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Hydrogen Treatment of Gold Contact on Silicon

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Plate of p-silicon of 0.35 mm thickness was the sample of present studies. Two gold film contacts of 50 nm thickness were deposited on the opposite surfaces of p-silicon sample. For the manufacturing of gold film contacts the method of direct contact heating in a tungsten boat was used. The surface of the silicon plate was activated before the deposition of gold by dipping the samples into a 0.5 % solution of hydrofluoric acid. The silicon wafer was then washed with distilled water, dried and placed in a container for substrates. After deposition of the gold film contact, the plate of p-silicon was cut in several samples. The hydrogen treatment of only one gold film contact was executed by means of electrolysis in 10 % water solution of H_2SO_4. The gold contact was the cathode and the graphite electrode was the anode. The second gold film contact was isolated during the electrolysis. The electrolysis lasted for 6 min. The current density during electrolysis was 117.5 A/m^2. The p-silicon samples with gold contacts processed by hydrogen were stored at room conditions. The time dependence of the volt-ampere characteristics of the samples was investigated. The resistance of the gold film contact increased in the first few hours after hydrogen processing. But then, during the week after hydrogen treatment, the resistance of the gold film contact constantly diminished. During the next week, the resistance of the gold film contact did not change. The hydrogen saturation of the gold film contact caused the significant reduction of the resistance of the gold contact. After treatment and exposure at room conditions, the final resistance of the gold film contact decreased by almost 1.5 times in comparison with the contact resistance before hydrogen treatment.

Keywords: *p*-silicon, Hydrogen treatment, Hydrogen, Gold contact, Diffusion, Resistivity.

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1. INTRODUCTION

The development of scientific and technological progress requires the search and study of materials with predetermined physical properties, as well as the creation and development of technologies that provide opportunities to obtain these materials. One of the ways to achieve these goals is the hydrogen treatment of materials. The hydrogen treatment of materials arose in the last quarter of the 20th century, and it is still actively developing. It has a significant contribution to the technology of the magnetic materials processing. The hydrogen treatment of the intermetallic compounds is known as the HDDR process allowed the creation of materials with the required magnetic properties. During HDDR technology, different affinity of the intermetallic compounds components to hydrogen was used, and significant acceleration of the diffusion of metal atoms saturated with hydrogen was observed [1].

Humanity has to develop efficient clean renewable sources of energy. Hydrogen energy is environmentally friendly technology. Its development requires the improvement of fuel cells, i.e. new technologies for the storage and supply of hydrogen [2]. The fuel cell is a complex device where the unique properties of the interaction of hydrogen with the condensed state of matter are used. Therefore, it is another example of the importance of studying the processes of hydrogen interaction with the condensed state of matter.

Mankind also needs the materials processing technology that could improve the performance of microelectronics. Silicon is the main material for the electronic industry today. Therefore studies of silicon-hydrogen interactions are interesting theme of modern studies [3-6]. Silicon is used during manufacturing various electronic components. Metallic contacts are presented in any electronic device. Properties of metal contacts on a semiconductor are based on the interaction of metal and semiconductor. Hydrogen can significantly affect the processes of metal-semiconductor interaction and change the operational properties of the contact. Thus, hydrogen treatment of the contacts can positively affect the performance properties and be proposed as a part of technological process of creating microelectronic devices.

2. CREATION OF FILM CONTACTS AND HYDROGEN PROCESSING

The gold film contacts were inflicted on the p-silicon plates with a thickness of 0.35 mm. A 50 nm thick gold film was deposited on the activated silicon surface. To produce the gold films, the method of direct contact heating in a tungsten boat was used. Energy was transmitted by phonons. The deposition was carried out inside the industrial system VUP-5M at a pressure in the working chamber of 10^{-3} Pa. Activation of the surface (substrate) of the silicon plate was performed by immersing the samples in a 0.5 % solution of hydrofluoric acid during 1-5 s. Subsequently the silicon plate was washed with distilled water, dried and placed into

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the container for substrates, which was immediately mounted in a working chamber for depositing a gold film. The deposition was carried out on a cold bed. The deposition rate of gold was 0.5 nm/s. After inflicting the contact film unto the one surface of the silicon wafer (substrate), the container for the substrates was removed from the VUP-5M. The silicon plate was turned over unto the surface with gold contact. The container with the silicon wafer was returned into the vacuum chamber VUP-5M. Then, according to the described method, a gold film was inflicted unto the second surface of the silicon wafer.

