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THE EFFECT OF THERMAL ANNEALING ON THE ELECTROPHYSICAL PROPERTIES OF SAMPLES n-Si<Ni,Cu>†

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This paper presents the results of studies of the effect of isothermal annealing at temperatures T = 673÷1473 K in the time interval 5÷60 minutes on the electrical properties of silicon, simultaneously alloyed with nickel and copper. Samples of n-Si<Ni,Cu> were obtained on the basis of the starting material - single-crystal silicon, grown by the Czochralski method with the initial resistivity ρ = 0.3 Ohm·cm. Diffusion was carried out at a temperature of 1523 K for 2 hours. After that, the samples were cooled at a rate of 0.1 K/s. The morphological parameters of impurity nickel and copper atom clusters formed in the bulk of silicon were measured by electron probe microanalysis on a modern Superprobe JXA-8800R setup. As it turned out, in the volume of n-Si<Ni,Cu> samples, clusters of impurity atoms with different geometric shapes are formed, the sizes of which reach up to 500 nm. The electrical properties of the samples were studied by the Hall effect method using an Ecopia HMS-7000 instrument. It was revealed that under the influence of thermal annealing (TA) at T≥1273 K, impurity clusters decompose, which leads to an increase in the resistivity of n-Si<Ni,Cu> samples. After exposure to TA at T=1273 K for 15 minutes, the density of impurity nanoaccumulations of acicular and lenticular shapes sharply decreases in the sample volume. Under the influence of TA at T = 1473 K for 10 minutes in the volume of the sample, the decay of impurity nanoclusters with a spherical shape is observed. Also presented are the results of changes in the density of impurity clusters, as well as structural analyzes of the samples before and after exposure to thermal annealing.
Keywords: *Silicon; Nickel; Copper; Impurity; Thermal annealing; Nanoclusters, Decay*
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INTRODUCTION

Currently, in the production of electronic devices, the base material is silicon, on the basis of which more than 90% of all semiconductor devices are produced. Therefore, the quality of this material significantly affects the development of modern semiconductor micro- and nanoelectronics. The manufacture of multifunctional integrated circuits is mainly carried out on single-crystal semiconductor wafers. Electrical, photoelectric, optical and other properties of semiconductor materials and structures based on them are determined by the presence of impurities and structural defects in crystals [1-4]. It should be noted that impurity defects can appear not only at the stage of obtaining materials, but also in the technological processes of manufacturing semiconductor devices [5-7].

Impurity defects formed during high-temperature diffusion doping of silicon single crystals with transition metal elements significantly affect their electrical, photoelectric, and optical properties [8-11]. Usually, when a silicon single crystal is doped with transition metal atoms, its thermal and radiation stability increases. In this direction, special attention is drawn to the behavior of impurity micro- and nanoinclusions under the influence of external influences. The state and behavior of impurity atoms of transition metals during heat treatment (HT) is of great interest from the point of view of controlling the electrophysical properties of silicon single crystals [12-15]. In this regard, this work is devoted to the study of the effect of HT on the resistivity of silicon doped with nickel and copper, as well as the kinetics of the decay of impurity nanoclusters under the influence of HT.

RESULTS AND DISCUSSION

Samples of n-Si<Ni,Cu> obtained on the basis of the starting material - single-crystal silicon, with resistivity ρ = 0.3 Ohm·cm, grown by the Czochralski method with crystallographic orientation (111), which are indicated in manufacturer's passport. The samples had the shape of a parallelepiped with the corresponding dimensions of 2×5×10 mm. Layers of impurity atoms were deposited on these samples, with nickel atoms 400 nm thick on one side of the sample and copper atoms 450 nm thick on the opposite side by vacuum deposition from a molybdenum boat heated to temperatures T_{Ni} ~ 1750 K and T_{Cu} ~ 1400 K. Simultaneous diffusion of nickel and copper into silicon was carried out in vacuum (10^{-5} Pa) at a temperature of 1523 K for 2 hours, after which the samples were cooled at a rate of 0.1 K/s. The results of our previous studies have shown that, at given diffusion parameters, nickel and copper impurity atoms diffuse into the entire volume of the sample. The resulting samples were subjected to isothermal annealing in vacuum (10^{-4} Pa) at temperatures T=673÷1473 K in the time interval 5÷60 minutes, followed by rapid cooling. After each stage of annealing, the electrical properties of the samples were studied. Structural studies were carried out by electron probe microanalysis on a modern Superprobe JXA-8800R setup. The electrical parameters of the samples were measured by the Hall effect method on an Ecopia HMS-7000 instrument. When measuring electrophysical parameters by the Hall

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effect method, the surface of the samples had dimensions of 1.8×5×5 mm. From each of the four corners on the sample surface, ohmic contacts were made using Au and In(50%)Sn(50%).

