Conference materials
UDC 504.064.36
DOI: https://doi.org/10.18721/JPM.163.170

Interdigital gold electrodes for a conductometric gas sensor on the glass surface

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Abstract. Modern cities with developed industries suffer from a large amount of emissions into the atmosphere. Therefore, for modern scientists, the task of creating sensors for environmental pollutants is urgent. This paper considers one of the tasks of creating a gas-sensitive element of a conductometric sensor for greenhouse gases in the atmosphere. An important component of a gas-sensitive element is a carrier substrate with a branched system of electrodes. The electrode system must be stable and have chemical, thermal, and mechanical resistance. The paper develops a technique for creating a system of gold electrodes for a gas-sensitive element on the surface of a glass substrate. The increasing mechanical strength of electrodes is considered. In general, the mechanical strength of thin films depends on the intralayer, interlayer bonding of components and adhesion to the carrier substrate. In this work, it is sufficient to use one numerical parameter, which characterizes the mechanical resistance of the layer as a whole. The method of determining nano hardness was used to control the mechanical strength of the electrodes. Nanohardness was measured by atomic force microscopy probe lithography.

Keywords: gas sensor, electrodes, PVD, adhesion, roughness, nanohardness, atomic force microscopy

Funding: The reported study was funded by the government assignment for FRC Kazan Scientific Center of RAS.

Citation: Nizameev I.R., Gainullin R.R., Nizameeva G.R., Lebedeva E.M., Kuznetsova V.V., Spiridonov S.V., Interdigital gold electrodes for a conductometric gas sensor on the glass surface, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.1) (2023) 384–389. DOI: https://doi.org/10.18721/JPM.163.170

Материалы конференции
УДК 504.064.36
DOI: https://doi.org/10.18721/JPM.163.170

Система встречно-штыревых золотых электродов для кондуктометрического газового сенсора на поверхности стеклянной подложки

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Аннотация. Современные города с развитой промышленностью страдают от большого количества выбросов в атмосферу. Поэтому перед современными учеными стоит задача создания датчиков загрязнителей окружающей среды. В данной работе рассматривается одна из задач создания газочувствительного элемента кондуктометрического сенсора парниковых газов в атмосфере. Важным компонентом газочувствительного элемента является несущая подложка с разветвленной системой электродов. Электродная система должна быть стабильной и иметь химическую, термическую и механическую стойкость. В работе разработана методика создания системы золотых электродов газочувствительного элемента на поверхности стеклянной подложки. Рассматривается методика увеличения механическая прочности электродов. Механическая прочность тонких пленок во многом зависит от внутрислойного, межслоевого сцепления компонентов и адгезии к несущей подложке. Для данной работе достаточным является использование одного числового параметра, характеризующего механическое стойкость слоя в целом. Для контроля механической прочности электродов использовался метод определения нанотвердости. Нанотвердость измеряли методом зондовой литографией на атомно-силовом микроскопе.

Ключевые слова: газовый сенсор, электроды, PVD, адгезия, шероховатость, нанотвердость, атомно-силовая микроскопия

Финансирование: Работа выполнена в рамках государственного задания ФИЦ КазНЦ РАН.

Ссылка при цитировании: Низамеев И.Р., Гайнуллин Р.Р., Низамеева Г.Р., Кузнецова В.В., Спиридонов С.В., Система встречно-штыревых золотых электродов для кондуктометрического газового сенсора на поверхности стеклянной подложки // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.1. С. 384–389. DOI: https://doi.org/10.18721/JPM.163.170

Introduction

The problem of air pollution with toxic gases is becoming more and more serious in the modern world. Therefore, to avoid negative consequences, it is necessary to develop new technologies for determining and controlling air pollution with toxic gases. Due to the growing demand, there is a wide variety of types of toxic gas sensors. Among the many types of sensors, conductometric sensors are among the most sensitive and accurate. Conductometric sensors allow the detection of gases at concentrations up to ppb units (one part in a billion). They operate based on a change in the electrical conductivity of the gas-sensitive element before and after the adsorption of the detectable component [1–3]. Semiconductor materials such as metal oxides are used as active elements in such sensors. Among various materials, the indicators most sensitive to gases are low-dimensional semiconductor structures, such as submicron fibers, due to their overdeveloped surface [4]. A conductometric sensor usually contains a substrate with two electrodes and a gas-sensitive element placed on them [5]. In this work, we assume the use of oriented networks of nickel oxide obtained by thermal oxidation from networks of metallic nickel. The main approaches to obtaining such material are presented in [6–8].

