Вісник ХНУ, серія «Фізика», вип. 23, 2015. с. 80-83

УДК: 537.312, 537.9, 53.082.7, 542.06.
PACS: 73.40.Jn, 81.07.Lk, 84.37.+q.

Study of tungsten point contacts' electric conductivity in a complex gas medium

A.S. Klimkin[1], V.A. Gudimenko[1], A. O. Gerus[1], V.V. Fisun[1], A.P. Pospelov, G[2].V. Kamarchuk[1]

[1] B.Verkin Institute for Low Temperature Physics and Engineering of NAS of Ukraine, 47 Prospekt Nauky., 61103 Kharkov, Ukraine
[2] National Technical University "Kharkov Polytechnic Institute", 21 Frunze Str., Kharkov, 61002, Ukraine
e-mail: klimkin@ilt.kharkov.ua

The electrical conductivity of tungsten point contacts has been investigated in multicomponent das medium. The complex gas mixture was the human exhaled gas. It has been found that the point contacts (PCs) demonstrate spectral type responses to the action of complex gas media. The spectral character of the time dependence of electrical conductivity is a unique feature observed for the first time on tungsten-based PC sensors in a multicomponent gas medium. The results obtained hold much promise of large-scale investigations on point contacts in multicomponent gas media which can provide the information required to estimate the individual contributions of the gas mixture components to the total response of point contacts.
Keywords: Yanson point contact spectroscopy, point contact, sensor, electrochemical synthesis, breath gas.

Исследована электропроводность вольфрамовых точечных контактов в многокомпонентной газовой среде. В качестве сложной газовой смеси использовался газ, выдыхаемый человеком. Обнаружено, что точечные контакты демонстрируют отклики спектрального типа на действие сложных газовых сред. Спектральный характер поведения временной зависимости электропроводности точечных контактов вольфрама в многокомпонентной газовой среде является уникальным и наблюдается впервые для чувствительных элементов на основе вольфрама. На основе полученных результатов открывается возможность проведения широкомасштабных исследований точечных контактов в многокомпонентных газовых средах. Это позволит получить информацию для определения вклада отдельных составляющих газовой смеси в суммарный отклик точечного контакта.
Ключевые слова: микроконтактная спектроскопия Янсона, точечный контакт, сенсор, электрохимический синтез, выдыхаемый газ.

Дослідження електропровідності вольфрамових точкових контактів в багатокомпонентному газовому середовищу. В якості складної газової суміші використовувався газ, що видихується людиною. Виявлено, що точкові контакти демонструють відгуки спектрального типу на дію складних газових середовищ. Спектральний характер поведінки залежності електропровідності точкових контактів вольфраму від часу в багатокомпонентному газовому середовищі є унікальним і спостерігається вперше для чутливих елементів на основі вольфраму. На основі отриманних результатів виникае можливість проведення широкомасштабних досліджень точкових контактів в багатокомпонентних газових середовищах. Це дозволе отримати інформацію для визначення внеску окремих складових газової суміші в загальний відгук точкового контакту.
Ключові слова: мікроконтактна спектроскопія Янсона, точковий контакт, сенсор, електрохімічний синтез, видихуваний газ.

Introduction

Intensive research has been carried out presently to develop high-sensitivity chemical nanosensors and sensing arrays [1]. The universal devices used to analyze gas media include a complex of similar sensing elements. The instruments capable of analyzing complex gas media are called "electronic noses". They incorporate several sensors responding to a particular gas or a group of gases [2]. In contrast to the conventional approaches of updating sensors primarily by enhancing their sensitivity, the "electronic nose" technology is concentrated on complex assemblies of relatively nonselective sensors [3]. This technology came with the advancement of computer engineering permitting real-time processing of multiparameter information. Despite the considerable progress in the technology of individual sensors, the development of "electronic nose" devices is still a labour-consuming process. Besides, the restricted real time data output imposes a limit on the number of sensing elements in current multisensory systems. In this context the urgent present-day challenge

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is to find alternative innovatory approaches to development and investigation of high-sensitivity devices for analyzing complex gas media.

The goal of this study was to develop point contact (PC) sensors capable of spectral-type responses to complex gas media and to investigate their electric properties in the process of their interaction with external agents.

Experimental technique

Point contacts formed between bulky tungsten electrodes (40 µm thick wires) have been investigated. The choice of tungsten was dictated by the peculiar structure of the electron shells of the W atom which determines the physical-chemical nature of tungsten oxides and is extensively exploited in sensor technologies [6, 7]. Point contacts with gas-sensitive properties [8, 9] can be modelled as a long metallic channel [10] coated with a semiconducting oxide layer. We sought to cover our W electrodes with a material that would respond to gas media in a wide range of compositions and concentrations. The surface treatment technology applied to our electrodes was based on electrochemical methods. Prior to treatment, the electrode surface was subjected to anodic cleaning in an aqueous 20% NaOH solution, the current density being 0.1 A/cm^2. The W wire electrodes fixed in the holder served as an anode. The cathode was a tungsten rod. After cleaning, an oxide layer was formed on the electrode surfaces by the cathodic method in an aqueous 20% $Na_2WO_4 + H_2O_2$ solution with the current density 0.04 A/cm^2. In this case the W electrodes used to form the contacts acted as a cathode and the bulky W rod was an anode. On completing the reduction process, the electrodes were washed thoroughly and treated thermally in a thermostat at T=50 °C for half an hour.

