The Effect of Annealing On The Crystal Structure of the Surface of Silicon Doped With Iron And Cobalt Ions

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Abstract: The paper reports results of the study of the distribution profiles of implanted iron and cobalt atoms in silicon as a function of the radiation dose and annealing temperature that was performed by applying the Rutherford backscattering spectroscopy (RBS). The effects of thermal annealing on the distribution of iron, cobalt, and in particular oxygen were studied. The authors strongly suggest that under certain heat treatment conditions and by applying specific radiation doses, the so-called epitaxial silicides will build on the surface of a single crystal, which can play the role of conducting or metal layers. One could consider theRBS method for analysis of both the topological distribution of dopants and the interaction of impurities.

Keywords: impurities, profiles, influence, thermal annealing, implanted atoms, thin layers, depth, radiation doses, structure, film

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1. Introduction

The current research in the field of two-dimensional and three-dimensional development of integrated circuits (ICs), aimed at increasing the speed of semiconductor devices while maintaining the size of active elements, improving the characteristics of contacts and local interconnects represents a significant task in silicon technology with the aim to achieve progress in microelectronics.

Silicides of transition metals that have high electrical conductivity and thermal stability, good adhesion to silicon and silicon oxide, resistant to corrosion and decomposition, and the ability to synthesize these compounds at relatively low temperatures are well suited for these goals. The scientific relevance of the problem of studying the process of defect formation of hidden layers of transition metals obtained by ion doping in silicon substrates is determined by the need for a deeper understanding of the basic processes occurring during the formation of these structures. From a practical point of view, these studies are relevant, first of all, in connection with the possibility of forming Si/CoSi2/Si, heterostructures suitable for use as local contacts and interconnects in three-dimensional metallization systems, as well as modern high-speed devices, such as, for example, transistors with a "permeable" or metal base.

The possibility of a detailed study of the Si-CoSi2system can serve as a model for studying the defect formation of other transition metals in silicon, as well as for studying the metal / silicon silicide phase boundary, in connection with its rather simple way to obtain and study it.

The fundamental principles of the formation of hidden thin conductive layers, promising for new generation microelectronic devices, are the laws of phase and defect formation during high-dose implantation. Despite the large number of studies on the structure and properties of ion-implanted layers, the mechanism of defect formation has not been sufficiently studied. In this regard, further study of the fundamental principles of solid-state ion doping of the epitaxial Fe and Co layers in silicon is very relevant. To obtain the most reliable results, it is necessary to use a set of complementary methods providing an unambiguous interpretation of experimental data.

Technique of investigation

Silicon implantation with cobalt and iron ions is used to create magnetic nanoclusters and metal silicides [1–4]. Composite materials based on magnetic nanoclusters are used in the development of new information storage

elements [5]. Metal silicides are also used as materials for contacts and interconnections of elements of integrated circuits.

Along with implantation of metal ions, which leads to the creation of metal silicides, implantation with small fluences of ions is also carried out in order to study the processes that occur during the early stage of mesotaxy. Moreover, due to the fact that the processes of atomic defect coalescence and spin percolation have not yet occurred [1], it becomes possible to study structural changes in silicon, for example, such as the formation of CoSi2 precipitates and annealing of radiation defects.

Ion implantation, depending on the dose and radiation energy, leads to a significant change in the composition, structure and properties of semiconductor materials. In this regard, silicon single crystals doped with Fe and Co ions with an energy of E = 20-50 keV are of particular interest, since at low radiation doses (D $\square$ 1015 cm-2) they can create electroactive centers with a high concentration that cannot be obtained by thermal diffusion ; at high doses of ions, metal silicides with new physical properties are formed. In particular, CoSi2 silicide films have a cubic lattice and have very small resistivities ($\square$ $\square$ 30-50 µOhm$\square$ cm), which is why they are very promising for the creation of microwave transistors with a metal and permeable base. However, such films are currently produced by MBE and TFE. A detailed description of the MBE installation and cleaning methods is contained in [6]. The preparation of latent conductive films of Fe and Co silicides by ion implantation and the study of their physicochemical, electrophysical, and structural properties are still under development.