The resistance values of n-Si<Ni,Cu> samples after diffusion annealing are ρ= 10^4 Ohm·cm. Such growth values of ρ compared to the original samples are due to the fact that the ejection atoms of impurities, both nickel and copper in silicon, have an acceptor character. The results of studying the dependence of ρ/ρ_0 on the annealing time in the sample show that at an annealing temperature of 673 K observations do not include significant changes in the value of ρ (curve 1, Fig. 1). In the subsequent value of thermal annealing (TA) at and 873 K for 30 minutes, there is a gradual increase in the value of ρ by approximately 50% (curve 2, Fig.1). With a further increase in time, the curve of this dependence slightly decreases and the value of ρ of the samples is $1.3{\cdot}10^4$ Ohm·cm. Under the influence of TA at T = 1073 K for 15÷20 minutes, a significant increase in the resistivity of the samples is observed, which increases almost 3 times (curve 3, Fig. 1). A further increase in the annealing time to 60 minutes does not lead to significant changes in the curve of this dependence.

The dependence of ρ/ρ_0 on the annealing time in n-Si<Ni,Cu> samples under the influence of TA at T = 1273 K is even more noticeable increase (curve 4, Fig.1). At this annealing temperature, in the initial 15 minutes, a sharp increase in the value of ρ/ρ_0 of the samples is observed, which reaches almost 7 times. With a further increase in time, it passes through a maximum, after which, over the next 25 minutes, there is a significant decrease in the value of ρ/ρ_0 and it is approximately 50%. Further, in the time interval of 40÷60 minutes, a moderate decrease in the curve of this dependence is observed and the final value of time, the value of ρ/ρ_0 decreases by approximately 40%.

The most significant increase in the dependence curve of ρ/ρ_0 on annealing time in n-Si<Ni,Cu> samples is observed under the action of TA at T = 1473 K (curve 5, Fig.1). During the initial 10 minutes, the value of ρ/ρ_0 of the samples increases by almost 2 orders of magnitude. And over the next 10 minutes, it decreases to approximately its original value. With a further increase in the annealing time to 60 minutes, it continues to moderately decrease and in the final time value it decreases, relative to the initial value, by almost 50%.

Therefore, under the influence of TA in the temperature range T=673÷1073 K, the dependences of ρ/ρ_0 values on time in n-Si<Ni,Cu> samples show the following trend: in the initial stages, with an increase in the TA temperature, the maximum of the curves of these dependences occurs earlier and the growth rate of the curves increases significantly. With a subsequent increase in the annealing time, the values of ρ/ρ_0 of the samples decrease, and the higher the value of the TA temperature, the more significantly it decreases.

The reason for such an increase in the curves of the dependences of the value of ρ/ρ_0 on the annealing time with an increase in the annealing temperature from 673 K to 1473 K annealing is associated with an increase in the concentration of electroactive impurity atoms of nickel and copper, which in turn depends on the decay of impurity clusters in the bulk of the samples. We have not measured the concentrations of nickel and copper impurity atoms in the volume of impurity clusters, and we will pay attention to this in our further studies.

In order to elucidate the cause of the origin of this phenomenon, we carried out complex structural analyzes of samples before and after exposure to TA. The results of analyzes in the n-Si<Ni,Cu> samples before TA exposure showed that nanoaccumulations of impurity Ni and Cu atoms with different geometric shapes are formed in their bulk (Fig. 2). Such impurity nanoaccumulations have needle-like, lenticular, spherical, and various polyhedral shapes. It should be noted that when measuring the morphological parameters of n-Si<Ni,Cu> samples using the Superprobe JXA-8800R electron probe analyzer, the probe excitation depth was 15–20 µm. The obtained results showed that impurity accumulations are unevenly distributed over the surface of the samples, their sizes reach from several nanometers to 500 nanometers, and their average density reaches ~10^3 cm^{-2}. We have not considered the problem of determining the ratio of quantitative indicators of nickel and copper impurity atoms in the volume of impurity clusters due to the limited capabilities of the measuring devices used by us, and in our further studies we intend to determine changes in these indicators before and after exposure to thermal annealing by comparison.

