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Effect of Annealing on the Crystal Structure of the Surface of Silicon Doped with Ni, Fe, and Co Ions

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Abstract—Ion-implanted Ni, Fe, and Co layers in silicon are experimentally investigated. It is established that at certain heat-treatment conditions and irradiation doses so-called epitaxial silicides form on the single-crystal surface, which can work as conductive layers or metal coatings.

Keywords: ion implantation, epitaxial silicides, molecular beam epitaxy, secondary-ion mass spectrometry, Auger electron spectroscopy

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INTRODUCTION

Ion implantation is one of the most effective ways of affecting the state and properties of solids. In contrast to the doping of silicon with foreign atoms with moderate (tens and hundreds of keV) energies in low (up to 10^{13} cm^{-2}) doses, which allows the control of some properties of silicon, the implantation of high-energy (up to 50 keV) ions in high (10^{15}–10^{17} cm^{-2}) doses makes it possible to form surface layers with impurity-atom concentrations similar to the Si-atom concentration or even higher. In other words, low-energy ion implantation can be a powerful tool for synthesizing novel thin-film materials with modified properties. However, to successfully use this technique, it is necessary to understand various processes that occur in a solid during ion implantation at the electronic and atomic levels.

The implantation of ions with different energies in different doses can significantly modify the composition, structure, and properties of semiconductors. In this respect, silicon single crystals doped with Ni, Fe, and Co ions with energies of $E = 20$–50 keV are of special interest, since, even at low irradiation doses ($D \leq 10^{15}$ cm^{-2}), they can form electrically active centers in high concentrations, which cannot be obtained by thermal diffusion; at high ion doses, metal silicides with new physical properties are formed [1, 2]. In particular, $CoSi_2$ and $NiSi_2$ silicide films have the cubic lattice and very low resistivity ($\rho = 30$–50 μΩ cm), which make them promising for application in microwave metal- and permeable-base transistors. However, such films are currently synthesized by molecular beam and solid-state epitaxy. The fabrication of buried conductive Ni, Fe, and Co silicide films by ion implantation and investigation of their physicochemical and electrical properties are still in an early stage of development.

The urgency of this study is associated with some unsolved problems concerning both the epitaxial-growth technique and understanding the physical aspects of the growth and effect of the structure on the physical properties of silicide films, which offer new opportunities for the creation of devices with unique capabilities.

The further development of microelectronics requires new extraordinary materials, which would ensure enhanced chip complexity and the improvement of functional electronic devices. In terms of this, silicides have the greatest potential for application.

The aim of this study is to investigate the effect of annealing on the crystal structure of the surface of silicon doped with Ni, Fe, and Co ions.

EXPERIMENTAL

We investigated concentration profiles for Ni, Fe, and Co atoms with an energy of $E_0 = 40$ keV implanted in silicon at irradiation doses of 10^{15}–10^{17} ion/cm^2. The initial material was KDB silicon with a resistivity of $\rho = 10$ Ω cm. The experimental techniques used were secondary-ion mass spectrometry, Rutherford backscattering, and electron microscopy.

The objects of study were single-crystal *n*- and *p*-Si ingots doped with boron and phosphorous, respectively, in concentrations from 10^{13} to 10^{18} cm^{-3}. The ingots were grown by the Czochralski technique and floating zone melting. Transition elements, including manganese, iron, cobalt, and nickel, were used as dopants. These impurities were chosen, first of all, o account of the fact that their behavior, as well as the

properties of silicon doped with them, remains understudied. On the other hand, the unfilled 3*d* shell of these impurities can cause as yet unrevealed features in their characteristics. We used the ion implantation technique. Ni, Fe, and Co ions with an energy of 40 eV along the ⟨111⟩ crystallographic axis were implanted in silicon using an ILU-3 installation. The concentration profiles of nickel, iron, and cobalt in silicon were obtained using a RIBER LAS-2200 secondary-ion mass spectrometer and by means of the installation described in [4]. The resistivity of the samples was measured using the four-probe technique.

The complex shown in Fig. 1 includes three growth chambers *1*, *2*, and *3*. Silicon,-cobalt disilicide $CoSi_2$, and calcium fluoride CaF_2 were grown in chamber *1*. The other chamber was equipped with three molecular beam sources, including two electron-beam evaporators *2* and *3* working as silicon and cobalt sources, respectively, and an effusion source *4* for CaF_2 deposition. A molybdenum holder with the sample *5* was placed into a chamber onto a manipulator *6*. The manipulator was equipped with a heater *7* and thermocouple *8* for changing the sample temperature from room to 1000°C accurate to ±0.5°C. To ensure uniform sample heating and deposition of the evaporated materials, the holder was rotated using an electric motor.