The resulting silicon wafer with gold film contacts was divided into samples for hydrogen treatment. The dimensions of each sample were approximately 0.8×5 mm. Volt-ampere characteristics of the samples were measured before hydrogen treatment. Subsequently the sample was placed into the bath for electrolysis (Fig. 1). One of the contacts (rear contact inside the bath in Fig. 1) and the lateral surfaces of the sample were isolated from contact with the electrolyte. The second one (upper contact in Fig. 2) was directly contacted with the electrolyte. The lower gold film contact was connected to the negative pole of the current source for electrolysis. The positive pole of the current source was connected to the graphite electrode. Thus, during electrolysis the upper gold film contact was a cathode, and the graphite contact was the anode. The tub was filled with 10 % water solution of sulfuric acid (H_2SO_4). Video camera was installed on top of the tub and during the electrolysis there was video control and video shooting of the entire process. Thus, the hydrogen treatment was provided to the upper gold film contact. Hydrogen could affect onto the lower gold film contact only after diffusion across the entire thickness of the silicon plate. The thickness of the silicon plate was 0.35 mm. Electrolytic saturation with hydrogen was carried out at room temperature. Current strength at electrolysis was 0.47 mA. During electrolysis, small hydrogen bubbles were constantly formed on the surface of the upper gold film contact.

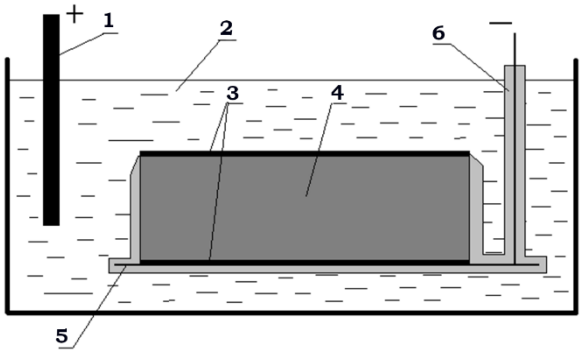

Fig. 1 – Sketch of bath for performing the electrolytic hydrogen saturation of the gold film contact on p-silicon. 1) graphite electrode (anode); 2) electrolyte (10 % water solution of H_2SO_4); 3) gold film contacts on silicon; 4) p-silicon crystal; 5) electrical connection of the bottom gold film contact with the negative pole of the current source (cathode); 6) insulator isolating the conductors (lower gold film contact on the p-silicon and the lateral surfaces of the p-silicon crystal) from the electrolyte

The density of the hydrogen bubbles on the surface was visually identical and time-independent through electrolysis. That is, the whole surface of the gold film contact is uniformly involved throughout the electrolysis process. The electrolysis process lasted for 6 min. After this, the sample was taken out of the tray and washed in distilled water. Subsequently the sample was dried in a flowing air at room temperature.

