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The Effect Of Annealing On The Crystal Structure Of The Silicon Surface Doped With Nickel Ions

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Abstract
The paper presents the results of a study of the distribution profiles of implanted nickel atoms in silicon as a function of the radiation dose and the annealing temperature using the Rutherford backscattering spectrometry technique (RBS). The effects of thermal annealing on the distribution of nickel and in particular oxygen are studied. It has been proven that under certain conditions of heat treatment and radiation doses, the so-called epitaxial silicides are formed on the surface of a single crystal, which can play the role of conductive layers or metallic coatings. The possibility of using the RBS technique for analyzing both the concentration distribution of doping impurities and the interaction of impurities is argued.
Keywords: impurities, profiles, influence, thermal annealing, implanted atoms, thin layers, depth, radiation doses, activation temperatures, ion implantation, epitaxial silicide.

Introduction

As is well known in silicon wafers doped with elements of transition groups, in particular nickel, a number of physical phenomena of scientific and practical interest were observed [1-5] .

Obtaining thin layers of implanted atoms in the near-surface region of silicon with given electro-physical properties and a certain thickness is important, in particular, for technologies for creating various sensors and high-sensitivity devices. The doping of elements of transition groups, in particular, nickel, is of utmost interest in this regard. From a technological point of view, it is impossible to create thin layers in silicon with a limited depth and sufficient concentration by using the diffusion method due to the large diffusion coefficient of these elements. Therefore, researchers resort to the method of ion doping. Since nickel impurities in silicon can be located both in the nodes and interstices of the crystal lattice and interact with lattice defects, their distribution during ion implantation and the mechanism of their activation are of particular interest. However, there are practically no works in the literature devoted to ion implantation and the investigation of the profile of the distribution of nickel in silicon over the depth.

Ion implantation, depending on the dose and energy of beam, leads to a significant change in the composition, structure and properties of semiconductor materials. In this regard, silicon single crystals doped with Ni ions with an energy of E = 20÷40 keV are of particular interest, since at low doses of radiation (D $<10^{15}$ cm^2) of high concentrations, which cannot be obtained by thermal diffusion; at high doses of ions, metal silicide are formed with new physical properties. However, such silicide are currently produced by the methods of MBE and TFE. The production of hidden conductive Ni silicide films by ion implantation and the study of their physicochemical and electro-physical properties are still in the development stage. In addition, the study of the structure of changes in very thin layers of the surface is associated with certain difficulties. First, the use of X-rays requires very complex methodological procedures. Since X-rays penetrate very deeply into the crystal, to obtain reliable results from the depth of interest to us, it is necessary to apply a layer of a film of a known and pure element to the sample surface.

On the other hand, it is very difficult to identify analytically the Regen reflexes associated precisely with the depth of interest. Therefore, without going into details of the type of structure and its parameters, we used the usual scanning electron microscope REM-200 to determine the structural changes.

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The Method Of Research

This paper presents a number of new original results on the study of the properties of the effect of annealing on the crystal structure of the surface of silicon doped with nickel ions. As is known among all transition elements in silicon, nickel has a sufficiently high solubility and a large diffusion coefficient. The choice of nickel as a compensating impurity is due to the fact that in a wide range of temperatures, the state of impurity atoms in the silicon lattice is fairly stable (100-450^{0}C) and, accordingly, the parameters of silicon doped by it. The technology of alloying silicon with nickel with specified parameters was developed and developed by us almost at an industrial level and does not require additional operations (mechanical, chemical, etc.), after diffusion doping. It is possible to dope Nickel-silicon plates of a sufficiently large area, more than 100 cm^2, which is very important for industrial and serial production of temperature converters with reproducible parameters.

Experimental studies have been carried out to see the concentration profiles of the distribution of Ni atoms implanted into silicon with an energy of E_0 = 40 keV with a variation of the radiation dose in the range of 10^{15} -10^{17} ion/cm^2. Silicon sample type- “silicon doped by boron” with a resistivity of ρ=10 Ω·cm was used as the source material. The studies were carried out using the methods of secondary ion mass spectrometry, back Rutherford scattering and electron Auger microscopy.

As objects of research, ingots of monocrystalline silicon of n and p - types doped with boron or phosphorus, respectively, with a concentration of from 10^{13} to 10^{18} cm^{-3}, grown by the Czochralski method and the technique where melting pot was not used most. Elements of the nickel transition group were chosen as impurities. The choice of these impurities was dictated by the fact that, on the one hand, their behavior and the properties of silicon doped with these impurities remained little studied, and on the other hand, the ability to identify new features associated with the presence of an unfilled 3d-orbital for these impurities. The ion implantation method was used.

