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Technological Features of Real Contact Systems' Production for Nanosystem Equipment

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In the article, the ways of increasing the efficiency of photoelectric transducers due to the application of SnO_2 | Zn_2O_3 – SiO_x – nSi – n + Si heterostructures and elaboration of the technology of contact systems production are dwelt upon. Physical processes, taking place in heterostructures, are empirically examined, the methodology and modes of their production are analyzed. It is sustained, that photoelectric transducers, produced on the basis of such structures, have significant advantages in comparison with foreign analogues. The authors proposed an alternative technology for creating contact systems to heterostructures and experimentally proved that annealed contact systems have advantages, primarily in terms of reducing the number of technological operations and are still relevant. The use of such a composition allowed to reduce the annealing temperature, which led to improved morphology of the obtained contact systems compared to traditional ones. It is proved that the application of such contact systems will increase the efficiency of photoelectric appliances due to simplicity of technological process and cheap materials, that will lead to the reduction of cost price of the product.

Keywords: Technology, Contact system, Photoelectric converters, Silicon structures, Heterojunctions, Parameters, Characteristics.

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1. INTRODUCTION

Fundamentals of contact systems' physics were founded at the end of the last century. A lot of scientists formed many physical representations about properties of contacts and their characteristics. The formation of such studies has contributed more high level of technologies. These technologies allowed to conduct active industrial production of devices on the basis of silicon with contact systems of rather high quality. But a lot of questions about technological features of contact systems' manufacturing remain controversial today, despite the large number of new experimental results, including results made on the basis of such materials as germanium, gallium arsenide, silicon carbide, heterostructures, etc.

The issue of studying the structure of contact systems, their physical properties and characteristics, have become relevant. The works of Tang [1] became significant, where special attention is paid to the nature (formation) of contacts. The author believes that the state of the metal and semiconductor surfaces plays a crucial role in the creation of contact systems.

However, there are other factors that researchers have noted, taking into account new approaches to the formation of contact systems on silicon. Their influence underlies a number of physical models. The most common are studies of Werner and Guettler, who did not answer questions about the nature and characteristics of contact systems on silicon and put a number of new [2].

A detailed analysis of the impact of metal output on the parameters of contact systems, which were obtained in particularly pure technological conditions, was given by Cowley and Zee [3]. Much of this research has been performed on contacts, where the pure surface of the semiconductor was created by special cleaning immediately before applying the metal in ultrahigh vacuum ($\sim 10^{-10}$ Torr), and later epitaxial build-up of metal in the same process as building semiconductor layers. Such technologies have virtually eliminated the possibility of oxidative or other origin of the layer at the metal-semiconductor interface. This stimulated additional interest in creating a cleaned semiconductor surface and developing high-quality contact systems.

It is also important to note that the parameters and characteristics of contact systems are significantly influenced by chemical and metallurgical processes that occur at the metal-semiconductor interface. For example, gallium arsenide does not interact (Ag), but metal arsenides (Al, Cu, Ni, Pd, Cr, Ti) and alloys with gallium (Au, Ni, Pd, Mn, Ti) have been invented. The same compounds were obtained by some researchers on the basis of silicon. The nature of the interaction in general corresponds to the thermodynamics of bulk materials, although the kinetics of the processes significantly affects the real range of interaction products. Of course, it is difficult and even impossible to obtain such systems under conditions (at room temperature).

The problem of forming reliable high-quality contact systems for nanosystem devices and integrated circuits remains a priority today. It consists in obtaining high-quality mechanical and heat-resistant contacts by studying and substantiating the effect of thermal annealing and insufficient adhesion of the metal-semiconductor contact and, as a consequence, increased voltage on the rectifier element. It should be borne in mind that in the process of establishing a metal-semiconductor contact, the interaction of these two materials is possible with increasing or decreasing the concentration of donors or acceptors in the semiconductor and therefore it is possible to obtain ohmic contact even on silicon. The same changes can occur as a result of further heat treatment. Thus, it is established that as a result of heat treatment

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of the aluminum-silicon contact, the semiconductor is doped with aluminum and the ohmic contact is formed to a sufficiently high-impedance p-type material.

