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OPTIMIZATION OF CHEMICAL SURFACE TREATMENT PROCESSES OF P-N JUNCTIONS IN THE PRODUCTION OF SILICON DIODES

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The quality of operation of active semiconductor structures, which include diodes, transistors, integrated circuits, etc., largely depends on the state of their surface layer in the region of the p-n junction exiting the surface. A multilayer film of moisture is deposited on the real surface of the semiconductor and contains many foreign impurities adsorbed from etchant and washing water. A significant part of these impurities is made up of positive ions of alkali metals. Under the action of a voltage applied to the junction, these ions drift in the moisture film, creating an ionic leakage current. The surface leakage current is often the main component of the reverse current through the p-n junction. Such important characteristics of diodes and transistors as the magnitude of the reverse current and the breakdown voltage of the p-n junction are largely determined by surface treatment. Surface treatment of a semiconductor is a very important technological operation in the process of manufacturing semiconductor devices and circuits. In connection with the development of micro- and nanoelectronics, the size of elements and dimensions of devices is decreasing and the surface to volume ratio is increasing, and, consequently, the degree of surface influence is increasing. The surface has a very strong influence on the operational characteristics of semiconductor devices: the stability of the characteristics and, consequently, the yield of suitable devices and their reliability during operation. Over time, the characteristics of the devices begin to degrade, that is, they change, go beyond the tolerances established by the standard, and the device fails. The change in the parameters of semiconductor devices begins with the surface and is associated *with the processes of adsorption-desorption, diffusion, etc. Therefore, special surface treatment methods are used in technology, aimed at improving and preserving the surface condition (surface passivation with a dielectric layer, sealing of devices, etc.). The article presents experimental results of studying the influence of various methods of chemical surface treatment of diode structures on their reverse current, and also analyzes possible mechanisms of this influence. The effectiveness of using the developed etchant based on chromium trioxide and sulfuric acid for photolithography on a chalcogenide glass layer for low-*temperature gettering processes in the production of silicon diodes is shown.

Key words: surface, p - n junction, varicap structures, surface effects, reverse current, chalcogenide glass, impurities.

Литвиненко В.М. Оптимізація процесів хімічної обробки поверхні p-n переходу у виробництві кремнієвих діодів

Якість роботи активних напівпровідникових структур, до яких відносяться діоди, транзистори, інтегральні схеми і ін., багато в чому залежать від стану їх поверхневого шару в області виходу на поверхню p- n *переходу. На реальній поверхні напівпровідника осідає багатошарова плівка вологи і міститься багато сторонніх домішок, адсорбованих з травників і промивної води. Помітну частину цих домішок складають позитивні іони лужних металів. Під дією напруги, прикладеної до переходу, ці іони дрейфують в плівці вологи, створюючи іонний струм витоку. Струм поверхневого витоку часто є основною складовою зворотного струму через* p-n *перехід. Такі важливі характеристики діодів і транзисторів як величина зворотного струму і пробивна напруга p - n переходу в великій мірі визначаються обробкою поверхні. Обробка поверхні напівпровідника є дуже важливою технологічною операцією в процесі виготовлення напівпровідникових приладів і схем. У зв'язку з розвитком мікро- і наноелектроніки відбувається зменшення розмірів елементів і габаритів приладів і збільшується відношення поверхні до об'єму і, отже, росте міра* *впливу поверхні. Поверхня дуже сильно впливає на експлуатаційні характеристики напівпровідникових приладів: стабільність характеристик і, отже, вихід придатних приладів і їх надійність при експлуатації. З плином часу експлуатації починається деградація характеристик приладів, тобто вони змінюються, виходять за встановлені стандартом допуски, і прилад виходить з ладу. Зміна параметрів напівпровідникових приладів розпочинається з поверхні і пов'язана з процесами адсорбції-десорбції, дифузії тощо. Тому в технології застосовуються спеціальні методи поверхневих обробок, спрямовані на поліпшення і збереження стану поверхні (пасивація поверхні шаром діелектрика, герметизація приладів тощо).*

В статті наведено експериментальні результати дослідження впливу різних методів хімічної обробки поверхні діодних структур на їх зворотний струм, а також проаналізовано можливі механізми цього впливу. Показана ефективність використання розробленого травника на основі триокису хрому та сірчаної кислоти для проведення фотолітографії по шару халькогенідного скла для процесів низькотемпературного гетерування у виробництві кремнієвих діодів.