The implantation of Ni ions into silicon was carried out on an ILU-3 unit with ion energy of 40 keV along the (111) crystallographic axis. The distribution profile of nickel in silicon was measured on a secondary-ion mass spectrometry unit LAS-2200 manufactured by Riber and on the apparatus described in (4). The specific resistance of the samples was measured by the four-probe method [9].

Figure 1 presents the analytical chamber. The complex consists of three growth chambers (1, 2 and 3). In chamber 1, epitaxial growth of silicon, cobalt di-silicide $CoSi_2$, and calcium fluoride CaF_2 was carried out. The other chamber was equipped with three sources of molecular beams: two electron-beam evaporators 2 and 3, serving as sources of silicon and cobalt, respectively, and an effusive source for precipitating CaF_2 4. A sample 5 mounted on a molybdenum holder was placed inside the chamber on the manipulator 6. The manipulator was equipped with a heater 7 and a thermocouple 8, allowing to control the temperature of the sample in the temperature range from room temperature to 1000^{0}C with an accuracy of + -0.5^{0}C. To ensure uniform heating of the sample and uniform deposition of evaporated materials, the holder with the sample was rotated using an electric motor.

The growth chamber was equipped with a fast electron diffractometer for reflection, allowing the structure of the crystal surface to be analyzed directly during growth. The diffractometer included an electron gun 9 and a luminescent screen 10. To control the composition of the atmosphere of the residual gases, a quadrupole gas analyzer 11 was used. In the analytical chamber 3, the grown epitaxial structures were investigated using Auger electron spectroscopy and secondary ion mass spectrometry. The vacuum in the system was maintained at 5x 5x10^{-9} Pa.

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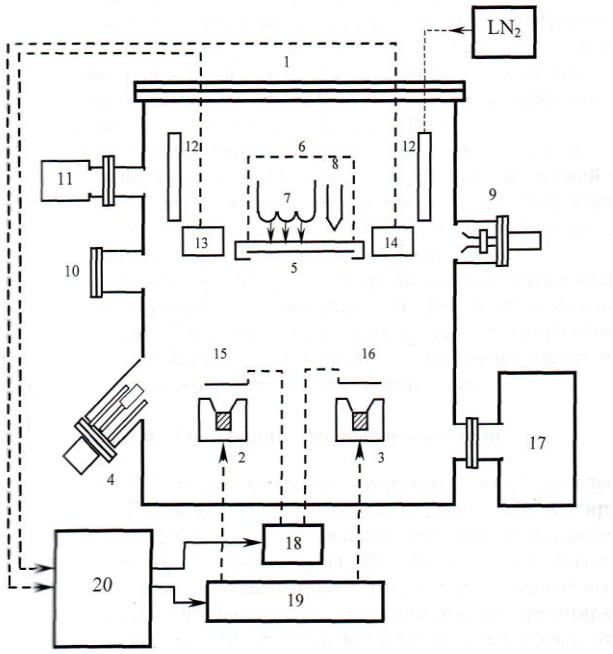

Figure1. Analytical growth chamber 1, 2, 3 –electron beam evaporators; 4-effusion source; 5 sample; 6-manupulator; 7-heater; 8-thermocouple "9-electron gun of a fast electron diffractometer; 10 luminescent screen; 11 quadrupole gas analyzer; 12 cryostat panel; 13.14-quartz deposition rate sensors; 15,16-flaps; 17-ion pump; 18-control valves with thermal; 19 power supplies for electron beam evaporators; 20 computer

Results Of Research

Figure 2 shows the backscattering spectra of He^+ ions from a Si (111) single crystal implanted with Ni^+ ions with a dose from 10^{15} to 10^{17} ion/cm^2.

It can be seen that the peak characteristic of Ni begins to appear on the spectrum at a dose of D≈10^{15} ion/cm^2. At the same time, the crystal structure of the surface and the electro physical properties of ion-doped layers were studied. The results of these experiments showed that at D≤10^{15} ion/cm^2, there is still no noticeable disordering of the surface layer, and the concentration of electroactive Ni atoms does not exceed $5\cdot10^{13}$ cm^{-3}.

