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Decay Of Ni Impurity Accumulations In Si Under The Influence Of Thermal Annealing

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Abstract: In this article, the effect of thermal annealing on the electrical conductivity of nickel-doped silicon single crystals is investigated. The results of analyses of morphological parameters of impurity accumulations of nickel under the influence of heat treatment, obtained using the method of electron microscopy, are presented. It is revealed that under the influence of thermal annealing at T=1173 K, impurity accumulations of nickel in silicon decay.

Keywords: Nickel, accumulations, silicon, thermal annealing, decay.

INTRODUCTION:

Currently, the influence of accumulations of impurity atoms on the properties of silicon, which is one of the main materials of modern electronics, is being studied in many leading scientific centers of the world. As is known, impurity accumulations significantly affect the electrophysical properties of silicon single crystals [1-4]. Particular attention is drawn to the behavior of impurity accumulations under the influence of external influences. The study of the nature of impurity atoms of transition metals, especially those in the bulk of silicon single crystals in the form of accumulations, during thermal annealing (TA) is of great interest from the point of view of controlling the electrophysical properties of silicon single crystals. The processes of self-organization of microparticles of nickel impurity atoms in silicon under certain thermodynamic conditions of diffusion alloying are investigated in [5, 6]. It is established that the concentration and distribution of impurity microparticles is mainly determined by the temperature and diffusion time, and by controlling the annealing temperature it is possible to vary the sizes of the resulting microparticles over a wide range d = 0.2-5 μm and their volume distribution. It was found that under the influence of thermal annealing, at T = 700 ° C, the ordering of impurity microparticles is observed.

The effect of thermal annealing on the electrical conductivity of cobalt-doped silicon single crystals at temperatures of 373÷1273 K was investigated in [7] in the time interval 5÷60 minutes. Also, an analysis of the sequence of decay of impurity accumulations under the influence of thermal annealing was carried out using the electron-probe microanalysis. On the basis of the experimental results obtained, two stages are identified in the kinetics of the change in the electrical properties of silicon with impurity accumulations. At the first stage of the TA, the impurity atoms located at the lattice sites are transferred to the interstices, leaving vacancies. In the second stage, impurity accumulations disintegrate, as a result of which the released impurity atoms pass into the free lattice sites, i.e. in the electroactive state, which leads to a sharp decrease in the value of the resistivity.

In this connection, in this work, the influence of TA on the electrical conductivity of silicon doped with nickel, as well as changes in the morphology of impurity accumulations under the influence of TA, was investigated.

METHOD

The studies were carried out on model samples of Si<Ni> n- and p-type. Samples were obtained on the basis of the initial single-crystal silicon of electronic conductivity of the KEF brand, with specific resistance ρ=10 Ω·cm. The diffusion of nickel in silicon was carried out at T=1523 K. The temperature in the furnace was measured with the help of a thermo-emf of a platinum-platinum-rhodium thermocouple. To obtain samples of n-Si <Ni>, the diffusion was carried out for t=1 hour. And samples of p-Si <Ni>, were obtained by diffusion annealing with a duration of t=2 hours. After the diffusion annealing, the Si<Ni> samples, both n- and p-type, were cooled at a velocity υ_{cool}=1 K/s. Samples were subjected to isothermal treatment at temperatures of 573÷1173 K, in the time interval 5÷120 minutes, followed by sharp quenching. After each annealing step, the electrical properties of the samples were investigated. In order to elucidate the effect of heat treatment on the morphology of impurity accumulations, the structural states of accumulations were studied before and after the effect of TA. Structural analysis of extrinsic accumulations was performed using the Superprobe JXA-8800R electron probe microanalyzer.

RESULTS AND DISCUSSIONS

The results of studies of the dependence of the value of the resistivity ρ on the annealing time in n-Si <Ni> samples with ρ_0 = 10^2 Ω·cm showed that during the maintenance process at a temperature of 673 K, in the time interval 5÷120 minutes no significant changes occur (curve 1 in Figure 1). Heat treatment of the samples at T = 873 K for 30 minutes leads to an increase in the value of ρ by almost 6 times (curve 2 in Fig. 1). With a further increase in the annealing time to 120 minutes, it decreases by ~ 15%. At subsequent TA, at T = 1073 K, in the time interval 20÷25 minutes, an even more significant increase in the value of ρ is observed approximately by one order in n-Si <Ni samples curve 3 in Figure 1). With an increase in the annealing time, the curves pass through a maximum, then the value of the samples decreases by approximately 10%. The dependence of the resistivity on the annealing time in n-Si <Ni> samples has a definite character, according to which the difference in the values of ρ and ρ_0 increases with increasing temperature TA.