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 silicon surface doped with iron and cobalt ions. The choice of iron and cobalt as a compensating impurity is due to the fact that in a wide temperature range, the state of the impurity atoms in the silicon lattice is quite stable (100-4500C) and, accordingly, the parameters of silicon doped with it. The technology of alloying silicon iron and cobalt with the specified parameters was developed and mastered by us practically at the industrial level and does not require additional operations (mechanical, chemical, etc.) after diffusion alloying. It is possible to alloy iron and cobalt onto silicon wafers of a sufficiently large area, more than 100 cm2, which is very important for industrial and serial production of temperature converters with reproducible parameters.

Experimental studies of the concentration profiles of the distribution of iron and cobalt atoms implanted in silicon with an energy of E0 = 40 keV were carried out with a dose variation in the range of 1015$\square$ 1017 ion/cm2. Boron-doped silicon grade silicon with a specific resistance of $\square$ =10 Ohm$\square$ cm was used as the starting material. The studies were carried out using the methods of secondary ion mass spectrometry, fast electron diffraction by reflection, Rutherford backscattering, SIMS and Auger electron microscopy.

As objects of research, we used ingots of p and p monocrystalline silicon doped with boron or phosphorus, respectively, with a concentration of 1013 to 1018 cm-3, grown by the Czochralski method and crucible-free zone melting. The elements of the transition group of iron and cobalt were selected as impurities. The choice of these impurities was dictated by the fact that, on the one hand, their behavior and properties of silicon doped with these impurities remained poorly studied, and on the other hand, the possibilities of revealing new features associated with the presence of an unfilled 3d shell in these impurities. The method of ion implantation was used. The implantation of iron and cobalt ions into silicon was carried out on an ILU-3 device at an ion energy of 40 keV along the crystallographic axis (100,111) at a constant ion current density of 10 µA/cm2. The distribution profile of iron and cobalt in silicon was measured on a Riber LAS-2200 secondary-ion mass spectrometric setup and on the setup described in [7]. The resistivity of the samples was measured by four probe methods.

Figure 1 shows the analytical chamber. The complex includes three growth chambers (1, 2 and 3). In chamber 1, epitaxial growth of silicon, cobalt silicide CoSi2, and calcium fluoride CaF2 was carried out. Another 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 the deposition of CaF2 4. 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 you to adjust the temperature of the sample in the temperature range from room temperature to 10000C with an accuracy of ±0.50C. To ensure uniform heating of the sample and uniform deposition of evaporated materials, rotation of the holder with the sample was provided using an electric motor.

The growth chamber was equipped with diffraction of fast electrons by reflection, which made it possible to analyze the structure of the crystal surface directly during the growth process. The diffractometer included an electron gun 9 and a luminescent screen 10.

A quadrupole gas analyzer 11 was used to control the composition of the residual gas atmosphere. In the analytical chamber 3, the grown epitaxial structures were studied by Auger electron spectroscopy, fast electron

diffraction by reflection, Rutherford backscattering, and secondary ion mass spectrometry. The vacuum in the system was maintained at $5 \times 10\text{-}9$ Pa.
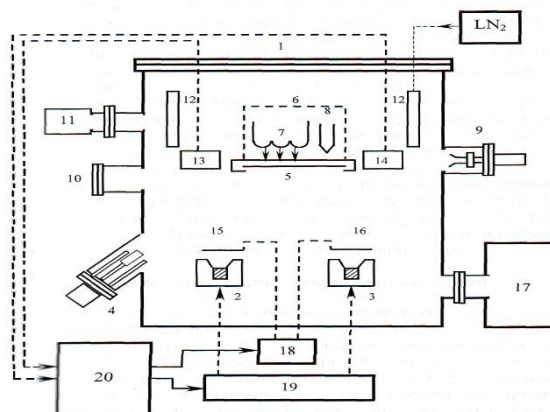