Ключові слова: *поверхня, p - n перехід, варикапні структури, поверхневі ефекти, зворотний струм, халькогенідне скло, домішки.*

Problem statement. The state of the surface of semiconductor device structures has no less strong influence on the parameters and characteristics of the devices than the physical properties of the semiconductor bulk. The cause of negative phenomena in semiconductor crystals with p-n junctions can be not only Tamm and Shockley levels, which occur even on the atomically pure surface of the semiconductor. Surface effects arise in the p-n junction when its surface is contaminated with metal impurities (Na, K, Cu, Au, Ni, etc.), which are in the form of ions and form a surface charge. These impurities can get onto the semiconductor wafers, for example, from etching solutions, quartz tubes of diffusion and oxidation furnaces, etc. [1]. In microelectronics technology, protection (passivation) of the surface of semiconductor devices and integrated circuits is always used. The best for this purpose is a thermally grown SiO_2 layer. However, even a surface protected by a dielectric layer does not always remain stable. Various chemical treatment methods are used to improve the surface condition. Many different chemical treatment methods have been developed to improve the surface properties of diode structures, but not all of them are effective in improving the reverse characteristics of diodes.

Formulation of the research goal. This work is devoted to the analysis of the negative impact of the surface on the electrical characteristics of semiconductor devices and the development of chemical treatment methods aimed at preventing this impact, i.e. aimed at improving the surface condition.

Chemical treatment technology and research on its effectiveness

In order to eliminate the undesirable influence of the surface state on the electrical parameters of semiconductor devices, various methods of chemical treatment of semiconductor structures have been developed, the use of which makes it possible to significantly improve the state of their surface. Chemical surface treatment operations precede all operations of the technological cycle of manufacturing semiconductor devices and microcircuits. Chemical treatment of semiconductor wafers and crystals is performed in solvents, acids and alkalis, water, using ultrasound, in aqueous solutions of surfactants, and also electrolytically [2].

The influence of chemical treatment of the surface of varicap structures on their reverse current was studied. Varicap structures were manufactured using standard planar epitaxial technology [2] on phosphorus-doped silicon epitaxial structures of n-type conductivity with a resistivity of 2 Ohm·cm and a thickness of 10 μm, grown on a silicon substrate oriented in the crystallographic direction (111). To manufacture varicap structures, the following main technological operations were performed: thermal oxidation of the plates at a temperature of 1050°C with the following alternation of cycles: oxidation in dry oxygen (10 minutes) - oxidation in humid oxygen (160 minutes) - oxidation in dry oxygen (10 minutes); I photolithography to open windows in the silicon dioxide layer for boron diffusion; boron distillation by the open tube method from the B_2O_3 impurity source at a temperature of 1080°C for 30 minutes in a mixture of argon (80 l/h) and dry oxygen (4 l/h); removal of borosilicate glass in a solution of hydrofluoric acid; boron distillation at a temperature of 1150°C in a dry oxygen environment (60 l/h) for 5,5 hours; II photolithography to open windows in the silicon dioxide layer to create ohmic contacts; formation of ohmic contacts: chemical deposition of nickel on both sides of the plate with subsequent annealing of the nickel film at a temperature of 700°C in an argon environment (140 l/h) for 25 min, carrying out the second stage of chemical deposition of Ni, applying an Au layer on both sides of the plate by galvanic deposition. Varicap structures rejected due to a high level of reverse current were used for the research. To confirm that these varicap structures were rejected due to the influence of surface effects on them, additional studies were conducted.