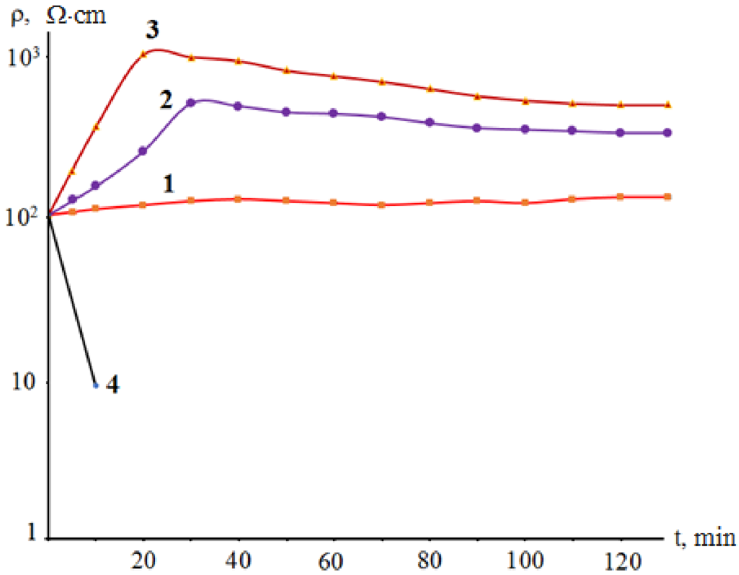

Fig. 1. Dependences of the value of ρ on the annealing time in samples of n-Si<Ni> at TA: 1 – 673 K; 2 – 873 K; 3 – 1073 K; 4 – 1173 K.

In the initial stage of the TA, at T = 1173 K, a sharp decrease in the value of ρ occurs for 8-10 minutes and it acquires the value of the original sample (curve 4 in Fig. 1). Such a character in the dependences of ρ on the TA time, in the samples of n-Si<Ni>, is explained by the fact that during the thermal annealing at T≥873 K, the impurity nickel atoms located at the lattice sites go to the interstices, leaving vacancies. With increasing temperature and time, a similar transition of impurity atoms increases, as a result of which the resistivity of the samples increases. In the subsequent value of the TA temperature at T = 1173 K, during ~ 10 minutes, impurity accumulations disintegrate, so that the released impurity atoms go to the free lattice sites, i.e. into the electrically active state, which leads to a sharp decrease in the value of ρ samples.

The results of similar studies of the dependence of the value of ρ on the annealing time, in p-Si<Ni> samples, with ρ_0 = 1.8 · 10^4 Ω·cm, showed that in TA at a temperature of T = 673 K, in the time interval 5÷120 min to significant changes does not lead (curve 1 in Figure 2). A marked decrease in the values of ρ samples is observed in the process of maintenance at T = 873 for 20 minutes and it is approximately 40% (curve 2 in Figure 2). Further increase in the TA time to noticeable changes in the value of ρ does not result. In the subsequent value of TA at T = 1023K in the time interval 10÷20 minutes, a sharp decrease in the resistivity to $\rho = 3 \cdot 10^3$ Ω·cm (curve 3 in Fig. 2) is observed in p-Si<Ni> samples. With an increase in the annealing time of up to 30 minutes, the curve passes through a minimum, after which the value of the samples increases by ~ 20%. In the samples of p-Si<Ni>, the dependence of ρ on the annealing time also has a certain character, according to which the minimum comes earlier with increasing temperature, and the growth rate of the curves increases.

In the process of TA, at T = 1173 K, a sharp increase in the value of p-Si<Ni> samples is observed for approximately 15 minutes, approximately 12-fold, and in the next 5 minutes it reaches its maximum, after which there is a sharp decrease in the value of ρ (curve 4 at Figure 2). In the further increase in the maintenance time, it continues to decrease and at t = 80 minutes reaches its minimum value $\rho = 8.5 \cdot 10^3$ Ω·cm. The observed decrease in the dependence of ρ on the TA time at T≥873 K, in p-Si<Ni> samples is explained by the increase in the concentration of electroactive nickel impurity atoms at the lattice sites, which previously are in an electrically neutral state in the form of NiSi and $NiSi_2$ complexes. The observed sharp increase in the ρ value of the p-Si <Ni> samples during the TA process at T = 1173 K for 20 minutes is due to the decay of impurity accumulations of nickel in silicon. It is assumed that the decrease in the value of ρ with a further increase in the TA time is due to the formation of new electrically active impurity cents.