3. VOLT-AMPERE CHARACTERISTICS OF GOLD FILM CONTACTS ON P-SILICON

One hour after hydrogen treatment, the measure of the volt-ampere characteristics of the sample was carried out. In Fig. 2, the volt-ampere characteristics of the sample are given depending on hydrogen processing in one of the directions of the current passing through the sample. Comparing the volt-ampere characteristics of the sample measured one hour after hydrogen treatment and before hydrogen treatment, it was determined that a larger difference of potentials should be applied to the sample to produce the same electric current. Thus, before hydrogen treatment when the voltage on a sample was 5 V, the current strength was 1.4 mA; an hour after the hydrogen treatment, the current strength was already 1.2 mA at the same voltage per a sample. That is, one hour after the hydrogen treatment, the electrical resistance of the sample increased. The next day, new measurements of the volt-ampere characteristics were carried out. Measurements were performed 22 hours after hydrogen treatment. According to the obtained results, it became clear that meanwhile as voltage on the sample was 5 V, the current was 1.4 mA. That is, after 22 hours after the hydrogen treatment, the electrical resistance of the sample became almost as much as before hydrogen treatment. We decided to repeat measurements of the volt-ampere characteristics of each day. The following measurements (carried out after about 24 hours) showed that the strength of the current in the sample increased every day, but the current growth rate gradually decreased. Volt-ampere characteristics were measured within two weeks. During one week the process of current growth through the sample was completed.

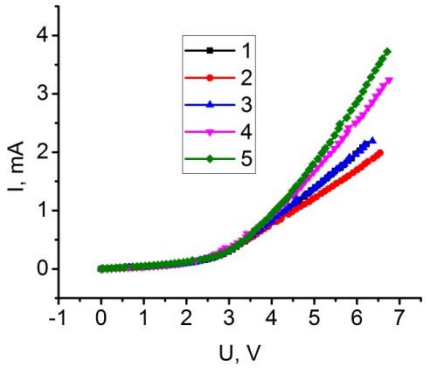

Fig. 2 – Volt-ampere characteristics of the sample when the electric current was in the positive direction: 1) before hydrogen treatment; 2) one hour after hydrogen treatment; 3) 22 hours after hydrogen treatment; 4) three days after hydrogen treatment; 5) a week after hydrogen treatment

Volt-ampere characteristics of the sample when the electric current had the opposite direction are given in Fig. 3. Analysis of the volt-ampere characteristics of the sample for the current in the opposite direction showed that the current increased for one hour after the hydrogen processing. Volt-ampere characteristic of the sample for measurements 22 hours after hydrogen treatment almost coincided with the characteristic before hydrogen treatment. That is, within experimental error, the electrical resistance of the sample 22 hours after the hydrogen treatment returned to the values that were before the hydrogen treatment. Observations in the following days shew that within experimental error, the volt-ampere characteristics do not change in the future.

Based on the volt-ampere characteristics for different times after hydrogen treatment, electrical resistance of the sample were obtained at applied voltage of 6 V. Time dependence of the electrical resistance of the sample for the first direction of current flow is demonstrated in Fig. 4.

Fig. 4 shows that one hour after hydrogen treatment, the electrical resistance of the sample increased. In the future, when the sample was stored at room conditions, the sample's resistance decreased monotonously. After one week, the resistance reduction of the sample ceased. Observation over the next week shew that obtained by means of the hydrogen treatment the new resistivity properties of the contacts do not change in the future. Thus, due to the hydrogen treatment of gold film contact on silicon, it was possible to reduce the electrical resistance of the contact by one and half times.

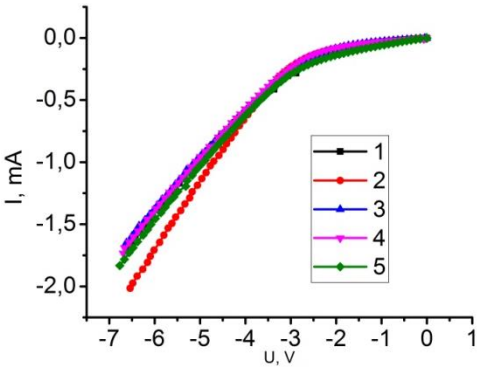

Fig. 3 – Volt-ampere characteristics of the sample when the electric current was in the opposite direction (red color - one hour after hydrogen processing)