Silicon wafers with formed diode structures were first treated in a hydrofluoric acid solution ($HF:H_2O = 1:10$) for 2 minutes followed by rinsing in distilled water (treatment mode 1). Next, a complex treatment of the wafers was carried out, consisting of: a) boiling in nitric acid (2 times for 5 minutes); rinsing in water; b) treatment in a hydrofluoric acid solution ($HF:H_2O = 1:10$) for 2 minutes; rinsing in distilled water; c) treatment in a peroxide-ammonia solution and subsequent rinsing in distilled water (treatment mode 2). Moreover, before chemical treatments, as well as after chemical treatment of the wafers in a hydrofluoric acid solution and after complex treatment, the value of the reverse current of the varicaps at a reverse voltage of 30V was measured on the same varicap structures. The results of the study are given in Table 1. As can be seen from Table 1, additional chemical treatment of the plates makes it possible to reduce the reverse currents of varicaps.

An effective method of cleaning semiconductor wafers from organic and mechanical contaminants and uncontrolled impurities is proposed [3]. This method involves a two-stage treatment in two baths with different solutions. The first bath contains a solution consisting of: sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) in the following ratio: $H_2SO_4 : H_2O_2 = 1:10$ at a temperature of 120±5°C.

Table 1

Results of measurement of reverse current of varicap structures at reverse voltage of 30 V

Varicap structure number	1	2	3	4	5	6	7	8	9	10
I_{rev}, μA to chemical processing	3,7	2,2	2,6	3,1	3,9	3,2	4,0	3,3	3,5	3,7
I_{rev}, μA after chemical treatment according to mode 1	2,9	1,7	1,7	2,5	3,1	2,4	2,9	2,8	3,1	3,3
I_{rev}, μA after chemical treatment according to mode 2	2,5	1,1	1,3	2,1	2,7	1,9	2,0	1,5	2,1	2,6

The second bath contains a solution consisting of: aqueous ammonia solution (NH_4OH), hydrogen peroxide (H_2O_2) and deionized water (H_2O) in the ratio: $NH_4OH:H_2O_2: H_2O = 1:4:20$ at a temperature of (55-65)°C. As the authors of the work explain, in the first bath the coarsest organic and fatty contaminants are removed, and in the second bath the areas of fatty coatings that were not removed during processing in the first bath are removed. Obviously, cleaning in H_2SO_4 makes it possible to remove adsorbed metal ions and dissolve oxide films on the surface of the semiconductor wafer, perhydrol decomposes with the release of oxygen: $H_2O_2 = H_2O+O$; atomic oxygen oxidizes both organic and inorganic contaminants. Alkali (NH_4OH) accelerates the decomposition reaction of perhydrol. As the authors showed, in comparison with the basic methods of processing semiconductor structures, the developed method makes it possible to improve the quality of cleaning and reduce the duration of the surface cleaning process.

The influence of surface treatment of silicon epitaxial structures before the first oxidation in various chemical reagents on the reverse currents of diodes made on their basis was studied [3]. The studied samples were cleaned before oxidation in the following components of chemical treatment: 1) ($HF:HNO_3$ =1: 19) - treatment for 20 s. 2) SRA - sulfa-raspberry anhydride (surfactant) - treatment for 25 min. 3) HNO_3 - treatment by boiling for 50 min. 4) Peroxide-ammonia solution ($H_2O_2+NH_4OH+H_2O$=1:1:4) - treatment for 7 min. 5) SMA+HNO_3 - treatment for 25 min. and 50 min. respectively. 6) SMA + ($HF:HNO_3$=1:19) + HNO_3 - treatment for 25 min., 20 s and 50 min. respectively. The treatment time in each of the studied components was selected experimentally. The oxidation of the studied samples was carried out in one technological process according to the mode: $T=1045^oC$; process time - 10 min.; medium - water vapor. The thickness of the grown oxide was 0,16 μm. After that, metallization of silicon structures and photolithography on a metal layer with a window diameter D =1000 μm were carried out to obtain metal-oxide-semiconductor structures (MOS structures).