Fig. 1. Analytical growth chamber: 1, 2, 3 — electron beam evaporators; 4-effusion source; 5-sample; 6-manupulator; 7-heater; 8-thermocouple "9-electron gun of a fast electron diffractometer; 10-fluorescent screen; 11-quadrupole gas analyzer; 12-cryopanel; 13.14-quartz deposition rate sensors; 15.16-flaps; 17-ion pump; 18-control dampers with thermal actuator; 19-power supplies of electron beam evaporators, 20-computers

Results and its discussion

Figure 2 shows the backscattering spectra of He+ 40 keV ions of different energies from a Si (111) single crystal implanted with Fe+ ions with a dose of 1015 to 1017 ion/cm2. It is seen that the peak characteristic of Fe begins to appear in the spectrum at a dose of D □ 1015 ion/cm2. At the same time, the crystal structure of the surface and the electrophysical properties of ion-doped layers were investigated.
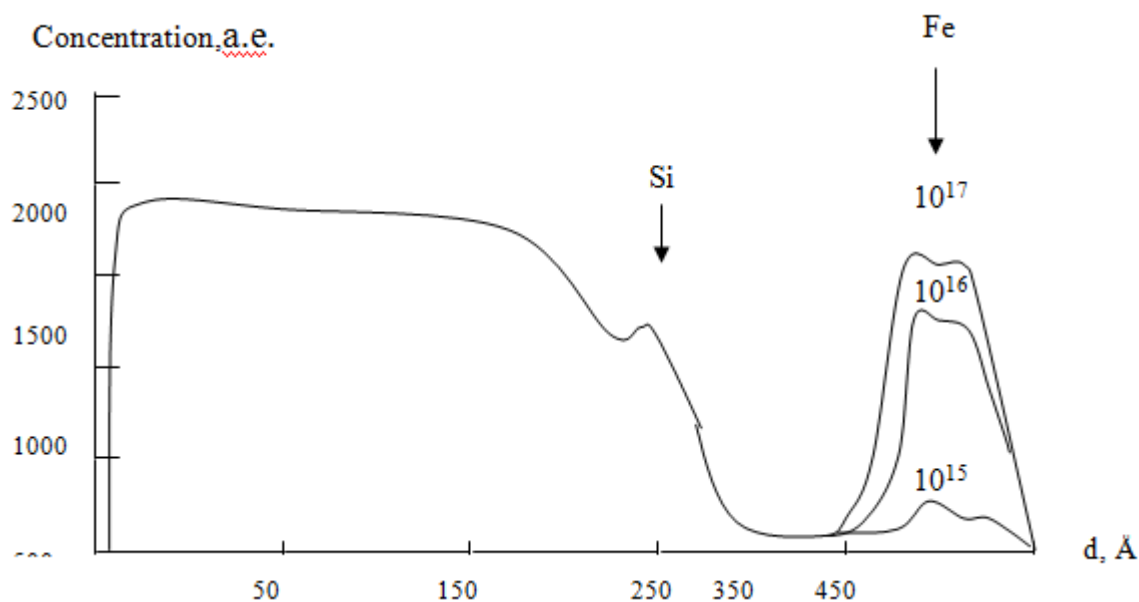

Fig. 2. The POP spectra of He+ ions on a Si single crystal doped with Fe ions with an energy of 40 keV with radiation doses of 1015-1017 ion/cm2.

The results of these experiments showed that at D □ 1015 ion/cm2, there is as yet no noticeable disordering of the surface layers, and the concentration of electroactive Fe atoms is □ 5□ 1013 cm3. An increase in the dose to 5□ 1015ion/cm2 practically does not lead to an increase in the concentration of electroactive Fe atoms. In this case, the surface region is partially disordered, and the backscattering peak from Fe becomes sharper and more intense. At an irradiation dose of D □ 1016 ion/cm2, an amorphization of the surface layer and a substantial increase in the Fe peak occur, and Fe+ Si cluster phases also begin to appear in separate sections of the ion-doped layer. These changes occurred up to a dose of (8□ 10) □ 1016 ion/cm2. A further increase in the dose does not lead to a noticeable change in the relative intensity of the peaks of Si and Fe.