The point contacts were prepared using a modified method based on the Fisun twist method [11] and the elements of the Chubov displacement technology [12]. These technologies have long been approved as efficient tools of the Yanson point contact spectroscopy. As with the twist technology, the contacts prepared were highly stable to external mechanical factors and retained their properties for a long time. The investigation was performed in a specially designed cell allowing a control gas feed.

The human exhaled breath was chosen as a complex gas mixture because it contains up to 2000 components of different endogenous and exogenous origin [13, 14]. About 600 of them are markers of various states of a human organism and can be used as a basis for developing new methods of medical noninvasive diagnostics [15]. Besides, the human breath gas is a readily available multicomponent gas mixture, which assists considerably attacking the problem of a functional gas-sensitive layer at the surface of a PC channel.

The current-voltage characteristics (IVCs) of the point contacts, the first IVC derivatives and the electrical PC resistance under ambient conditions were measured. Also, the time dependences of the electrical resistance of the PCs exposed to human breath gas were obtained. The time dependence of the electrical conductivity of a point contact interacting with a gas medium is taken as a response signal of PC sensors. The measurements were made using an original point contact spectrometer developed at the B.I.Verkin ILTPE, NAS of Ukraine. This is a multifunctional automated measuring setup capable of simultaneous five-channel high-precision signal recording. The recorded data were analyzed using a special software packet.

Results and discussion

The investigation was performed on 52 point contacts demonstrating a spectral type signal in response to the complex gas mixture (breath gas). This behavior of the gas sensor based on a tungsten compounds is unusual for conventional gas sensors, and was observed for the first time in the study. It should be noted that the gas-sensitive elements used in current sensor technologies demonstrate simple behavior of the signal in response to one- or several-component gas mixture which reduces to a “yes-no” signal and is seen as a step or a Dirac delta function in the response curve [6, 7, 16].

The typical time dependences of the electrical resistance of tungsten PCs in the breath gas medium are illustrated in Fig.1.

The PCs respond to the gas medium immediately or with a short delay after feeding the gas to the contact, i.e., the response time of the contacts is small. The amplitude of the electrical conductivity variations is over 100% with reference to the starting signal level. The time dependence of the electrical resistance has a distinct spectral character. It is quite nonmonotonic and contains a number of maxima and minima varying in both intensity and reactivity rise rate. The duration of the PC spectrum of the breath gas profile is about 100-150 sec. The PC resistance decreases due to the interaction between the PC and the gas medium and becomes stable at ~0.7 R_0, where R_0 is the starting PC resistance before the onset of interaction. Note that the samples were irresponsive to the pulse of atmospheric air: the electrical conductivity of the PCs remained invariant for an hour, i.e., during the whole experiment.

The nonlinear behavior of the electrical conductivity of tungsten PCs in a gas medium and the parameters of PC-based sensors can be interpreted readily in terms of the fundamental properties of point contacts considered in Yanson point contact spectroscopy [17, 18]. The high sensitivity of point contacts to gas media is determined first of all by the unique distribution of the potential over a point contact [19]. When current flows through the “electrode-PC-electrode” system, a drop of voltage occurs only