To perform accurate measurements of the electrical signal, the electrodes must be stable in the environment of the studied gases and have good adhesion to the substrate surface. First of all, this work is devoted to improving the stability of the measured values of the final conductometric sensor by increasing the mechanical resistance of its current-measuring part. This is very important when thin-film structures are used as a gas sensitive element. Within the framework of this study, the authors did not set themselves the goal of directly increasing the sensitivity of the final gas sensor. This task is the next step in the development of the conductometric sensor.

Inert metals are usually used as conductive electrodes: silver, gold, platinum, and palladium. Thin gold films are well suited for electrodes because they are highly conductive and resistant to oxidation [9]. Various approaches are used to deposit gold electrodes on the surface of substrates, such as ion-beam sputtering, thermal vacuum evaporation, molecular beam epitaxy, and magnetron

sputtering. It is known that adhesion depends on the coating method, and the best results are obtained with magnetron sputtering. This method makes it possible to obtain uniform and reliable films. Its results are easily reproducible, and this method is often used for large-scale coatings of thin films [10]. With repeated use of conductive metal films for electrical measurements, mechanical defects and damage in the contact areas of the measuring probes inevitably occur. Therefore, the task of increasing the mechanical resistance of the metal layer is very important when creating conductometric gas sensors. In this paper, we propose a method for creating electrodes of a gas-sensitive element from a thin layer of gold, as well as a method for increasing the mechanical strength of the layer to penetrating influences. Micro- and nano hardness is used as a numerical measure of mechanical strength. A well-known option for increasing the adhesion strength of a gold film to glass is the preliminary deposition of a metal sublayer that has good adhesion to the substrate [11–13]. Pretreatment of the glass substrate can also improve the adhesion of gold electrodes to the surface. Three types of methods are used in glass etching: mechanical, wet, and dry. In many studies, glass is etched using hydrofluoric acid HF [14]. Other methods, such as laser radiation, can also be used for etching [15].

Materials and Methods

In this work, silicate glass was chosen as the target substrate, on the surface of which interdigital gold electrodes were formed by photolithography. The surface morphology of the glass substrate, as well as the roughness, was studied by atomic force microscopy (AFM) MultiMode V. The observation was carried out in intermittent-contact mode. Microscopic images were obtained with a resolution of 512×512 pixels per frame at a scanning speed of 1 Hz. The study of the nano hardness of metal layers was carried out using probe lithography. Probe lithography was carried out on a MultiMode V atomic force microscope in the contact mode. Phosphorus-doped RTESP silicon cantilevers with a nominal elastic coefficient of 50 N/m were used to mark the film surface. The force of pressing the probe to the surface was controlled by creating a different deflection of the cantilever console. The clamping force was determined according to Hooke's law as the product of the coefficient of elasticity of the cantilever and its deflection. The determination of the microhardness of the metal coating was carried out according to the following procedure: using a micro indenter, one or another force was created on the film with a known value in millinewtons, and the resulting depression was studied on AFM MultiMode V. The depth of the formed submicron defect on the surface was measured by the profile of the AFM image of this area. Next, a graph of the dependence of the depth of the created defect on the impact force was plotted. The deposition of a metal layer to create a system of electrodes was carried out according to the standard photolithography technique: a film photoresist was exposed to radiation with a wavelength of 395 nm for 7 sec. through a photomask with the necessary pattern; after the development of the photoresist, magnetron sputtering of the metal layer was carried out in an argon medium.

Results and Discussion

The creation of a system of gold electrodes on the glass surface was carried out by magnetron sputtering, after applying the photoresist, its exposure, and development. The structure of the film deposited in this way is homogeneous and is represented by the same type of nanoparticles with sizes of 150−200 nm, which densely cover the entire area (Fig. 1, *a*). The film thickness was determined by scanning the metal-glass transition region. For the gold layer, it averaged 380−420 nm (Fig. 1, *c*). The nano hardness of the gold layer was studied by applying recesses on the surface using a nanoprobe of an atomic force microscope. In Fig. 2, *c*, the recesses made with different forces are visible.

The clamping force was determined from the deflection of the cantilever with a known spring constant (50 N/m). Further, the recess depth was determined by the AFM method. In this work, the determination of the standardized value of nano hardness is not the main goal. The relative value is sufficient because the interest is the change in nano hardness upon modification of the film structure. For simplicity and clarity, the measure of nano hardness in the work is the ratio of the probe pressing force to the depth of the recess created in this case: $G = F / h$. Thus, studies of the nano hardness of a gold film (Au), a gold film with a copper sublayer (Cu-Au), and a gold film with a nickel sublayer (Ni-Au) were carried out (Fig. 2).