Of interest is the nature of the distribution of metal atoms in depth in Si, depending on the radiation dose. At medium doses (D $\square$ 1015- 1016 cm-2), the distribution profile has a very complex shape with several maxima.

The bulk of the implanted atoms are located in the surface region to a depth of d $\square$ 300 Å. At d $\square$ 400 Å, the concentration of iron decreases sharply with increasing d, and at a depth of 800–850 Å its value does not exceed 1-2 at%.

At high radiation doses (D > 1017 ion/cm2), a single maximum appears in the place of several maxima, and the iron concentration on the surface decreases sharply. The latter is explained by an increase in the rate of atomization of surface atoms. At D $\square$ 1017 ion/cm2, the Fe distribution has a Gaussian shape, the maximum is formed at d $\square$ 400-450 Å at surface layers.

The maximum iron content is $\square$ 30-35 a.e. %. A further increase in the ion dose leads to a shift of the maximum toward the surface and its broadening. This is due to both intense spraying of the surface layers and an increase in the density of the surface layers due to the formation of metal silicides [8-10]. The concentration of iron in the region of a broad maximum was 35–40 at%. In these layers, FeSi2 type compounds predominantly formed.

A different picture is observed in Fig. 3. The backscattering spectra of He+ 40 keV ion energies from a Si (111) single crystal implanted with Co+ ions with a dose of 1015-1017 ion/cm2 are presented.
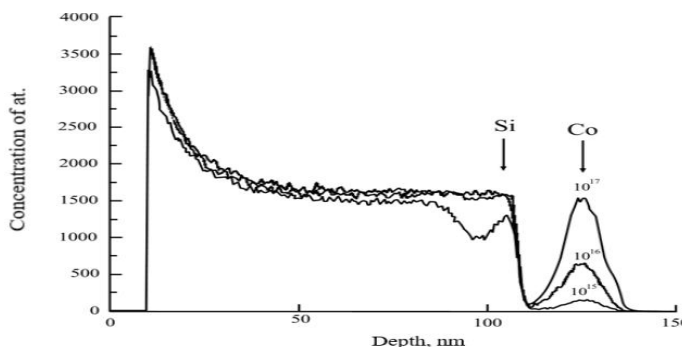

Fig. 3. The POP spectra of He+ ions on a Si single crystal doped with Co ions with an energy of 40 keV with radiation doses of 1015-1017 ion/cm2.

Investigations were made of samples of silicon implanted with cobalt ions under various conditions (various doses), both immediately after implantation and after heat treatment. The experimental results, in the form of RBS spectra, are presented below. It can be seen that the peak characteristic of Co begins to appear at a dose of дозе D $\square$ 1015 ion/cm2, that cobalt is buried, the distribution maximum is at a distance of about 120 nm, which is not in bad agreement with the data obtained using SIMS. It was found that with increasing dose, the peak corresponding to the scattering of helium ions by cobalt increases, as well as a change in the shape of the spectrum (decrease in the scattering yield on the matrix) at the depth of the impurity. After thermal annealing at 10000 for 30 minutes. the distribution profile of cobalt is noticeably narrowed and the concentration at the distribution center increases. In this case, the cobalt concentration in the region of a broad maximum was 30-35 at%. In these layers, mainly CoSi2 type compounds formed. At the same time, a sharp decrease in the spectrum for silicon indicates a noticeable annealing of radiation defects in silicon. In all the spectra, after annealing, small peaks are visible in the silicon spectrum — this is oxygen. Apparently, during the heat treatment there was not a good vacuum, as a result of which silicon oxide SiO2 appeared on the samples.