As a result of the experiment, the voltage-farad characteristics of the MOS structures treated with the above chemical reagents were measured. The quality of the chemical treatments was assessed by the value of the total surface charge of the MOS structures Q_{SS} and the density of surface states N_{SS} for each type of chemical treatment, which were calculated using the constructed voltage-farad characteristics of the MOS structures. The smallest value of the total surface charge and density of surface states (respectively $Q_{SS} = 2,8 \cdot 10^{-10}$Cl and $N_{SS} = 1,4 \cdot 10^{11}$cm^{-2}) was obtained when using treatment in a surfactant. Also, the quality of the studied chemical treatments was assessed by the yield of suitable diode structures manufactured using standard planar-epitaxial technology on silicon epitaxial structures of n-type conductivity with a resistivity of 2 Ohm·cm. and 10 μm thick, the cleaning of which before the first thermal oxidation was carried out using these chemical components (see Table 2).

Table 2

The effect of different chemical treatment methods on reverse currents of diode structures

Method of chemical treatment	Output of suitable diode structures, %
Treatment in SRA+ (HF:HNO_3=1:19) + HNO_3	63
Treatment in HNO_3	69
Treatment in HNO_3 + SRA	65
Treatment in SRA	70
Treatment in (HF:HNO_3=1:19)	73
Treatment in peroxide-ammonia solution	76

Thus, the optimal from the point of view of ensuring the minimum value of the total charge on the surface of diode structures and the highest yield of usable diodes (see Table 1) is the treatment in a peroxide-ammonia solution. The most acceptable from the point of view of ecology and economy is the treatment of the surface of diode structures in sulfa-raspberry anhydride, which does not contain components harmful to service personnel, which eliminates the need to use special equipment and protective equipment. At the same time, a sufficiently high yield of usable diodes is ensured.

Development of an etchant for chalcogenide glasses. The development of low-temperature gettering methods using chalcogenide glass films aimed at removing contaminants from the surface of the p-n junction and increasing the reliability of silicon diodes has necessitated the search for an etchant composition for chalcogenide glass that eliminates the disadvantages of known etchants. Performing photolithography on a layer of chalcogenide glass is a difficult task, since the quality of the photolithography process depends on a large number of different factors. Most often, alkaline etchant based on NaOH and KOH are used to dissolve glassy chalcogenide films [2]. Also, as etchant for chalcogenide glass, the following can be used: an aqueous solution of dimethylamine and a solution of potassium dichromate in diluted sulfuric acid. The main disadvantage of the first three etchants is the solubility in them of almost all photoresists used in the electronics industry, which excludes the use of these etchants for performing photolithography. In addition, etching of semiconductor device structures in solutions of alkalis NaOH and KOH leads to contamination of the surface of the p-n junction with positively charged ions K^+ and Na^+, which causes an increase in its reverse current due to the ionic leakage current. The last of the four etchants considered above includes potassium dichromate. During its dissociation, positively charged potassium ions appear in the etching solution, which, as noted above, leads to an increase in the leakage currents of the p-n junctions processed in the etching solution.

Based on the task, we have developed an etchant for photolithography on a layer of chalcogenide glass, which includes chromium trioxide, sulfuric acid and water. The distinctive features of the etchant are as follows: firstly, the vast majority of photoresists are resistant to the effects of this etchant; secondly, the composition of the etchant does not contain substances containing sodium and potassium ions. The etchant was tested in the production of silicon diodes with a mesa structure.

Table 3

Results of control of the appearance of the plates after photolithography on the glass layer

Composition of glass	Glass layer thickness, μm	Digestion time, s	The ratio of herbal ingredients	Photolithography process quality
$Ge_{33}As_{12}Se_{55}$	0,40	360	3:1:96	satisfactory – along the edge of the plate, grinded
$As_{32}S_{62}J_6$	0,40	330	3:10:87	satisfactory – glass residue in windows along the edge of the plate
$Ge_{28}Se_{66}Sb_6$	0,45	305	30:1:69	good – no etching or glass residue
$Ge_{28}Se_{66}Sb_6$	0,40	290	30:10:60	good – no etching or glass residue
$Ge_{33}As_{12}Se_{55}$	0,40	90	9:3:88	good – no etching or glass residue