The growth chamber contained a high-energy electron backscattered diffractometer, which allows the crystal structure of the surface to be analyzed during growth. The diffractometer comprised an electron gun *9* and a luminescent screen *10*. The residual gas composition was controlled using a quadrupole gas analyzer *11*. The grown epitaxial structures were investigated in the analytical chamber *3* using Auger electron spectroscopy, secondary-ion mass spectrometry, and X-ray photoelectron spectroscopy. The residual pressure in the system was 5×10^{-9} Pa.

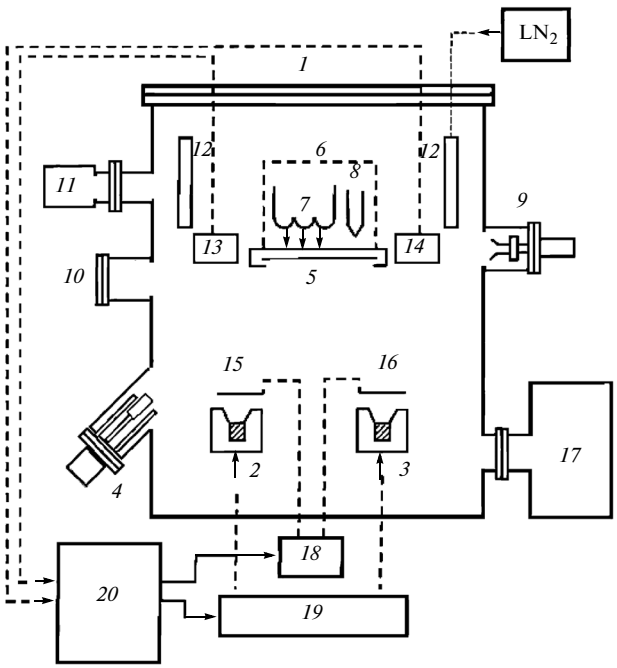

Fig. 1. Analytical growth chamber: electron-beam evaporators *1, 2*, and *3*; effusion source *4*; sample *5*; manipulator *6*; heater *7*; thermocouple *8*; electron gun of a high-energy electron diffractometer *9*; luminescent screen *10*; quadrupole gas analyzer *11*; cryopanel *12*; quartz deposition-rate sensors *13* and *14*; shutters *15* and *16*; ion pump *17*; shutter control with a thermal drive *18*; electron-beam evaporator power sources *19*; and computer *20*.

RESULTS AND DISCUSSION

Investigation of the structural variations in ultrathin surface layers poses certain difficulties. First, the use of X-rays is associated with very complex procedures. Since X-rays penetrate very deep into a crystal, the sample surface should be coated with a film of some well-studied pure element to obtain reliable results at a specified depth.

On the other hand, it is hard to analytically distinguish X-ray reflections related to specified depths. Therefore, without going into details of the structure and its parameters, we investigated variations in structure using a conventional SEM-200 scanning electron microscope.

Figure 2 shows electron microscopy images of the Si surface before and after ion doping and after heat treatment at different temperatures. It can be seen that pure silicon has a smooth uniform surface, since the samples were polished (Fig. 2a). After ion doping, the electron microscopy images significantly change, depending on the irradiation dose and ion type. The surface becomes rough or opaque (Fig. 2b).

High-temperature annealing greatly affects the implanted samples. At low irradiation doses and annealing at temperatures of up to 800°C, no significant variations are observed in the samples doped with Fe. The electron-microscopy images of the samples annealed at a temperature of 800°C and more contain bordered areas typical of single crystals. Elemental Auger electron spectroscopy analysis of the borders showed that they consist mainly of Si and Fe atoms and, partially, of oxygen. The amplitude distribution of silicon and iron Auger peaks allows us to conclude that these areas are $FeSi_2$-type silicides.

Similar images were obtained for the other dopants. Under irradiation with Ni ions at a dose of 10^{16} ion/cm^2, bordered areas arise at a temperature of 850°C and more (Fig. 3a). Under irradiation with Co at a dose of 10^{16} ion/cm^2, these areas arise at temperatures above 950°C (Fig. 3b).