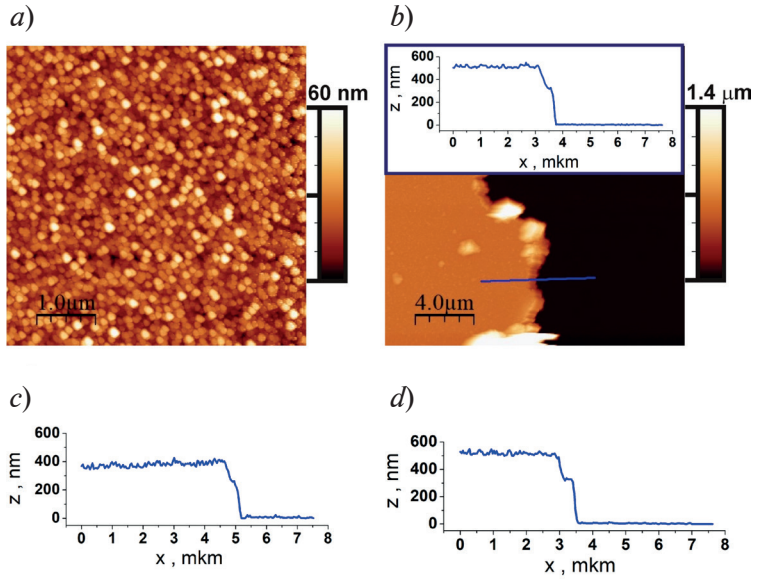

Fig. 1. AFM image of the gold film surface (*a*); film-substrate transition region and section profile along the blue line for the Ni-Au film (*b*); profile of the film-substrate transition region for the bare Au film (*c*) and for the Cu-Au film (*d*)

With an increase in the pressing force of the probe to the gold film, an almost linear increase in the recess depth is observed (Fig. 3, *a*). On average, $G = 1.0 \pm 0.1$ μN/nm for a pure gold layer.

To increase the mechanical strength and adhesion of the metal film to the substrate, options for applying copper and nickel sublayers were considered. Sublayers were also deposited by magnetron sputtering. The sublayer thickness was almost 100 nm, and the total thickness of the Cu-Au and Ni-Au films was about 500 ± 20 nm (Fig. 1, *b* and 1, *d*).

The mechanical strength of Cu-Au and Ni-Au films was determined by the same method as for the Au film. It was found that the value of G increases with an increase in the pressing force of the probe to the surface of both films (Fig. 3, *a*). This demonstrates an increase in the nano hardness of the layer when approaching the sublayer. This phenomenon can be associated with an increase in interlayer adhesion within the film, as well as with an increase in the adhesion of the layer to the substrate as a whole. Changes in the adhesion of a layer to a substrate, as well as interlayer adhesion and internal interactions of nanolayers, were studied in detail in [13]. For the Cu-Au layer, the maximum calculated value $G = 1.8 \pm 0.1$ μN/nm, which is achieved at a recess depth of 150–170 nm. It should be noted that the value of G for the Cu-Au film at low values of the applied force is commensurate with the Au film, which can be explained by the weak influence of the sublayer when the probe is slightly immersed in the film. Nano hardness of the Ni-Au film $G = 2.2 \pm 0.1$ μN/nm. If the probe immersion depth does not exceed 80 nm, the value of G exactly coincides with the value for a pure gold layer ($G = 1.0 \pm 0.1$ μN/nm). However, with further deepening into the material of the layer, the nano hardness sharply increases.

The metal electrodes obtained by the described method in practice have low mechanical resistance. The number of cycles of approach-withdrawal of measuring contacts, after which the electrical properties of the conductive layer of the contact zone are preserved, does not exceed 100. Therefore, to further increase the mechanical strength of the layer of electrically conductive tracks, an investigation was carried out to increase the adhesion of the layer to the substrate.