As a starting material for the manufacture of diodes, phosphorus-doped silicon epitaxial films with a thickness of 9 μm and a resistivity of 0,75 Ohm · cm were used. Diode structures were manufactured using standard mesa-epitaxial technology [2]. The ohmic contact to the p-region was formed by sputtering an aluminum film in a vacuum with its subsequent annealing at a temperature of T=783K. After obtaining mesa-structures, a chalcogenide glass film was deposited on the plates. Then, photolithography was performed on the glass layer using the FP-RN-27V photoresist and an etchant based on chromium trioxide and sulfuric acid. The limits of the quantitative composition of the etchant components were selected from the point of view of the etching rate of glassy films, as well as the quality of the photolithography process - the presence of film etchings, glass residues in the windows after photolithography, etc. (see Table 3).

It has been experimentally established that the chromium trioxide content in the etchant plays a decisive role in the etching rate. When the chromium trioxide content in the etchant increases from 3 to 15%, the etching rate increases. A further increase in the chromium trioxide content in the etchant leads to a gradual slowdown in the etching rate. When the chromium trioxide content in the etchant is >30%, the glass etching rate decreases significantly. A significant decrease in the etching rate is also observed in cases where etchants with a chromium trioxide content of < 3%. As it was established, with an increase in the sulfuric acid content in the etchant from 1 to 10%, the etching rate increases slightly. A further increase in the sulfuric acid content in the etchant practically does not increase the etching rate of chalcogenide glass films.

From the obtained experimental data, the limits of the quantitative composition of the etchant components were determined, which allow photolithography on a layer of chalcogenide glass of satisfactory quality. These limits of the etchant components have the following ratios, wt. %: chromium trioxide: 3 - 30; sulfuric acid: 1 - 10; water: 60 - 96. Along with the study of the influence of the quantitative composition of the etchant components on the quality of photolithography, a comparison of the influence of the etchant based on chromium trioxide and sulfuric acid and the etchant based on potassium bichromate and sulfuric acid on the reverse currents of mesa structures was carried out. Table 4 shows the results of the rejection of batches of mesa structures with protection of the p - n junction by a film of chalcogenide glass $Ge_{33}As_{12}Se_{55}$ when using a known and developed etchant for photolithography on a layer of glass. Moreover, each batch of mesa structures was divided in half, and photolithography on these halves was carried out using different etchant. The suitability criterion: $I_{rev} \leq 0{,}05$ μA at $U_{rev} = 30$ V. The experimental results shown in Table 4 can be explained as follows. As noted above, potassium dichromate is used as a glass oxidizer in the composition of the known etchant. When the latter dissociates, positively charged potassium ions appear in the etchant solution. The composition of the developed etchant does not include components containing alkali metals. This can explain the higher values of the percentage yield of suitable mesa structures, in the manufacture of which the developed etchant was used (see Table 4).

Table 4

Effect of etchant for chalcogenide glasses on reverse currents of mesa structures

Batch numbers of mesa structures	Yield of suitable mesa structures, %	
	Mesa – structures on which photolithography on a glass layer was carried out using the developed etchant $CrO_3:H_2SO_4:H_2O = 9:3:88$	Mesa – structures on which photolithography on a glass layer was carried out using the well-known etchant $K_2Cr_2O_7:H_2SO_4:H_2O = 9:3:88$
1	75,4	74,1
2	77,3	75,1
3	69,4	68,8
4	73,4	70,6
5	71,6	69,5

Conclusions. Thus, the review and analysis of the influence of the surface on the reverse characteristics of p - n structures and the methods used to prevent this influence indicate the need to use methods of chemical surface treatment of semiconductor structures in the production of semiconductor devices and integrated circuits. The use of methods of chemical surface treatment of semiconductor device structures in serial production makes it possible to significantly improve the functional characteristics of semiconductor devices and integrated circuits and increase their reliability. An etchant has been developed for photolithography on a layer of chalcogenide glass based on chromium trioxide and sulfuric acid. It is shown that the use of an etchant in the production of semiconductor diodes made it possible to significantly increase the yield of suitable devices.

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