Our investigations showed that upon heating the samples doped at radiation doses of $D \le 10^{15}$ ion/cm^2 at temperatures of $T \ge 650$°C, the concentration of active atoms in the surface layer sharply grew. Choosing the annealing temperature and time, one can

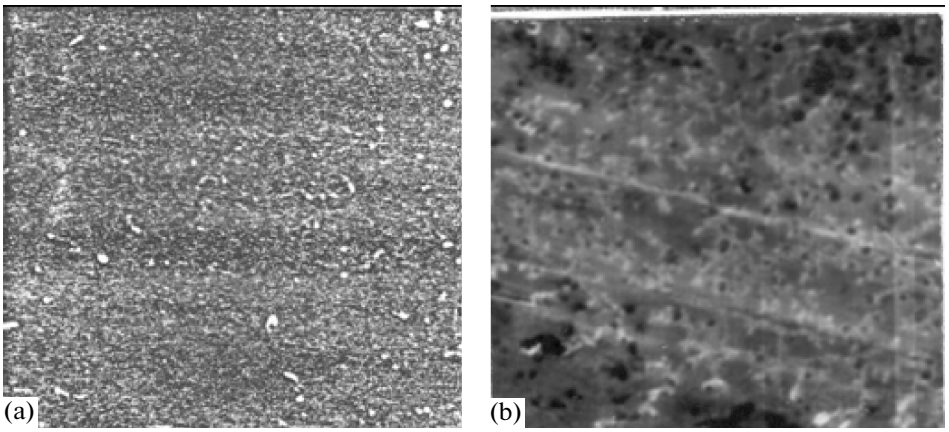

Fig. 2. Electron-microscopy images of the surface of (a) pure silicon and (b) silicon doped with Fe^+ ions.

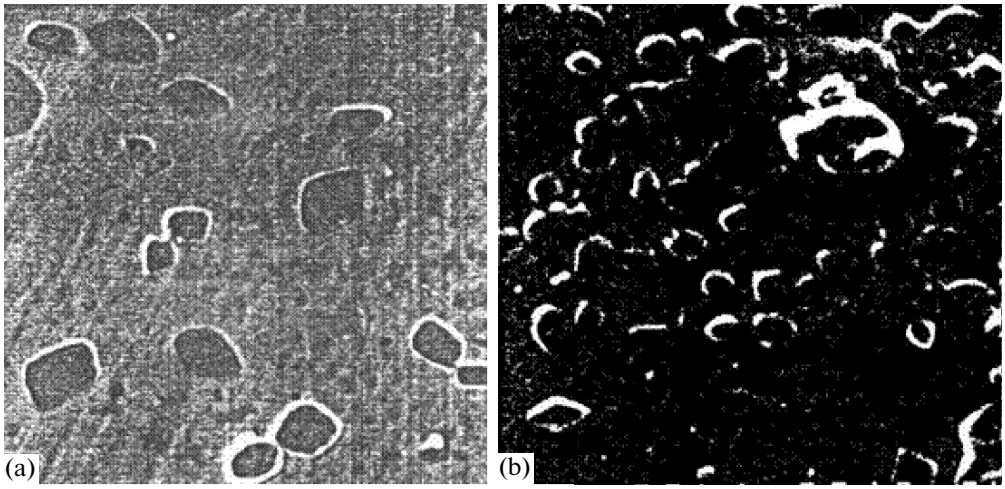

Fig. 3. Electron-microscopy images of a silicon surface (a) irradiated with Ni^+ ions at a dose of 10^{16} ion/cm^2 and annealed at a temperature of 850°C and (b) irradiated with Co ions and annealed at a temperature of 950°C.

obtain a uniform impurity distribution in the bulk of the crystal up to a certain depth.

Upon annealing at $T \sim 750$°C, the concentration of electrically active Ni and Co atoms increases to $(2–5) \times 10^{15}$ cm^{-3}, which exceeds that upon diffusion doping by a factor of 4 or 5. A further increase in temperature negatively affected the concentration of electrically active Ni atoms. Starting from 1000°C, this concentration was comparable with that obtained upon diffusion doping. For silicon samples doped with Ni and Co, the concentration of electrically active atoms noticeably grew at annealing temperatures above 600°C. As the annealing temperature was increased (600–1250°C), the Ni and Co concentrations steadily grew from 10^{15} to 6×10^{17} cm^{-3}. The latter value is the highest concentration of electrically active atoms attained upon diffusion doping. Analysis of the concentration profiles showed that for all impurity atoms activation occurs only in a thin surface layer and the concentration profile of electrically active atoms is steadily descending deep in the crystal rather than the Gaussian one. These experiments showed that complex surface processes depend on temperature and dopant dose.