To increase the adhesion of the photoresist and the resulting metal layer to the surface of the glass substrate, the surface roughness of the glass was increased by applying a layer of etch paste (TAIR). After the matting process of the glass substrate, its roughness R_a increased from 0.55 nm to 165 nm. The metal layer deposited on such a surface has noticeably greater mechanical resistance. For the numerical characterization, the same technique was used for the unmodified glass substrate. However, it has been found that the pressing force of the probe lithography nanoindenter is insufficient to cause noticeable mechanical defects on the surface of the metal

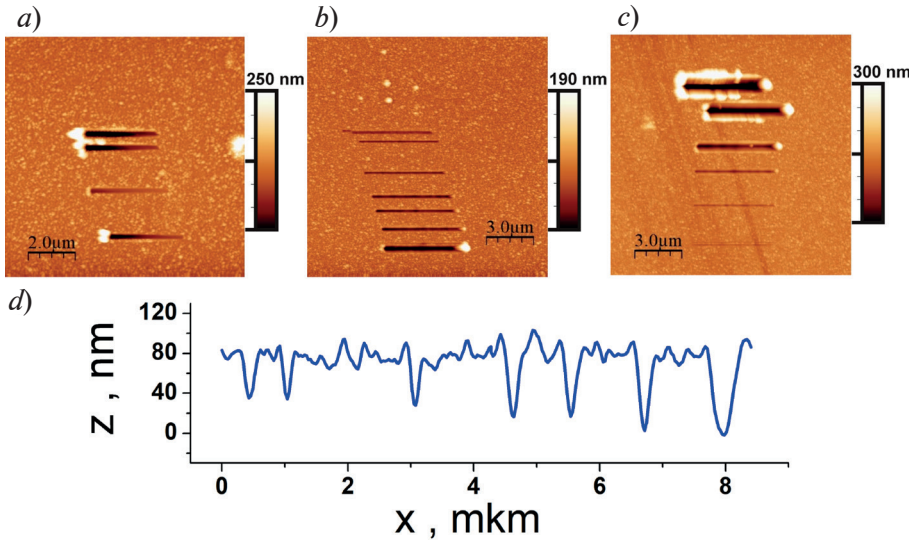

Fig. 2. AFM images of the Ni-Au (*a*), Cu-Au (*b*) and Au (*c*) film surfaces with visible recesses created by probe lithography with different forces; profile of the AFM image of the region with recesses for the Cu-Au film (*d*)

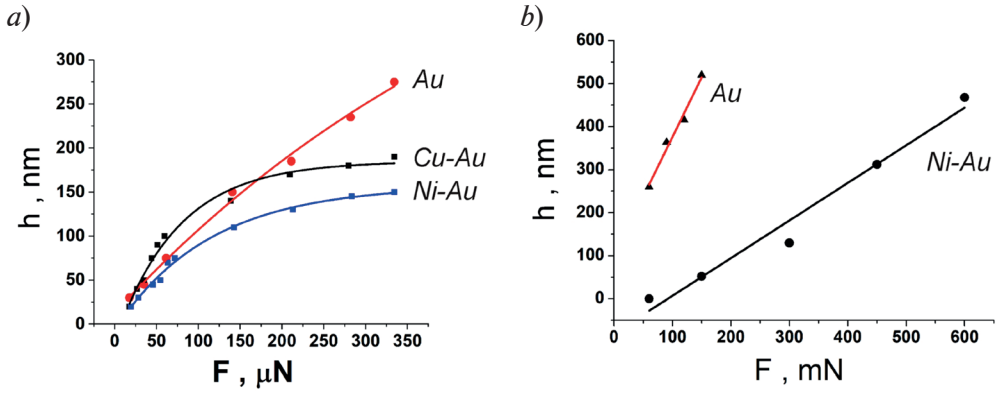

Fig. 3. Depth of recesses created by probe nano-lithography VS the probe pressing force (*a*); depth of recesses created by micro indenter VS the microprobe pressing force (*b*)

layer thus created. Therefore, a micro indenter was used with the possibility of setting the probe pressing force up to several hundreds of millinewtons. The results are shown in Fig. 3, *b*. The G value for the pure gold layer is 350 ± 50 μN/nm and for the Ni-Au layer on the modified glass substrate $G = 1200 \pm 300$ μN/nm.

Conclusion

As a result of the study, it was found that the mechanical resistance of the electrode system of the gas-sensitive element of the conductometric sensor can be significantly increased by creating a metal sublayer of nickel. The numerical values of the nano hardness of the created layer of electrically conductive tracks are determined. It is shown that the nano hardness of gold electrodes more than doubles in the case of a nickel sublayer. It has also been shown that the adhesion of the metal layer of the electrodes to the glass substrate can be increased many times over by etching the substrate. An increase in layer adhesion leads to an increase in its hardness and mechanical resistance. An increase in hardness by several hundred times was recorded. However, this increases the roughness of the electrically conductive layer and becomes commensurate with its thickness.

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Received 07.07.2023. Approved after reviewing 16.08.2023. Accepted 16.08.2023.