The authors believe that the parameters of the metal-semiconductor transition have a significant impact on the oxide layer formed at the boundary between these two materials. Most semiconductors always have their own "oxide" on the surface. For example, silicon is always covered with an oxide film with a thickness of at least 25 Å, which grows on its surface in the air, even at room temperature. This intermediate layer, firstly, reduces the density of surface states, secondly, with an increase in the thickness of the oxide layer, a transition to the MES structure is possible, and thirdly, an additional oxide layer reduces tunneling currents, both forward and reverse. Finally, if in the case of ideal metal-semiconductor contact the current consists of the main carriers, then in the presence of an intermediate oxide layer, the injection of non-basic carriers is possible, which, in turn, changes the overall mechanism of current passage. The presence of an intermediate oxide layer increases the resistance of the contact system [4-6].

Therefore, the analysis of the influence of technological factors on the quality of contact systems showed that, despite their formation to various semiconductor devices of nanosystem technology, they must have the following general properties:

– a linear volt-ampere characteristic in the range of operating currents;

– the minimum value of the contact resistance;

– minimal generation of non-basic media;

– the possibility of connecting to the contact pads of the terminals by thermal compression, ultrasonic grinding or soldering;

– good adhesion, flat and uniform fusion front;

– small difference in the temperature coefficients of linear expansion of contact material and semiconductor, high mechanical strength;

– high corrosion resistance.

According to the above requirements, contact systems can be characterized by:

– the value of contact resistance R_k;

– the value of specific contact resistance ρ_k;

– maximum current density;

– linearity of the volt-ampere characteristic j;

– the range of operating contact temperatures;

– noise level in the mode of operating currents;

– the depth of penetration of the contact material into the volume of the semiconductor;

– the strength of the connection of the contact pad to the semiconductor substrate.

2. DESCRIPTION OF THE OBJECT AND METHODS OF RESEARCH

Contact systems made of n and nn^+-Si, p and pp^+-Si are subject to a number of requirements, the fulfillment of which largely depends on the electrical and mechanical properties of manufactured semiconductor devices and their stability. The requirement that largely determines the quality of contact systems is the value of their specific transient resistance ρ_k, which must be small enough. Typically, probe methods are used to determine the value of the resistivity, which is used to measure the impedance of the contact pads. In turn, the measured resistance depends on both the contact resistance and the spreading resistance in the semiconductor. At the same time, all of the above methods have a sufficient error and do not allow creating automated measuring systems on their basis.

Two methods for determining ρ_c were proposed [10] by Reeves and Harrison: the method of separate current and voltage measurement (SCVM) and the method of "extra resistance measurement" (ERM). The essence of these methods was to determine the resistivity for contact pads by the formula:

$$\rho_c = R_c \cdot A_c,$$

where A_c is the area of the contact window equal to $= 24.2 \times 10^{-8}$ cm^2.

Thus, to obtain high-quality contact systems it is necessary to provide:

– a small value of the potential barrier in the metal-semiconductor contact (achieved by choosing the material from which the base contact is made);

– maximum movement of the areas adjacent to the contact (achieved by local doping of the contact area);

– the minimum life of minority carriers in the contact area (achieved by the choice of alloying substances with a large cross section of capture).

The most successful methods are the manufacture of contact systems using an alloy containing impurities of the same type as those contained in the semiconductor with where the contact is made (donors – for electronic semiconductors, acceptors – for holes).

Today, the Ti/Al/Ni/Au metallization system and its variations are widely used. However, such contact systems do not meet a number of requirements due to poor morphology of the contact surface. The authors believe that this problem can be solved by forming non-annealing contacts and alloy contacts using refractory metals as a barrier layer. In the first case, it is necessary to use technologies for growing high-alloy semiconductor layers or ion implantation of Si in the subcontact areas to improve characteristics of contact systems. Despite some advantages, for example, in the development of transistors of higher frequency ranges, this approach leads to a significant complication of technology and increase technological operations in their manufacture. The technology of forming alloy contact systems is a spraying of metallization followed by thermal annealing, which is much easier, because it allows the formation of contact in one operation of explosive photography and from a technological point of view. However, this approach also has a number of difficulties: the development of molding modes is reduced to optimizing the composition and thickness of metal layers and the annealing mode.