Figure 4 shows the distribution profiles for a current of 10 µA, which, as we saw from the experimental spectra, is sufficient for the self-annealing process. The profiles for the same sample are also shown here, but after annealing with a temperature of 1000°C. it is very clearly seen that a layer of cobalt disilicide was formed.
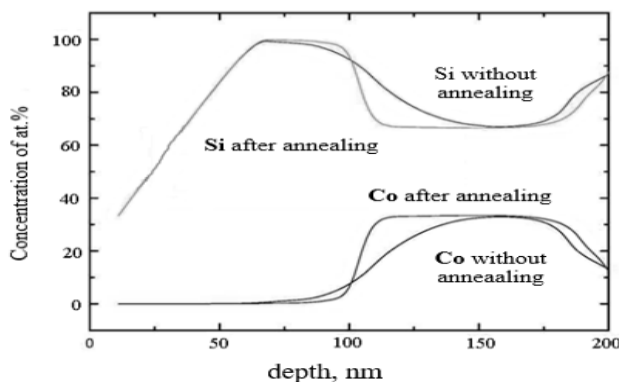
Fig. 4. Co distribution profiles in Si with an energy of 40 keV and a dose of 1017 ion/cm2before and after annealing.

At the same time, the crystal structure of the surface and the electrophysical properties of ion-doped layers were investigated. Fig. 5. Electronic pictures are presented obtained from the Si surface to ion doping, after ion doping, and also after heat treatment at different temperatures.
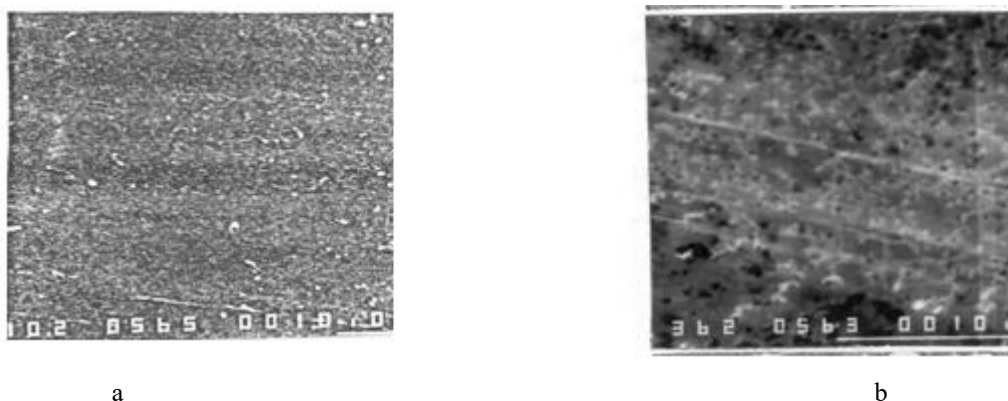

a

b

Fig. 5. Electron - microscopic pictures of the surface of pure silicon (a) and the surface of ion-doped, Fe+ (b).

As can be seen from the figure, in the case of pure silicon, the electronic picture has a continuous and uniform appearance, since the samples were ground and polished (Fig. 5.a.). After ion doping, depending on the radiation dose and type of ions, the electronic picture changes significantly. The view of the picture from a smooth surface goes over to a rough or dull picture (Fig. 5.b.).

Temperature annealing strongly affects the state of implanted samples. At low values of the radiation dose and thermal annealing in the case of Fe up to 8000C, no significant changes in the electronic picture occur. At a temperature of 8000C and higher, some edged regions characteristic of single crystals are observed in the picture. An elemental analysis of these fringes by Auger electron spectroscopy showed that they consist mainly of Si and Fe atoms and partly oxygen. The amplitude state of the Auger Auger peaks of silicon and iron suggests that these regions are FeSi2 type silicides.

Similar patterns are observed in the case of Fe at an irradiation dose of 1016ion/cm2 with Fe ions. The edged regions appear at a temperature of 8000Cand higher (Fig. 6.a). In the case of Co, at a radiation dose of 1016 ion / cm2, staining is detected at a temperature above 9500C (Fig. 6b).
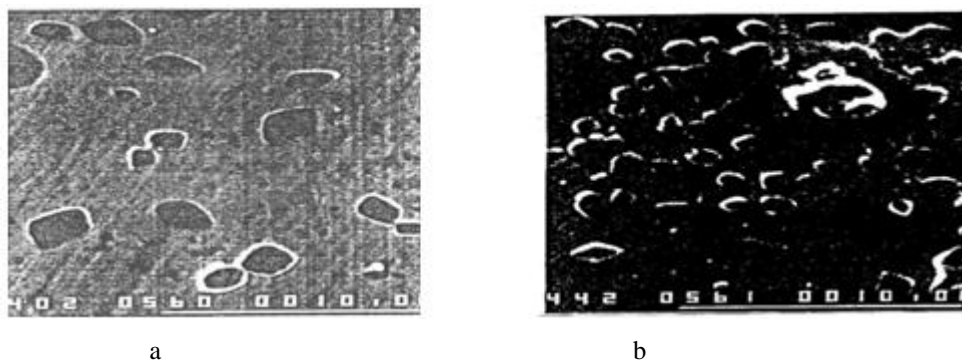
a	b

