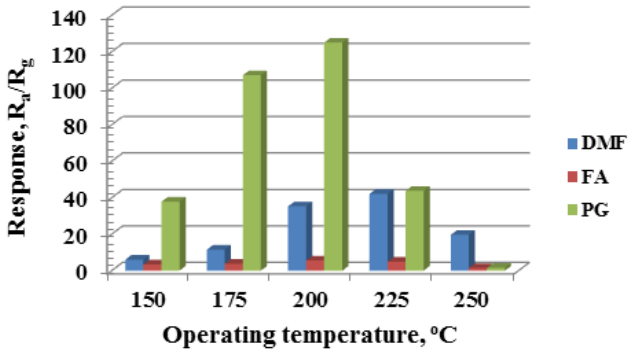


Fig. 10 – Comparison of responses of SnO_2/MWCNTs sensors to 650 ppm PG, 500 ppm DMF and 1160 ppm FA vapors exposure of various operating temperatures
Рис. 10 – Сравнение откликов SnO_2/MWCNT сенсоров к парам 650 ppm пропиленгликоля, 500 ppm диметилформамида и 1 160 ppm формальдегида в зависимости от рабочей температуры подложки

Sensors were manufactured using hydrothermal synthesis and sol-gel methods. Investigations of response/recovery characteristics in the 50–300°C operating temperature range reveal that the optimal operating temperature for PG, DMF and FA vapor sensors, taking into account both high response and acceptable response and recovery times, was about 200 and 220 °C respectively. A sensor response dependence on gas concentration in all cases was linear [21].

The minimal PG, DMF and FA gas concentrations at which the perceptible signal was registered were 13 ppm, 5 ppm and 115 ppm respectively.

Conclusion

Information about chemical warfare agents and toxic industrial chemicals and semiconductor gas sensors for its detection is reported. The review is based on the open-source literature. SnO_2 is the most studied material and SnO_2-based gas sensors have been used to detect CWAs and TICs, but other semiconductor metal oxide such as ZnO, TiO_2, WO_3, CuO, In_2O_3 have also been considered. The resistance variation under influence of sarin and yperite for the Co-doped SnO_2 sensor are reported. Response of SnO_2/MWCNTs thick-film PG sensors vs operating temperature reported at the DMF vapor exposure.

Investigations of response/recovery characteristics in the 50–300°C operating temperature range reveal that the optimal operating temperature for PG, DMF and FA vapor sensors, taking into account both high response and acceptable response and recovery times, was about 200 and 220°C respectively. A sensor response dependence on gas concentration in all cases was linear. The minimal PG, DMF and FA gas concentrations at which the perceptible signal was registered were 13 ppm, 5 ppm and 115 ppm respectively.

Acknowledgments

This work was carried out in the frame of the NATO EAP SFPP 984597 project.

Благодарности

Эта работа выполнена в рамках проекта НАТО EAP SFPP 984597.

References

[1] Lee D.-D., Kim J.-C Semiconductor gas sensors for chemical warfare agents In*: Semiconductor gas sensors* (Editors R. Jaaniso and O. Tan) WP. 2013 Oxford, 467–490.

[2] Qing Zhua, Wei-Heng Shiha, Wan Y. Shihb. Enhanced dimethyl methylphosphonate (DMMP) detection sensitivity by lead magnesium niobate-lead titanate/copper piezoelectric microcantilever sensors via Young's modulus change. *Sensors and Actuators B,* 2013;182:147–155.

[3] Comini E., Baratto C., Concina I. et al. Metal oxide nanoscience and nanotechnology for chemical sensors. *Sensors and Actuators B,* 2013;179:3–20.

[4] Yoo R., Cho S., Min-Jung Song and Lee W. Highly sensitive gas sensor based on Al-doped ZnO nanoparticles fordetection of dimethyl methylphosphonate as a chemical warfareagent stimulant. *Sensors and Actuators B,* 2015;221:217–223.

[5] Aroutiounian V.M., Arakelyan V.M., Aleksanyan M.S. et al. Sensor for Detection of Chemical Agents Made of Co-Doped SnO_2. *Armenian J. Physics,* 2017;9:P122–127.

[6] Adamyan Z. N., Sayunts A., Aroutiounian V. et al. Study of Propylene Glycol, Dimethylformamide and Formaldehyde Vapors Sensors Based on MWCNTs/SnO_2 Nanocomposites. *Sensors & Transducers*, 2017;213:38–45.

[7] Adamyan Z. N., Sayunts A., Aroutiounian V.et al. *AMA-Conferences Proc_SENSOR*-2017 P5.5. MWCNTs/SnO_2 Harmful Gas Sensors, 2017, pp. 708–713.

[8] Alizadeh T., Soltani L.H. Reduced graphene oxide-based gas sensor array for pattern recognition of DMMP vapor. *Sensors and Actuators B,* 2016;234:361–367.