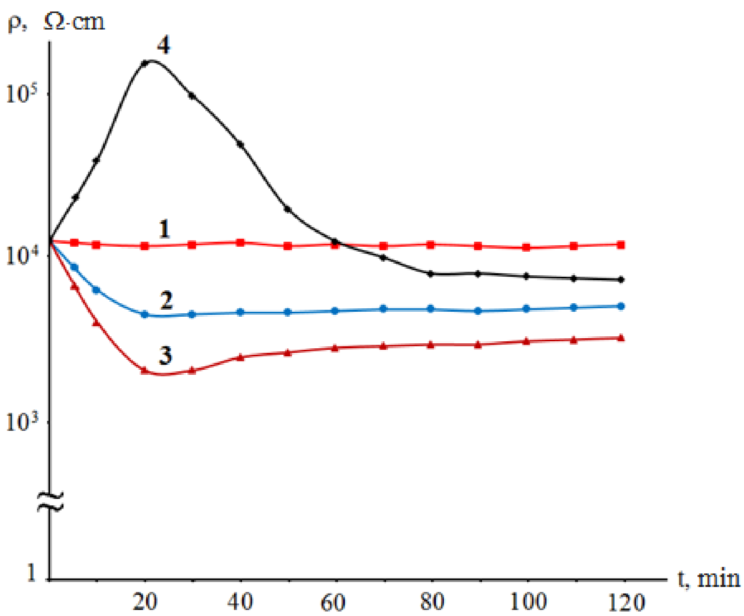

Fig. 2. Dependences of the value of ρ on the annealing time in p-Si <Ni> samples at TA: 1 – 673 K; 2 – 873 K; 3 – 1073 K; 4 – 1173 K.

To determine the nature of this change in the electrical conductivity of Si <Ni> n- and p-type samples, under the influence of TA, microstructural analyzes of impurity accumulations were carried out using an electron probe microanalyzer before and after the TA. The results of structural studies of n-Si<Ni> samples showed that accumulations with sizes up to ~ 6 μm are formed in their volume, and accumulations with maximum dimensions of ~ 2-3 μm are observed in p-Si<Ni> samples. It was revealed that these micro inclusions have different morphologies. In Fig. 3 shows images figure of impurity accumulations in p-Si<Ni> samples, before and after TA at T=1173 K, in the secondary-electron mode. As can be seen from Fig. 3 impurity accumulations with relatively small sizes (up to 1 μm), having needle-shaped, disk-like and lenticular forms, under the influence of TA, disintegrate. And larger micro inclusions are subject to partial decay, i.e. after the impact of the TA, splitting of the surface layers of such accumulations is observed.

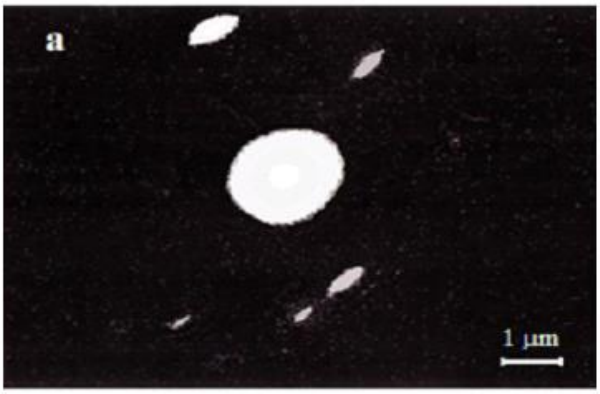

Fig. 3. Accumulations of impurity atoms of nickel in p-Si<Ni> samples before (a) and after (b) TA at T = 1173 K.

CONCLUSION

Thus, the results obtained show that under the influence of TA at T <873 K, the electrical properties of the Si<Ni> n- and p-type samples remain without significant changes. That at temperatures of 873÷1073 K for 5÷30 minutes, in samples of n-Si <Ni> leads to an increase in the value of ρ, which is explained by the transition of impurity nickel atoms from the lattice sites to the interstitial sites, leaving vacancies. With increasing temperature, a similar transition of impurity atoms increases, as a result of which the resistivity of the samples increases. In p-Si <Ni> TA samples at temperatures of 873÷1073 K for 5÷20 minutes leads to a decrease in the value of ρ, which is due to an increase in the concentration of electroactive impurity nickel atoms due to the transition from electrically neutral states in the form of NiSi and $NiSi_2$ complexes. At T = 1173 K for samples n-Si <Ni> for 8-10 minutes, and for samples of p-Si<Ni> for 20 minutes leads to the decay of impurity accumulations, which is confirmed by the results of electron probe microanalysis.

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