Electrochemical behavior of silicon in etching solutions of hydrofluoric and nitric acids

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Topicality. It is impossible to imagine the modern world without computers and telephones. Ability to store information or quickly find some queries - all these features provide different types of integrated circuits housed in our devices. An integrated circuit is a set of electronic circuits on a single small flat piece (chip) of a semiconductor material, which is usually silicon. Smaller transistors are integrated into a piece of silicon (there are 7-nm processor technologies for 2019). And transistors are not only getting smaller, but their number in one integrated circuit can reach billions and will only grow according to Moore's Law. Such continuous and rapid development of integrated circuits, reducing the development of structures leads us to the problem of correct identification of different areas of this technology, such as p-domains and n-domains that form p-n conductivity, and in modern more complex structures and p-n-p and n-p-n transitions, on the lowest layers of any modern transistor. N-type structures are doped with elements of the fifth group of the Mendeleev table (for example, phosphorus), so they have electronic conductivity. Structures of the same p - type are doped with elements of the third group, which provides their hole conductivity. It is necessary to more clearly identify the transition between p- and n-doped structures, which is a more difficult task due to the reduction of structures. Electrochemical study of the etching rate of structures with different conductivity in solutions of hydrofluoric and nitric acid will allow a clearer understanding of the nature of the process and will help identify the most favorable conditions for the process on more complex structures used today.

Connection of work with scientific programs, plans, topics. The dissertation work was made according to the plans of research works of LLC Reatiss.

Aim and objectives of the study: To scientifically substantiate and electrochemically investigate the effect of different light intensities on the etching rate of structures with electron and hole conductivity, which are silicon wafer, in hydrofluoric and nitric acid, and to provide the possibility of using the data on real chips transitions.

To achieve this goal the following tasks were solved:

- Assess the current state of the problem of digestion of silicon in hydrofluoric and nitric acid.
- Obtaining volt-ampere characteristics in a mixture of solutions of hydrofluoric and nitric acid with different ratios of components.
- Obtaining volt-ampere characteristics at different degrees of illumination of visible light and in the dark.
- Obtaining a volt-ampere characteristic in the reverse voltage supply mode to determine the effect of etching in solutions of a certain concentration.
- Construction of curves of dependence of speed of etching of elements with various conductivity on intensity of illumination, tension and current.

The **object** of study is a physical-chemical process on silicon wafer doped with elements of the third and fifth groups of the periodic table to create structures with different conductivities.

The **subject** of research - electrochemical process of development of zones with electronic and hole conductivity in solutions of hydrofluoric and nitric acid at different light intensities.

Research methods:

- Voltammetry (for scientific substantiation of the process)
- Using a light meter (to determine the intensity of light during digestion)
- Optical microscopy (to establish the etching zones on the sample and visually assess the intensity of the process)
- Electron microscopy (for more detailed determination of the structure of silicon during etching, and to determine the intensity of etching of small structures)

Scientific novelty of the obtained results:

- Establishing the dependence of the intensity of digestion on the degree of illumination.
- Establishing the dependence of the intensity of digestion on the concentration of herbal components.
- Setting the dependence on the voltage supply mode (direct and reversible).

Practical novelty of the obtained results:

- Determination of light intensity to ensure the greatest photo effect during digestion.
- Determining the optimal concentration of herbal solution to achieve the desired effect under different conditions.

Structure and scope of work. The master's thesis consists of an introduction, three sections, conclusions, a list of references. The total volume of 85 pages, including 4 tables, 31 figures, 3 annexes. The list of references includes 36 references.

The first section provides a literary overview of the state of development of basic information about silicon, what distribution it has as an element, what are its main properties, why it is important in today's world, where it is used, how it is mined, what has a crystalline structure. The following information provides the semiconductor properties of silicon and the energy zones of semiconductors, and the band gap of semiconductors is described in more detail. Then, information is given about the emitting impurities of semiconductors and doping technologies, which alloying elements are used, why they are added to the structure of silicon and what methods are now common. Next, we talk about the photosensitivity of semiconductors and their photoconductivity. Then the role of metallization in integrated circuits is considered, how the structure of making contacts to silicon is now developed, what they are and why it is important. Etching of silicon in solutions of nitric and hydrofluoric acid is also considered.

The second section describes creating a reliable contact between silicon and metal, various methods of achieving strong contact between metal and

semiconductor are considered. Various methods are described - chemical, electrochemical and mechanical, and drawings of electrodes and methods of their collection are given. The final version of the electrodes used in further studies is also presented. In addition, the section discusses the creation of an electrochemical cell for research. Namely, the construction materials of the electrode holder are considered, and a simplified diagram of the appearance of the structure is given.

The third section shows what reagents were used in the work. The results of verification of the created silicon-copper contact in hydrofluoric acid solution are also provided. The effect of light on the digestion process in different solutions of hydrofluoric and nitric acid is discussed, the behavior of silicon depending on the concentrations of the components of the etching solution is studied and the behavior of silicon in the etching solution depending on lighting is studied. In addition, the use of reverse voltage supply mode is described. Obtained SEM - images of the structure of silicon after etching in a mixture of nitric and hydrofluoric acids.

General conclusions

In the course of work, according to the set tasks, strong contact metal-semiconductor was created thanks to what it was possible to remove correct I – V characteristics in the further research in solutions of various structure. Contact was obtained mechanically and chemically by ultrasonic polishing and contact exchange in the process of applying a solution of copper sulfate with hydrofluoric acid. The resulting contact provided a resistance of the structure of 105 Ohm / mm. A study of the behavior of silicon in etching solutions containing hydrofluoric and nitric acid in different ratios and under different light intensities. It is established that in the range 0–0.5 V in solutions containing nitric acid there is a drop in current from what should be theoretical, due to the formation on the surface of a layer of SiO_x, which prevents the reaction at the rate to be observed. It was determined that despite the increase in the concentration of hydrofluoric acid, the solution under study did not show an increase in current values and is not promising in terms of digestion. This may be due to the lower electrical conductivity of the solution. Whereas in the case of using a solution with a higher content of nitric acid, the value of electrical conductivity is

higher, due to the fact that nitric acid is a strong acid and dissociates almost completely, in contrast to hydrofluoric acid with a degree of dissociation in dilute solutions of about 9%. In general, it can be noted that the effect of light intensity on the etching solutions is significant, so the use of herbalists should be in a controlled lighting mode, if necessary, the intensification process must use additional light sources. Examining the anodes with an optical microscope, it was also found that in a solution with a higher content of nitric acid, the dissolution process is more uniform, which is reflected by the change in the larger area of the electrode immersed in the solution. Cathodes used in solutions of different compositions and in different modes of lighting and voltage supply remained unchanged, so we can conclude that even a small current protects the plate from etching and is sufficient. The use of reverse voltage mode allows you to understand that the possible etching rate when using solutions having nitric acid are much higher than those obtained using the direct voltage mode. However, the value of the reverse voltage in this mode is quite significant. The voltage of 6.5 V is not enough to dissolve the SiO_x film on the surface, and the reaction occurs with the same intensity as in the direct mode. Whereas a voltage of 12.5 V is sufficient, and you can see that the reaction is more intense. The results are confirmed by studying the samples in an optical microscope.