Fig. 6. Electron microscopic images of the surface irradiated with Fe+ ions with a dose of 1016 ion/cm2after thermal annealing at a temperature of 8000C (a), for cobalt at a temperature of 9500C (b).

The results of these experiments prove that complex surface processes depend on the type of temperature and the dose of dopants [11-12]. Completely different results are obtained when doping silicon samples with large doses. Fig. 7. Electronic images of the surface of silicon doped with Fe ions with a dose of 1017ion/cm2 after annealing at a temperature of 8000C are presented. As can be seen from the figure, the edged regions seemed to merge, forming a continuous layer in the form of a single crystal with a large number of defects.
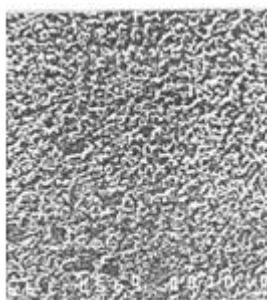

Fig. 7. Electron - microscopic pictures of the surface doped with Fe + ions with a radiation dose of 1017ion/cm2after thermal annealing at 8000C.

The same results were obtained for silicon doped with Co ions with an irradiation dose of 1017ат/cm2, the annealing temperature of the formation of "epitaxial" silicide layers 9000-10000C(Fig. 8).

Fig. 8 Micrograph of the surface of silicon doped with Co + ions with a dose of 1017 ion / cm2 after thermal annealing at 9500C.

A further increase in the annealing temperature to 11000C leads to a significant change in the state of the surface. The electronic picture passes from the "epitaxial" to the amorphous surface (Fig. 9).
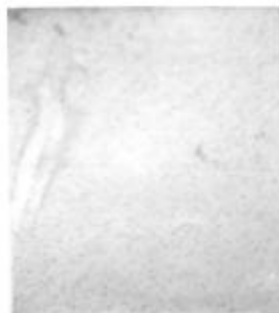
Fig. 9. A micrograph of the surface of silicon doped with Co+ ions with a dose of 1017 ion/cm2 after thermal annealing at a temperature of 11000C.

These changes relate not only to the structure, but also to the composition of the surface [13]. The peaks of the alloying elements decrease markedly in amplitude, which indicates the decomposition of silicide layers and the partial evaporation of alloying impurities.

Conclusion

Studies have shown that ion doping strongly affects the surface structure depending on the dose and ion energy. After alloying, the surface becomes rough. This structure is strongly affected by temperature annealing. At temperatures above 8000C, some edged regions characteristic of a single crystalsis formed on the surface.

Structural changes depending on radiation dose and annealing temperature. For example, for iron with an irradiation dose of 1017 ion/cm2, after annealing at a temperature of 8000 C, a single-crystal type layer with a large number of defects is formed on the surface. A further increase in temperature to 11000C leads to the formation of an amorphous layer on the surface.

The analysis of the effect of the accumulated dose and high-temperature annealing on defect formation in ion-implanted layers is carried out. The latent cobalt disilicide layers in silicon were studied, obtained by ion-beam synthesis under various implantation and annealing modes.

It is shown that a change in the dose taken changes the depth and thickness of the cobalt disilicide layers. By varying the dose, one can change the depth and thickness of the CoSi2. layer.

It was shown that, under the influence of high-temperature annealing, there is a significant decrease in the yield of alpha particles scattered on silicon and cobalt in the RBS channeling spectra, which indicates that most radiation defects are eliminated and the crystallinity of the structure of the implanted layer improves.

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