The results obtained upon the doping of silicon samples at high irradiation doses are quite different. Figure 4 shows electron-microscopy images of the surface of silicon doped with Fe ions in a dose of 10^{17} ion/cm^2 after annealing at a temperature of 800°C. Annealing strongly affects the implanted samples. In the case of Fe, no significant variations are observed at low irradiation doses and annealing temperatures of up to 800°C. At a temperature of 800°C and more, the surface contains bordered areas typical of single crystals. Elemental Auger electron spectroscopy analysis of the borders showed that they consist mainly of Si and Fe atoms and, partially, of oxygen. The amplitude distribution of silicon and iron Auger peaks allows us to conclude that these areas are $FeSi_2$-type silicides. It can be seen that the bordered areas are

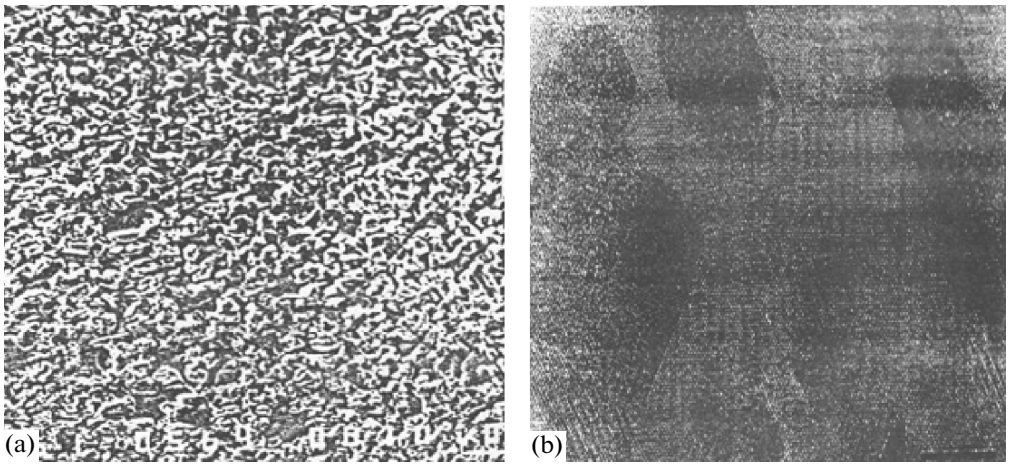

Fig. 4. Electron-microscopy images of a silicon surface (a) doped with Fe^+ ions at a dose of 10^{17} ion/cm^2 and annealed at a temperature of 800°C and (b) doped with Co^+ ions at a dose of 10^{17} ion/cm^2 and annealed at a temperature of 950°C.

to some extent merged with the formation of a continuous layer with a large number of defects. Similar results were obtained for silicon doped with Co and Ni ions at an irradiation dose of 10^{17} ion/cm^2. In the case of Ni, epitaxial silicide layers form at 850–900°C and, in the case of Co, at 900–1000°C (Fig. 4b).

As the temperature is further increased to 1100°C, the surface state significantly changes, transforming from epitaxial to amorphous. These variations concern both the structure and composition of the surface. The dopant peaks noticeably decrease, which is indicative of decomposition of the silicide layers and the partial evaporation of dopants [3–5].

CONCLUSIONS

Study of the concentration profiles of dopants with deep levels in silicon after heat treatment in different modes showed that, by choosing the annealing temperature and time, one can obtain uniform impurity distribution in the bulk of the crystal up to a certain depth and a subsequent relatively sharp concentration drop for each dopant. Comparative analysis of the impurity concentration profiles showed that a sharp concentration drop cannot be achieved upon diffusion doping because of the formation of different silicides. The impurity concentration for the uniform portion grows proportionally to the irradiation dose and, at a dose of 10^{17} ion/cm^2, exceeds the equilibrium impurity concentration upon diffusion doping by two or three orders of magnitude.

It was proved that at certain heat-treatment conditions and irradiation doses, so-called epitaxial silicides form on the crystal surface, which can serve as conductive layers or metal coatings.

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