[9] Patil L.A., Bari A.R., Shinde M.D. et al. Detection of dimethyl methyl phosphonate – a simulant of sarin: The highly toxic chemical warfare – using platinum activated nanocrystalline ZnO thick films. *Sensors and Actuators B,* 2012;161:372–378.

[10] Lee S.C., H.Y. Choi, S.J. Lee et al. The development of SnO_2-based recoverable gas sensors for the detection of DMMP. *Sensors and Actuators B,* 2009;137:239–245.

[11] Choi N.J., Kwak J.H, Lim Y.T. et al. Devices and chemical sensing applications of metal oxide nanowires. *Sensors and Actuators B,* 2005;108:298-306.

[12] Lee S.C., Kim S.Y., Lee W.S. et al. Effects of Textural Properties on the Response of a SnO_2-Based Gas Sensor for the Detection of Chemical Warfare Agents. *Sensors,* 2011;11:6893–6902.

[13]. Liu L., Zhang Y., Wang G., et al. Nano-composite sensors composed of single-walled carbon nanotubes and polyaniline for the detection of a nerve agent simulant gas. *Sensors and Actuators B*, 2011;160:448–456.

[14]. Dar G.N., Metal Oxide Nanostructures and Their Applications Thesis, Patras, Greece, 2013, p. 154.

[15] Chen T., Liu Q.J., Zhou Z. L. and Wang Y.D. A high sensitivity gas sensor for formaldehyde based on CdO and In_2O_3 doped nanocrystalline SnO_2 Nanotechnology. *Nanotechnology*, 2008;19:095506.

[16] Yang Sh,. Liu Yu, Chen W. et al. High sensitivity and good selectivity of ultralong MoO_3 nanobelts fortrimethylamine gas. *Sensors and Actuators B*, 2016;226:478–487.

[17] Xing R., Xu L., Yong-sheng Zhu et al. Three-dimensional ordered SnO_2inverse opals for superior-formaldehyde gas-sensing performance. *Sensors and Actuators B*, 2013;188:235–247.

[18] Lin Shiwe, Jian WuAkba S.A. A selective room temperature formaldehyde gas sensor using TiO_2 nanotube arrays. *Sensors and Actuators B*, 2011;156:505–512.

[19] Castro-Hurtado I., Herrán J., Mandayo G.G. and Castaño E. Studies of influence of structural properties and thickness of NiO thin films on formaldehyde detection. *Thin Solid Films*, 2011;520:947–955.

[20] Aroutiounian V.M. Gas sensors based on functionalized carbon nanotubes. *Journal of Contemporary Physics*, 2015;50:333–390.

[21] Adamyan Z., Sayunts A., Aroutiounian V. et al. Nanocomposite sensors of propylene glycol, dimethylformamide and formaldehyde vapors. *J. Sens. Sens. Syst*., 2018;7:31–41.

I Международная научно-практическая конференция
«ТЕОРЕТИЧЕСКИЕ И ПРИКЛАДНЫЕ ВОПРОСЫ КОМПЛЕКСНОЙ БЕЗОПАСНОСТИ»

(28 марта 2018, г. Санкт-Петербург)

Цель конференции – публикация и апробация результатов научных исследований ученых, студентов, аспирантов, докторантов и практикующих специалистов в области управления рисками и обеспечения безопасности.

По результатам конференции издается сборник материалов конференции (с присвоением кодов УДК и ББК и рассылкой по основным библиотекам), присвоением номера ISBN.

Основные направления конференции:

СЕКЦИЯ 1. Современные аспекты международной и военной безопасности. Проблемы противодействия терроризму и экстремизму.
СЕКЦИЯ 2. Предупреждение возникновения чрезвычайных ситуаций, их развитие и ликвидация последствий.
СЕКЦИЯ 3. Пожарная и промышленная безопасность. Проблемы безопасности жизнедеятельности.
СЕКЦИЯ 4. Вопросы природопользования, экологии и охраны окружающей среды.
СЕКЦИЯ 5. Безопасность на транспорте.
СЕКЦИЯ 6. Информационная безопасность и защита информации.
СЕКЦИЯ 7. Актуальные вопросы обеспечения социальной безопасности и демографии.
СЕКЦИЯ 8. Управление рисками и обеспечение экономической безопасности.
СЕКЦИЯ 9. Правовые аспекты в сфере безопасности.
СЕКЦИЯ 10. Образование и воспитание в области управления рисками и безопасности.

Сборники конференции представлены в свободном бесплатном доступе в полнотекстовом формате в научной электронной библиотеке в целях создания Российского индекса научного цитирования (РИНЦ) на сайте http://elibrary.ru.

http://to-future.ru/konferencii/kb/about_kb