Many contact systems based on refractory metals Cr, Hf, V, Ta, Mo, etc. are known and studied today [3-7], the most interesting one is the Mo/Al/Mo/Au system. Based on it, it is possible to obtain contact systems with resistance not worse than standard Ti/Al/(Ni, Ti)/Au systems, as well as relatively smooth surface morphology and high thermal stability. Its main advantages are a wide range of annealing temperatures (700-900 °C), while for standard contact systems based on Ti/Al/x/Au it is already from 750 to 850 °C, as well as the ability to obtain ohmic contacts at lower temperatures (500 °C) using pre-plasma chemical treatment in $SiCl_4$ [8]. However, the study of the peculiarities of the formation of contacts based on Mo/Al/Mo/Au and the study of the mechanism of its formation to heterostructures is a difficult task. It is necessary to take into account: the sequence and thickness of the metal layers; temperature, duration and conditions of thermal annealing; conditions and methods of metallization spraying; polarity of the semiconductor surface; the presence of its own oxide and various contaminants on the surface of the semiconductor; design and quality of epitaxial structures.

The authors proposed a technology for creating contact systems and experimentally proved that for the formation of annealed contact systems, a smaller number of technological operations should be performed compared to heterostructures.

The ways of increasing the efficiency of photoelectric transducers (PETs) due to the application of SnO_2 | Zn_2O_3 – SiO_x – nSi – n^+Si heterostructures and elaboration of the technology of contact systems production are dwelt upon. Physical processes, taking place in heterostructures are empirically examined, the methodology and modes of their production are analyzed. It is sustained, that PETs, produced on the basis of such structures, have significant advantages in comparison with foreign analogues. The technology of production of Al-Cu-Si contact systems is elaborated, their parameters are investigated, and their tests are performed.

One of the major aims in the engineering of solar elements is increasing their efficiency. For effective transformation of solar radiation into electric energy due to the division of electron-hole pairs by internal electric field, the depth of stratification of the field, that separates them, should be sufficient for penetration of the main stream of photons. In silicon, the solar energy is adsorbed in the layer of 0.003 μm in depth [10].

It is claimed [11], that the highest efficiency of PET is found in the spectrum of wavelengths from 0.4 to 9 μm, that is on the borderline of visible and infrared radiation.

The analysis demonstrates [11] that the displacement to the short-wave spectrum increases the efficiency of energy transduction. However, in the conditions of reality, it is necessary to work in the spectrum close to infrared, i.e., of short waves. It can be explained by the fact, that the atmosphere is more transparent for them. To achieve that, the depth of the internal field stratification should be enlarged. In case the wavelength is less than 1.1 μm, PETs are not sensitive to the photons stream, as far as their energy is not sufficient for generation of charge carriers.

The problem of increasing PET sensitivity can be solved by means of choosing SNS (semiconductor – nonconductor – semiconductor) heterostructure, that constitutes its fundamentals, and by means of application of high-quality contact systems.

In SNS structures, the surface layer is a wide-band semiconductor, which is separated from the layer of semiconductor with less width of the prohibited area with the help of thin layer of nonconductor. In view of this, the upper semiconductor should have good optical transparency, and the lower – have the width of the prohibited zone, which enables the maximum solar spectrum absorption. As for the nonconductor layer, scientists claim that it improves the parameters of PET in case it is not thick [11].

3. DESCRIPTION AND ANALYSIS OF THE RESULTS

It was empirically proved by means of a series of experiments, that the SnO_2 | Zn_2O_3 – SiO_x – nSi – n^+Si structure corresponds to the requirement of heterostructures of PET. Besides, a thin layer of a wide-band semiconductor creates a barrier as a course of contact with it through a thin layer of nonconductor, semiconductor with less width of prohibited zone. As a result, a pseudo p-n – transition is performed. A thin layer of nonconductor between semiconductors determines the amount of current of tunneling. If the layer of nonconductor is diminished, the amount of current increases. Significant diminishing of nonconductor layer can lead to such an increase of the amount of current, that may cause the basic semiconductor to lose the state of heat equilibrium. It makes the concentration of charge carriers close to the surface higher to a certain constant point. After that, the surface layer can be treated as a quasi-doped. The current of the main charge carriers from the valence band of the basic semiconductor is blocked by the prohibited zone of the wide-band semiconductor. It significantly increases the efficiency of the structure [12, 13].

For the production of PET, the authors selected the SnO_2 | Zn_2O_3 – SiO_x – nSi – n^+Si heterostructures. For their production, Si structures of nn^+-type of conductivity, 76 mm in diameter were used. The preparation of the surface was done by means of its treatment in the HF + H_2O = 1:3 solution for 1-3 min with eventual rinsing in distilled water and drying at a temperature of 150 °C during 2 h. Noticeable results can be observed after treatment with ammonia-peroxide solution.