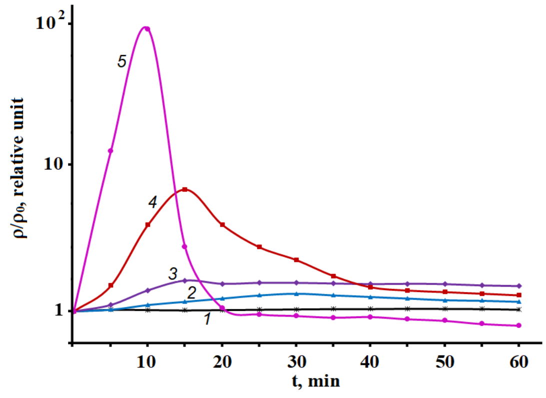

Figure 1. Dependence of the value of ρ/ρ_0 on the annealing time in n-Si<Ni,Cu> samples at TA:
1 – 673 K; 2 – 873 K; 3 – 1073 K; 4 – 1273 K; 5 – 1473 K

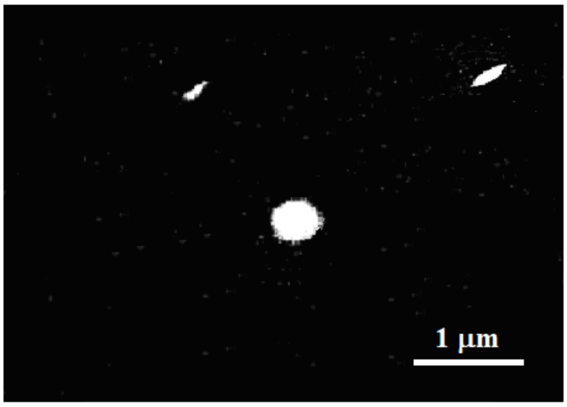

Figure 2. Micrographs of impurity nanoaccumulations in n-Si<Ni,Cu> samples before heat TA

The results of the structural analysis of the Si<Ni,Cu> samples subjected to thermal annealing in the temperature range T=673÷1073 K showed that the impurity nanoaccumulations formed in their volume after exposure to TA remain in this temperature range. This shows that impurity nanoaccumulations of Ni and Cu atoms formed in the bulk of single-crystal silicon are resistant to TA at temperatures T≤1073 K.

The obtained results of similar studies with n-Si<Ni,Cu> samples after exposure to TA at T=1273 K for 15 minutes showed that the density of impurity nanoaccumulations with needle-shaped and lenticular shapes in the sample volume decreases sharply (Fig.3). The micrographs obtained with a microprobe analyzer clearly show that, under the influence of TA, nanoaccumulations with similar shapes decay. With an increase in the value of TA up to T = 1473 K for 10 minutes, the decay of impurity nanoaccumulations with spherical shapes is observed in the sample volume (Fig.4). Impurity atoms split off from nanoclusters pass into nodes and interstices of the silicon crystal lattice. Such a course of the decay process of impurity nanoaccumulations shows that the sequence of decay of nanoaccumulations mainly depends on their geometric shape. Consequently, it turns out that impurity nanoaccumulations with a spherical shape are more resistant to external influences.

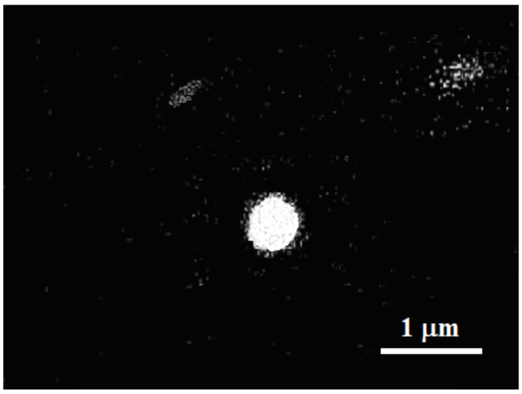

Figure 3. Micrographs of impurity nanoaccumulations in n-Si<Ni,Cu> samples after TA at T=1273 K