Increasing the dose to 5.10^{15} ion/ cm^2 practically does not lead to an increase in the concentration of electroactive Ni atoms. In this case, the near-surface region is partially disordered, and the backscatter peak from Ni becomes clearer and more intense. At a dose of 10^{16} ion / cm^2, the amorphization of the surface layer occurs and significant growth of the Ni peak, and in some parts of the ion-doped layer cluster phases of Ni + Si begin to appear. These changes occur before the dose $(8\div10)\cdot10^{16}$ ion/cm^2. A further increase in the dose does not lead to a noticeable change in the relative intensity of the Si and Ni peaks. Therefore, the dose D≈10^{17} ion /cm^2 can be taken as a dose of saturation.

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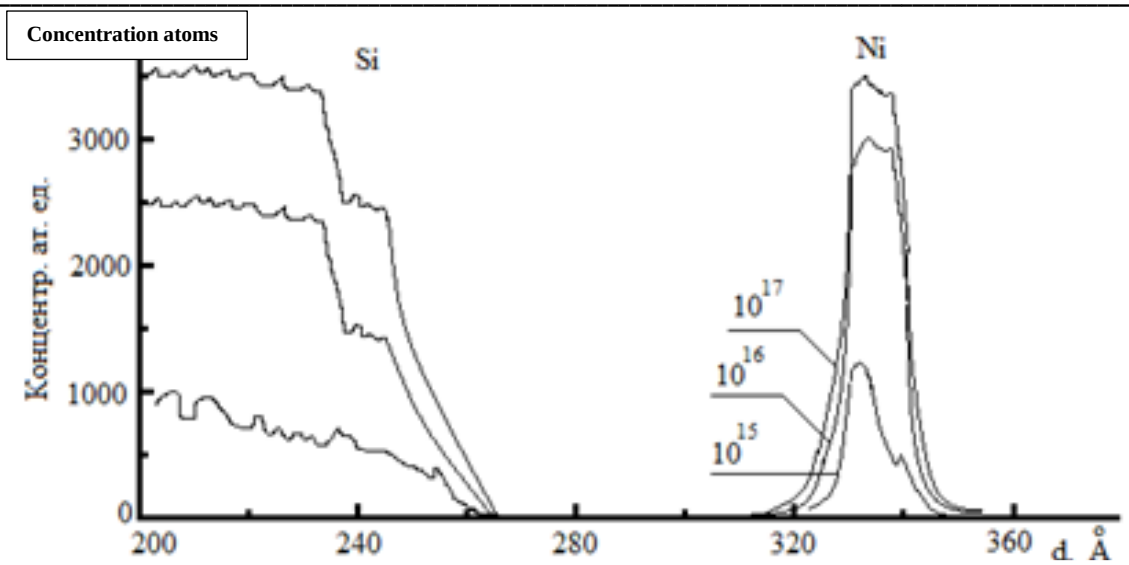

Figure2. RBS spectra of He^+ ions on a single crystal of Si doped with 40 keV Ni ions with doses of $10^{15} \div 10^{17}$ ion/cm^2

Increasing the dose to 5.10^{15} ion/ cm^2 practically does not lead to an increase in the concentration of electroactive Ni atoms. In this case, the near-surface region is partially disordered, and the backscatter peak from Ni becomes clearer and more intense. At a dose of 10^{16} ion / cm^2, the amorphization of the surface layer occurs and significant growth of the Ni peak, and in some parts of the ion-doped layer cluster phases of Ni + Si begin to appear. These changes occur before the dose $(8 \div 10) \cdot 10^{16}$ ion/cm^2. A further increase in the dose does not lead to a noticeable change in the relative intensity of the Si and Ni peaks. Therefore, the dose $D \approx 10^{17}$ ion /cm^2 can be taken as a dose of saturation.

For the purposeful modification of the properties of ion-doped materials in many cases it is required after implantation annealing. As is well known, even at low radiation doses, the concentration of electrically active metals in Si is ten times less than the concentration of the impurity introduced. After implantation annealing can increase the concentration of electroactive atoms. Such annealing is especially necessary for samples implanted with high-dose ions. Therefore, at high doses of irradiation, the surface region is completely depreciated and homogeneous metal compounds are not formed.

Figure 3. shows the distribution profiles of Ni in Si for two doses of radiation. Profiles were obtained by VIMS [10].

The results of the study showed that when the samples were heated

As can be seen from the figure, the maximum distribution in depth is not very different from Fe in Si and is 335 Å.