The initial mixture for heterotransition, the so-called ITO-mixture, consisted of the following: 7g $InCl_3 \cdot 4H_2O$ + 0.25 ml $SnCl_4 \cdot 5H_2O$ + 50 ml C_2H_5OH. The produced mixture was thoroughly mixed and kept during 2 h at room temperature.

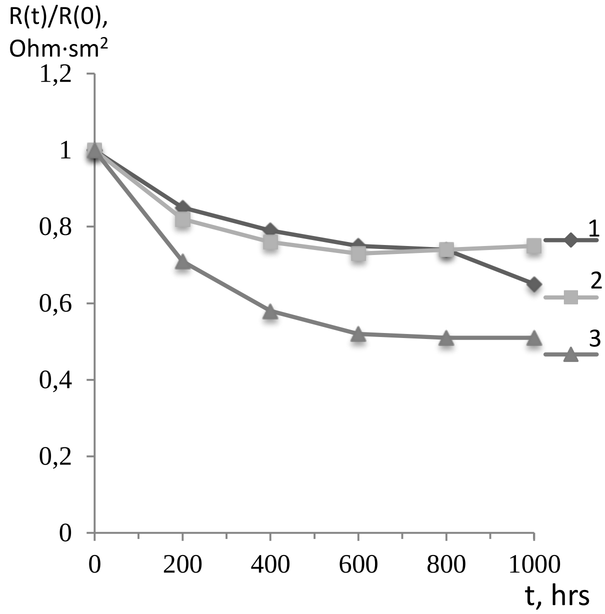
The formation of heterotransitions was performed by the method of pulverization of the solution made on silicon epitaxial structure, heated to the temperature of 350-430 °C. For the sake of keeping the temperature on the level, the plating was performed by means of periodicity of pulverization: 2-5 s – spraying, 10-12 s – a pause. Pulverization was done with the help of deliberately designed appliance. The function of the spray gun was played by compressed air. The heating of the backing took place with the help of a furnace with smoothly regulated output. The pulverization lasted till the first blue color appeared, that corresponded to the thickness of the oxide layer of ~ 80 Å. The application of heterotransitions significantly diminishes the expanse of electric energy of PET due to their surface recombination, increase of sensitivity in the "violet" range of the spectrum, where photons' energy is high, and widening of spectrum sensitivity. Besides, the structures of semiconductor-nonconductor-semiconductor type are marked by the simplicity of technology, low-temperature processes required and their high productivity.

The research demonstrated that one of the ways of increasing the efficiency of PET production is the improvement of the technology of contact systems processing [12].

The authors elaborated the Al-Cu-Si contact system, which is marked by increased stability to electromigration, and which prevents silicon erosion in contact windows simultaneously. The function of the backing was done by silicon plates of nn^+-type with resistivity of 0.3-5 Ohm·cm. The plates' diameter was 78 mm, their width was 500 μm.

On corresponding batches of plates, the layers of Al, Al-Cu (2 %) Al-Cu (2 %) – Si (1 %) 0.6 μm thick were pulverized. Immediately before the sedimentation, the plates were polished in the solution of HF (concentrated) for 25 s, after the etching they were washed in hot and cold distilled water, in alcohol and dried up in the thermostat. After that, the plates were put into the camera of the vacuum pulverization device. The interval between the processing and loadings of the camera was 25 min. After the formation of the adjusted topology of metallization, the plates were exposed to nitrogen burning with a temperature of 450 ºC during 10 min and the protective coat of SiO_2 of 0.9 μm thick was applied. It was followed by the oxide removal from the excretive grounds and the splitting into separate crystals was completed. The quality test of instrument structures was held by means of measuring contact resistance of contact systems. The amount of resistivity ρ for Al-Cu-Si contacts was (0.78-1.55) 10^{-6} Ohm·cm^2.

For quality tests of contact systems, the authors investigated the dependence of contact resistance at a temperature of 150 ºC. Produced structures were exposed to this temperature for 1000 h. The contact resistance was measured after 200, 400, 750 and 1000 h of exposure. The dependence of normalized contact resistance $R(t)/R(0)$ on the duration of exposure for Al-Cu-Si (graph 1), Al-Cu (graph 2) and Al (graph 3) metallization is provided in the Fig. 1.