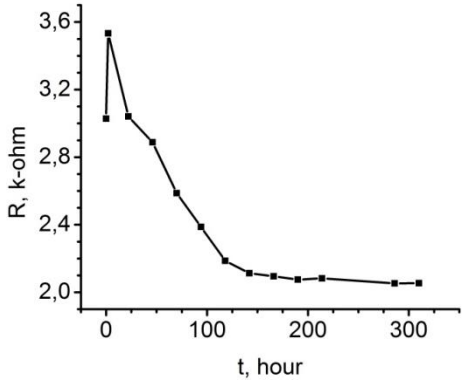

Fig. 4 – Time dependence of the sample electrical resistance after hydrogen treatment

4. DISCUSSION OF RESULTS

Let us consider the details of the electrolysis process. The difference of potentials between the cathode and the anode does not exceed 30 V. This means that the energy of positive hydrogen ions does not exceed 30 eV. Ions with such energies, mainly protons, remain on the surface of the film contact or in the first near-surface layers of a crystalline lattice of gold. At a current density of 1.2 A/cm^2, the contact surface is quickly saturated with hydrogen. Some part of hydrogen forms a molecule that is visually observed in experiment. The bubbles of hydrogen are formed on the surface. The other part of the electrolytic hydrogen diffuses into the gold contact toward the silicon wafer. The gold film acts like a hydrogen membrane. There are many defects at the gold-silicon interface. It is well known that the various defects of the crystal lattice are good traps for hydrogen [7]. Thus, the first part of hydrogen diffusing through the gold film is captured by defects at the gold-silicon interface. The second part of hydrogen after passing the "membrane" continues to diffuse in silicon until silicon saturates with hydrogen. Thus, during electrolysis, hydrogen saturation occurs at the gold-silicon interface. This saturation is not time-reversible, as evidenced by further observations.

Saturation with hydrogen of the layer at the gold-silicon interface provokes more profound transformations than saturation of hydrogen defects at the boundary of distribution. Saturation of defects most likely causes changes of the contact resistance in the first hour after electrolysis. Changes in the electrical resistance of the contact throughout the week cannot be explained by the simple diffusion of hydrogen in the opposite direction that is degassing of the sample, since the degassing time should be comparable with the saturation time. However, the saturation lasted for 6 min, but the transformation in the sample took place for a week. Such a long process of transformation can be explained by the fact that the studied process (or even several processes) was caused by the diffusion of atoms of gold, silicon, oxygen and other impurities in silicon. In a condensed state at room temperature, for the diffusion exchange of atoms of a gold film and a silicon plate, it takes much longer than 300 hours to be observed in the experiment. The phenomena of significant acceleration of the diffusion of metal atoms, for example, were observed in the diffusion phase transformation of intermetallic [1, 7]. It is known that the hydrogen saturated crystalline metal lattice causes an increase of the number of equilibrium vacancies in the nodes of a crystal lattice in several orders of magnitude [8]. The increase in vacancies at the nodes of the crystal lattice has created conditions for accelerating the diffusion of atoms of gold, silicon, oxygen and atoms of impurities in a layer at the gold and silicon interface. Thus, hydrogen saturation during electrolysis has created conditions for the accelerated exchange of atoms at room temperature in the layer at the boundary of gold-silicon distribution [9].

In most cases, metals on silicon form non-ohmic contacts. Gold contacts are no exception. Volt-ampere characteristics of such contacts are nonlinear and asymmetric with respect to the alteration of the polari-

ty applied to the sample. In the most cases, the electrical resistance of the gold contact on silicon varies significantly with the change of the polarity of the voltage. Since in the experiment on the sample two contacts are used, then when the voltage is changed, the electrical resistance of such a sample is always determined by the greater resistance of one of the contacts. After hydrogen processing, the electrical resistance of the sample significantly decreased for one voltage polarity on the sample, but did not change for the opposite voltage on the sample. This can be explained by the presence of two contacts on the sample. One contact was under hydrogen treatment and its properties have been changed. The second contact was not and its properties haven't been changed. If the total resistance of the sample gives the resistance of the treated contact, we observe a decrease in resistance. If the main contribution to the sample resistance is the resistance of the untreated sample, we observe the constant resistance of the sample before and after processing.