Experiments have shown that, in the case of *Ni*, at high doses of irradiation of 10^{17} ions / cm^2, an epitaxial film of *Ni* silicide is formed during annealing at a temperature of $850^0 \div 900^0$C.

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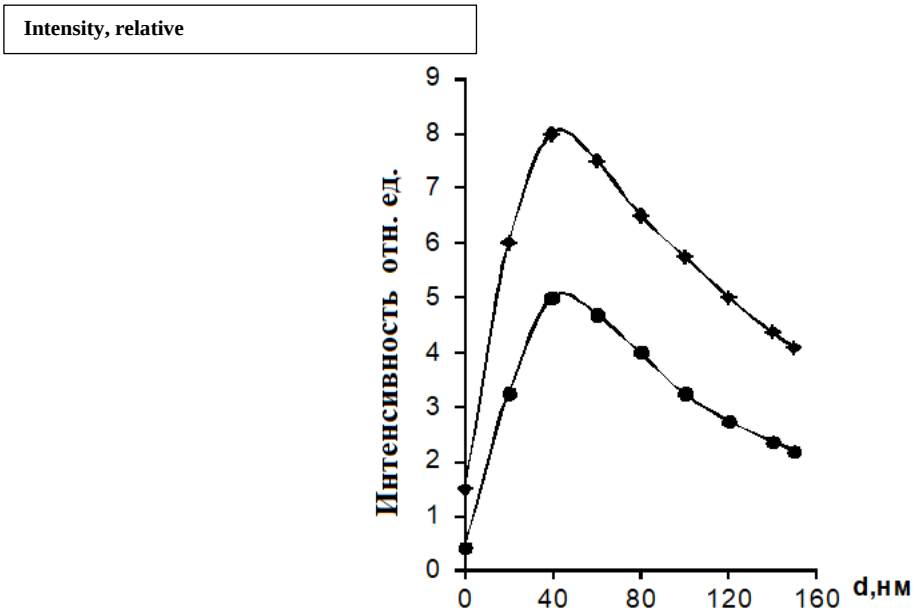

Figure3. The distribution profiles of doped Ni atoms in Si doped with a dose of $10^{16} \div 10^{17}$ ion/t/cm^{2}obtained by the VIMS method.

to T≥650°C, doped with a dose of D≤10^{15} ion / cm^2, a sharp increase in the concentration of active atoms in the surface layer was observed. By choosing the temperature and duration of annealing, it is possible to achieve a uniform distribution of impurities in the crystal volume to a certain depth.

Figure 4 presents electron microscopic images of the Si surface before ion doping, after doping, and after treatment at different temperatures.

As can be seen from the figures, in the case of pure silicon the surface is smooth and uniform, since the samples were ground and polished (Fig. 4a). After ion doping, depending on the radiation dose and the type of ions, the electron microscopic picture changes significantly (Figure 4b).

Discussion Of Research

Temperature annealing strongly affects the state of the implanted samples. At low doses of radiation and thermal annealing up to 800^{0}C in the case of Ni, no significant changes occur. At a temperature of 800^{0}C C and higher, an electron-microscopic image of the surface shows some edged regions characteristic of single crystals. The elemental analysis of these "edging" by the method of electronic Auger spectroscopy showed that they consist mainly of Si and Ni atoms and partially oxygen. The amplitude distribution of Auger peaks of silicon and nickel suggests that these regions are silicides of the $NiSi_2$ type.