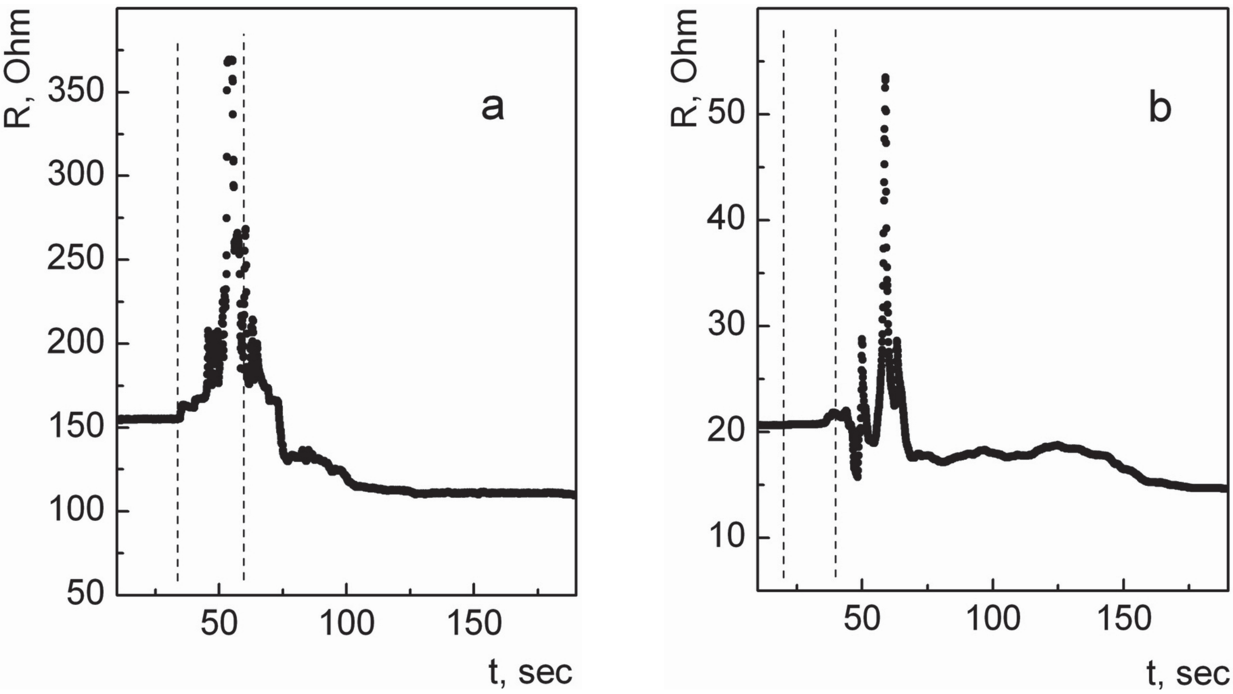

Fig.1. The time dependence of the electrical resistance R of tungsten point contacts in the medium of human breath gas. The vertical dash lines show the pulse duration of the exhaled gas. a – R_0=155 Ohm, b – R_0=21 Ohm.

at the point contact. It is therefore the point contact that determines the electrical resistance of the whole system. As a result, the possible contribution of the current-feeding electrodes to the gas-caused changes in the electrical conductivity of the system is negligible [8]. As a nanoscale object, a point contact has a very high surface-to-volume ratio [9], which in turn determines the ultrahigh sensitivity of point contacts to gases.

The short relaxation times of PC sensors are accounted for by the unique conditions induced by the current flow in the PC. The classical experimental investigations of the electron-phonon interaction in the context of Yanson point contact spectroscopy at helium temperatures show that the current density in contacts can be as high as 10^9-10^{10} A/cm^2 [20]. A very high current density (10^6-10^7 A/cm^2) was also observed in the narrowing area of point contacts while investigating the PC sensitivity to gases at room temperature [8]. In this case the point contacts retained their physical properties and stable mechanical parameters, i.e., no heating or destruction of the sample material occurred. This behavior is due to the fact that, unlike conventional bulk conductors, in the point contacts obeying the criteria of Yanson point contact spectroscopy [17] the nonequilibrium current states of charge carriers and the thermal effects are separated. When current flows in conventional homogeneous conductors and nanostructures, the nonequilibrium and thermal effects are distributed uniformly over the whole volume, which leads to heating and melting of such objects even at densities about 10^2-10^3 A/cm^2. In point contacts the current carriers are in a nonequilibrium excited states. They scatter at the adsorbed atoms and molecules and stimulate their desorption by transferring them excess energy of the electrons. This accounts for the short relaxation time of PC sensors and their instantaneous response to gas mixtures.

The nonmonotonic behavior and the spectral character of the responses of tungsten-based point contacts to gas media can be attributed to the unique fundamental properties of these nanostructures. It should be noted that point contacts are nanostructural objects whose behavior is of quantum nature [21]. They can thus be used as an efficient tool of investigating and applying various quantum effects. For example, the PC spectra of the electron-phonon interaction recorded in terms of Yanson point contact spectroscopy [17, 18] can be used to obtain information about the energy states of the components of a physical quantum system through finding the function of the electron-phonon interaction and the function of the phonon density of states in a solid. The exhaled gas is a complex mixture with a great number of interactions of its components. As a result, the components of the gas medium form a certain profile of the exhaled gas accounting for the state of the organism. Knowledge of the profile enables us to analyze the exhaled gas which contains information about the adsorption energy of the components of the gas medium. Owing to the quantum nature of their electric properties, point contacts are able to detect fine changes in the surface states of the conducting channel [21] that are caused by the adsorption of external agents. This permits us to register spectral-type response signal with PC sensors [5]. In this case the relaxation time of a PC sensor is in some way analogues to the energy extent of the PC spectrum of the electron-phonon interaction because it describes the integral energy of adsorption of the exhaled gas components.

The absence of relaxation of a point contact in reference to the starting electrical resistance may be connected with the chemical interaction of some breath gas components with the PC material.

Conclusions

To sum up, we note that the revealed time dependence of the electrical conductivity of tungsten point contacts in a multicomponent gas medium demonstrates a unique behavior observed for the first time in W-based sensors.

The complex response detected in this study can testify about a novel mechanism of gas sensitivity operating in point contacts.

The results reported have been made possible by the efficient original technology developed to form point contacts.

The data obtained open the way to large-scale investigations of point contacts in multicomponent gas media. The new approach will provide information required to estimate individual contributions of the gas mixture components to the total response of a point contact.

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