1 – for Al-Cu-Si;
2 – for Al-Cu;
3 – for Al

Fig. 1 – The dependence of normalized contact resistance on the duration of exposure

The analysis of the stability of contact systems before electromigration demonstrated, that the Al-Cu-Si systems did not prove any refusal either in the process of exposure to a temperature of 150 ºC, or in the course of electromigration tests, whereas for the Al and Al-Cu structures, a significant quantity of refuses was observed. Thus, after 1000 h of exposure at a temperature of 200 ºC, 2 of 15 Al structures and 2 of 15 Al-Cu structures demonstrated refuses. As a result of electromigration tests during 256 h at a temperature of 215 °C, there were 14 refusals (with 20 tested structures) for Al and 7 refusals for Al-Cu.

The investigation of the surface morphology of the borderline of metal-silicon, which was estimated by means of scanning with the help of an electronic microscope, was completed as well.

The casings, in which test structures were preserved, were depressurized in advance, and the protective nonconductor coating and metal layer were one by one removed from the surface of the test crystal. The analysis of the samples, tested under the temperature of 200 ºC during 1000 h, demonstrated, that on the borderlines of Al-silicon and Al-Cu-silicon the erosion of silicon was observed. For Al-Cu-Si structures, only a small amount of silicon precipitate was noticed. It was proved that both erosion areas and silicon precipitate are unevenly distributed in the contact window, their density is higher at the periphery in comparison with the core area. Silicon erosion in the contact window causes a short circuit of *p-n* transitions. An insignificant increase in resistance of Al-Cu-Si contacts after 750 h of exposure to the temperature of 200 ºC is explained by the silicon precipitate split-off or the growth of silicon epitaxial layer in the contact window.

4. CONCLUSIONS

In the course of the analysis of Al-Cu-Si structures neither in the process of exposure to the temperature of 200 ºC, nor in the course of electromigration tests, there were no refusals observed, only insignificant amount of silicon precipitate was noticed. For Al and Al-Cu structures, a significant amount of refusals and silicon erosion are characteristic.

It is well known that the value of contact resistance mainly determines the characteristics of photoelectric instrument structures. The most low-Ohm contact was performed by the method of vacuum pulverization with the further annealing in nitrogen environment with a temperature of 450 ºC during 15 min. The minimum value of surface resistivity of Al-Cu-Si with the depth of *p-n* transition of 0.30 μm was 0.78·10^{-6} Ohm·cm^2.

The variation of the contact resistance points out the necessity of thorough preparation of contact windows before the contact. It was also proved that cleaning of the backing surface in the processing camera of the vacuum device immediately before the metal coating significantly diminishes the variation of the contact resistance.

All in all, it is advisable to apply Al-Cu-Si contact systems for a series of photoelectric appliances. Technological processes of the obtained systems do not demand any complicated equipment, the applying of precious metals and require a small amount of operations. The optimal width of the layers in the recommended contact system was approximately 500 Å.

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Технологічні особливості виготовлення реальних контактних систем для приладів наносистемної техніки

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У статті розглянуті шляхи підвищення ефективності фотоелектричних перетворювачів за рахунок застосування гетероструктур SnO_2 | Zn_2O_3 – SiO_x – nSi – n^+Si і опрацювання технології виробництва контактних систем. Емпірично досліджено фізичні процеси, що відбуваються в гетероструктурах, проведено аналіз методологій та режимів їх отримання. Розглянуто значні переваги фотоелектричних перетворювачів на основі представлених структур в порівнянні із закордонними аналогами. Авторами запропонована альтернативна технологія створення контактних систем до гетероструктур і експериментально доведено, що відпалені контактні системи мають переваги, в першу чергу, з точки зору зниження числа технологічних операцій і до цього часу являються актуальними. Використання такої композиції дозволило знизити температуру відпалу, що привело до покращення морфології отриманих контактних систем у порівнянні з традиційними. Доведено, що застосування таких контактних систем дозволить підвищити ефективність фотоелектричних приладів за рахунок простоти технологічного процесу і дешевих матеріалів, що приведе до зниження собівартості виробу.

Ключові слова: Технологія, Контактні системи, Фотоелектричні перетворювачі, Кремнієві структури, Гетеропереходи, Параметри, Характеристики.