It is also necessary to take into account the actual state of the surface of the silicon plate during the deposition of the gold film contact. Before depositing gold on the surface of silicon, the surface activation was carried out by immersing the plate into a solution of hydrofluoric acid for a few seconds. Next, the silicon plate was washed with distilled water and dried in air. After preparing the surface, it is not ideal where there are only silicon atoms on the surface of the crystal. Usually, a dielectric amorphous silicon oxide layer was formed on the surface. Then, a gold film was deposited on this layer. That is, before hydrogen treatment the gold film contact on silicon is such a structure where there is a thin layer of dielectric between gold contact and silicon. This layer creates an additional barrier when electric current passes through a contact. During hydrogen treatment, the dielectric amorphous layer is saturated with hydrogen. In this layer hydrogen keeps longer than in crystalline silicon or gold contact film. The presence of hydrogen creates conditions under which there is a change in the chemical composition of the layer. Instead of a layer of silicon oxide there is a layer of silicon enriched with gold. Perhaps it does not happen on the entire contact plane; "pieces of oxide" of silicon are stored in some places [10]. To clarify the mechanism of transformation, we are going to perform additional experiments using electron microscopy, secondary ion mass spectrometry and other techniques. We hope to create a hydrogen processing technology that will allow to control the changes of the characteristics of metal contacts on silicon.

The applied electrolytic doping with hydrogen of the gold film contact can be replaced by controlled irradiation by low-energy protons. Proton beams can have small sizes. Energy, direction of irradiation and value of integral doze of proton beams are well-controlled. In the case of low-energy protons, it is possible to achieve high purity of doping in p-silicon. Proton irradiation is also definitely interesting to study the stability of electronic components in a radiation environment.

5. CONCLUSIONS

In the work, a change in the electrical resistance of a silicon sample with two gold film contacts was studied. Due to the hydrogen processing of the gold film contact with silicon, it was possible to significantly reduce the electrical contact resistance. Changes in the electrical characteristics of the gold film contact on silicon lasted within a week. The saturation with hydrogen of the gold film contact was due to electrolysis in a 10 % water solution of H_2SO_4.

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Воднева обробка золотого контакту на кремнії

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Зразком для досліджень була пластина *p*-кремнію товщиною 0.35 мм. До протилежних поверхонь p-кремнієвого зразка було нанесено два золотих плівкові контакти товщиною 50 нм. Для виготовлення золотого плівкового контакту використано методи прямого підігріву контакту в вольфраму човні. Поверхня кремнієвої пластини була активована для відкладення золота шляхом занурення зразків у 0.5 % розчин плавикової кислоти. Після цього кремнієву пластину промили дистильованою водою, висушили і помістили в контейнер для субстратів. Після відкладення золотих плівкових контактів пластину p-кремнію розрізали на декілька зразків. Водневій обробці було піддано лише один контакт за допомогою електролізу в 10 % водяному розчині H_2SO_4. Золотий контакт був катодом, а графітовий електрод був анодом. Другий золотий плівковий контакт був ізольований під час електролізу. Електроліз тривав 6 хвилин. Щільність струму під час електролізу складала 117.5 А/м^2. Оброблені воднем p-кремнієві зразки з золотими контактами зберігалися в кімнатних умовах. Досліджено часову залежність вольт-амперної характеристики зразків. Опір золотого плівкового контакту збільшився в перші кілька годин після водневої обробки. Але потім, протягом тижня після цього, опір золотого плівкового контакту постійно зменшувався. Протягом подальшого тижня опір золотого плівкового контакту не мінявся. Насиченість воднем золотого плівкового контакту викликала значне зниження опору золотого контакту. Після водневої обробки та витримки в кімнатних умовах остаточний опір золотого плівкового контакту знизився майже в 1.5 рази у порівнянні з опором контакту до водневої обробки.

Ключові слова: *p*-кремній, Воднева обробка, Водень, Золотий контакт, Дифузія, Питомий опір.