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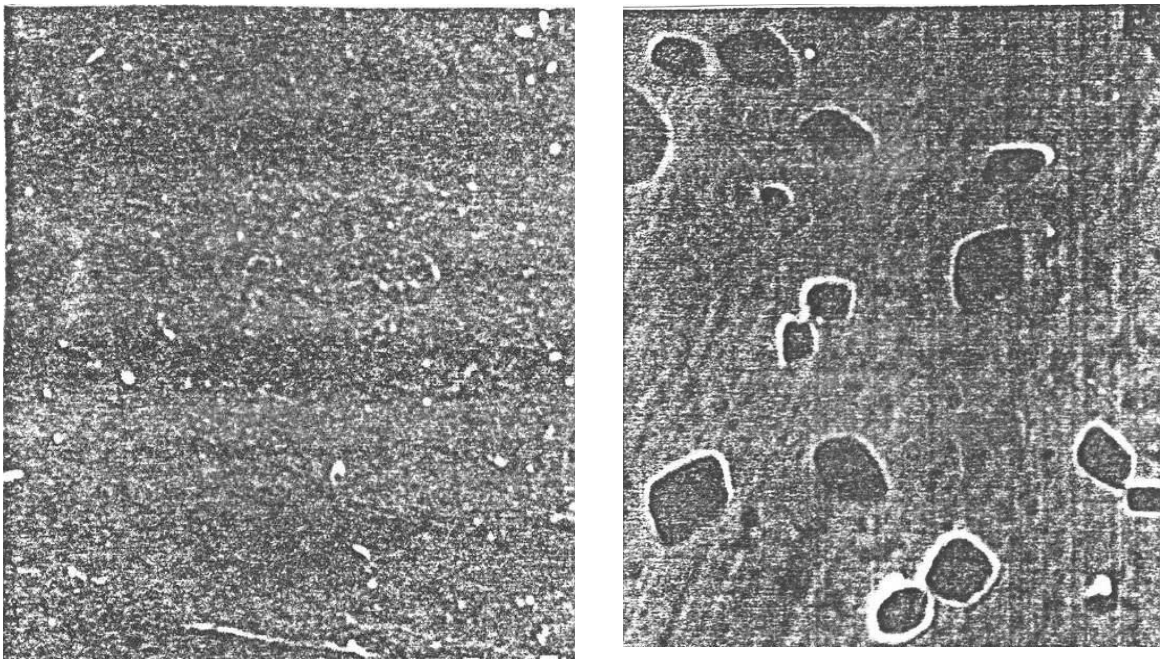

(a) (б)

Figure4. Electron microscopic pictures of the surface of pure silicon (a) and the surface irradiated with Ni^+ ions with a dose of 10^{16} ions / cm^2 after annealing at a temperature of 850^0C (b).

In the process of heat treatment at T ≈ 750 ° C, the concentration of electroactive Ni atoms increases to $(2\div5)\bullet10^{15}$ cm^{-3}, which is 4–5 times more electroactive nickel atoms than with diffusion doping. A further increase in temperature adversely affected the concentration of electroactive nickel atoms. Starting from a temperature of 1000 ° C, it was comparable to the concentration of electroactive atoms, which is obtained by diffusion doping. For samples of silicon implanted with Ni, a noticeable increase in the concentration of electroactive atoms occurred at annealing temperatures above 600 ° C. With an increase in the annealing temperature ($600–1250^0C$), the concentration of electrically active Ni atoms increased monotonically within $10^{15}\div6\cdot10^{17}$ cm-3, and, moreover, the highest concentration of electroactive atoms, achieved by diffusion doping. The study of the distribution profiles has shown that for impurity atoms, activation occurs in a thin surface layer. Moreover, the distribution of the concentration of electroactive atoms in a thin layer is not Gaussian, but monotonously decreasing deep into the crystal [6-8] .

Temperature annealing strongly affects the state of the implanted samples. At small irradiation doses and thermal annealing in the case of Ni up to 800^0C, there are no significant changes in the electronic picture. At a temperature of 800^0 ° C and above, some edged regions characteristic of single crystals are observed in the picture. Further increase ща annealing temperature up to 1100^0 ° C leads to a significant change in the surface state. The electron picture goes from the "epitaxial" to the amorphous surface. These changes relate not only to the structure, but also to the composition of the surface. The peaks of the alloying elements decrease markedly in amplitude, which testifies to the decomposition of the silicide layers and the partial evaporation of the alloying impurities. The results of these experiments prove that complex surface processes depend on temperature and dose of dopants [11-14]

Conclusion

Analysis of the data evidences that during the process of ion implantation nickel distribution maximums as in the surface so across the depth changes in dependence to the concentration and measurement of oxygen. One can assume that the nickel ions are largely displaced by oxygen.

The above assumption is well grounded if oxygen in silicon matrix is not in chemically bound state. The process of ion implantation does not only influence oxygen state but also influences the state of defects. The generated defects as on the surface so in the bulk of silicon open free radicals, oxygen in particular.
The experimental results well correspond to similar results obtained during secondary ion-mass spectrometry (SIMS). One can note the possibility of using Res Rutherford backscattering spectrometry technique (RBS) for analysis of concentration distribution of dopants as well as interaction of impurities.

Analysis of the results of research shows that ion doping of silicon with transition metals has several advantages compared with diffusion doping:

* Activation of impurities directly in the process of implantation or during low-temperature annealing;
* a sharp increase in the concentration of electro-active atoms in the thin surface layer;
* getting sharp n-p transitions;
* obtaining thermally stable alloy layers.

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