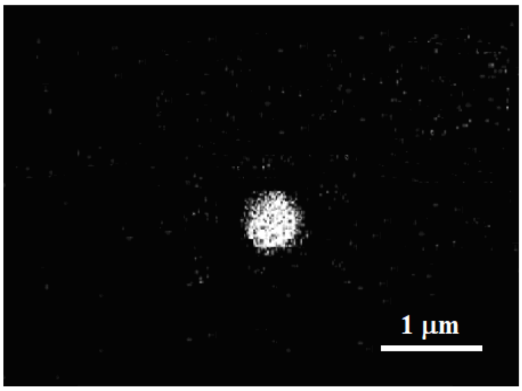

Figure 4. Micrographs of impurity nanoaccumulations in n-Si<Ni,Cu> samples after TA at T=1473 K

CONCLUSION

Thus, on the basis of the experimental results obtained, two stages can be distinguished in the kinetics of changes in the electrical properties of silicon with impurity nanoaccumulations under the influence of TA in the temperature range T=673÷1073 K. At the first stage of TA, the concentration of vacancies in the crystal structure of silicon increases and due to this impurity atoms located in the interstices, in an electrically neutral state, begin to move to the nodes of the crystal lattice. As a result, the value of the resistivity of the samples in the initial period of TA increases and reaches its maximum value. At the second stage, so if with a further increase in the TA time, due to a decrease in the excess concentration of vacancies in the crystal lattice, the transition of impurity atoms to lattice sites slows down. And this leads to a decrease in the resistivity of the samples.

Under the influence of TA at 1273 K for 15 minutes, as well as at 1473 K for 10 minutes, impurity nanoaccumulations decay, as a result of which the released impurity atoms pass into free lattice sites, so if in an electroactive state, which leads to a sharp increase in the specific sample resistance. With a further increase in the annealing time to 60 minutes due to a decrease in the concentration of excess vacancies, this transition is weakened, and the formation of various silicide complexes such as Ni_xSi_y, Cu_xSi_y, or $Ni_xCu_ySi_z$ in the electrically neutral state gradually becomes predominant, which leads to a significant decrease in the resistivity of the samples.

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ВПЛИВ ТЕРМІЧНОГО ВІДПАЛУ НА ЕЛЕКТРОФІЗИЧНІ ВЛАСТИВОСТІ ЗРАЗКІВ n-Si<Ni, Cu>

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У даній роботі представлені результати досліджень впливу ізотермічного відпалу при температурах T = 673÷1473 K до в інтервалі часу 5÷60 хвилин на електричні властивості кремнію, одночасно легованого нікелем і міддю. Зразки n-Si<Ni,Cu> були отримані на основі вихідного матеріалу - монокристалічного кремнію, вирощеного за методом Чохральского з початковим питомим опором ρ = 0,3 Ом·см дифузію проводили при температурі 1523 K до протягом 2 годин. Після цього зразки охолоджували зі швидкістю 0,1 K/s. Морфологічні параметри кластерів атомів домішок нікелю і міді, що утворилися в об'ємі кремнію, були виміряні методом електронно-зондового мікроаналізу на сучасній установці Superprobe JXA-8800R. як виявилося, в об'ємі зразків n-Si<Ni,Cu> утворюються кластери атомів домішки різної геометричної форми, розміри яких досягають до 500 нм. Електричні властивості зразків вивчали методом ефекту Холла за допомогою приладу Ecopia HMS-7000. Виявлено, що під впливом термічного відпалу (TA) при T ≥ 1273 до відбувається розкладання кластерів домішок, що призводить до збільшення питомого опору зразків n-Si<Ni, Cu>. Після впливу TA при T = 1273 до протягом 15 хвилин щільність наноакумуляцій домішок голчастої і лінзоподібної форм в обсязі зразка різко зменшується. Під впливом TA при T = 1473 до протягом 10 хвилин в обсязі зразка спостерігається розпад домішкових нанокластерів сферичної форми. Також представлені результати зміни щільності кластерів домішок, а також структурні аналізи зразків до і після впливу термічного відпалу.

Ключові слова: *кремній; нікель; мідь; домішка; термічний відпал; нанокластери; розпад*