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Interaction between Nickel Atoms and Nanoclusters of Manganese Atoms in Silicon

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ABSTRACT: The present paper presents research of interaction of Manganese and Nickel atoms in silicon lattice. It was revealed that in the result of such interactions multiple charged nanoclusters of Manganese atoms and clusters of Nickel atoms are destroyed and significant changes in magnetic and photoelectric properties of samples occur. The results are explained by formation of electro-neutral complexes between atoms of Nickel and Manganese $Ni^- Mn^{++}$ in silicon lattice, i.e. binary clusters $Ni^- Mn^{++}$ type are formed.

KEY WORDS: Nanoclusters of Manganese atoms, positive magnetoresistance, negative magnetoresistance, concentration of nickel, manganese atoms, Cluster of Nickel atoms, complex.

I. INTRODUCTION

As was shown in [1, 2], under certain thermodynamic conditions, nickel atoms in the silicon lattice create electron-neutron clusters with sizes from several nanometers to several microns. Manganese atoms create clusters of 4 atoms. In samples with clusters of manganese atoms, a number of new physical phenomena are observed, such as an abnormally large negative magnetoresistance, as well as high impurity photoconductivity. Of great interest is the study of the interaction between clusters of nickel and manganese atoms in the silicon lattice in order to determine the possibility of controlling the properties of the material, as well as their interaction in the formation of binary clusters consisting of nickel and manganese atoms.

II. THEORETICAL ANALYSIS

The interaction of clusters of impurity atoms with a different nature is of great scientific and practical interest. Since, firstly, such studies make it possible to reveal the specific features of the interaction of clusters of impurity atoms, to assess their stability and state in the lattice, secondly, to determine the possibilities of self-organization of binary clusters taking into account various impurity atoms, and finally to elucidate the mechanisms of self-organization and kinetics of formation of atomic clusters. Controlling the composition, structure, and size of both monoatomic and binary clusters of impurity atoms in a crystal lattice with a different nature makes it possible to determine the functional capabilities of such materials.

III. EXPERIMENTAL PART

As was shown in [3], multiply charged nanoclusters of manganese atoms are formed only in compensated samples, where manganese atoms are in the Mn^{++} state. The formation of clusters of nickel atoms in silicon does not depend on the type and concentration of the initial impurity atoms. Manganese was diffused from the gas phase, and nickel from the deposited metal layer onto the silicon surface. Three batches of samples were made: the first batch of samples only for diffusion of nickel atoms, the second batch of samples only for diffusion of manganese, the third batch of samples for simultaneous diffusion of nickel atoms sprayed on only one surface of the sample and from the gas phase of manganese. Samples were placed in separate pumped-out quartz ampoules; diffusion was carried out together in the temperature range $T=975\div1150$ °C with a step of 25 °C. The diffusion time was 60–90 minutes. After diffusion, the ampoules were cooled and the samples were subjected to mechanical and chemical treatment under identical conditions.

IV. RESULTS AND DISCUSSION

The electrophysical parameters of the samples were measured by the Hall effect method. The results of the study are shown in the table.1, and kinetics of the formation of impurity atoms. ter taking into account various impurity atoms and finally find out the mechanisms of self-organization.

Table 1.
Electrophysical parameters of samples Si <B,Mn>, Si <B,Ni,Mn>, Si <B,Ni> at various temperatures

№	Diffusion temperature	Samples	$\rho, \Omega \cdot \text{cm}$	Type
1.	T=975 °C	Si<B,Mn>	11,57	p
		Si<B,Ni,Mn>	9,46	p
		Si<B,Ni>	8,2	p
2.	T=1000 °C	Si<B,Mn>	48,97	p
		Si<B,Ni,Mn>	8,43	p
		Si<B,Ni>	8,14	p
3.	T=1025 °C	Si<B,Mn>	$5,09 \cdot 10^2$	p
		Si<B,Ni,Mn>	8,72	p
		Si<B,Ni>	8,14	p
4.	T=1050 °C	Si<B,Mn>	$2,01 \cdot 10^3$	p
		Si<B,Ni,Mn>	8,58	p
		Si<B,Ni>	8,1	p
5.	T=1075 °C	Si<B,Mn>	$8,26 \cdot 10^4$	n
		Si<B,Ni,Mn>	$1,02 \cdot 10^2$	p
		Si<B,Ni>	8,0	p
6.	T=1100 °C	Si<B,Mn>	$5,07 \cdot 10^3$	n
		Si<B,Ni,Mn>	$9,22 \cdot 10^2$	p
		Si<B,Ni>	7,9	p
7.	T=1125 °C	Si<B,Mn>	$1,67 \cdot 10^2$	n
		Si<B,Ni,Mn>	$6,19 \cdot 10^2$	n
		Si<B,Ni>	7,85	p
8.	T=1150 °C	Si<B,Mn>	$1,6 \cdot 10^2$	n
		Si<B,Ni,Mn>	$5 \cdot 10^2$	n
		Si<B,Ni>	7,8	p

As can be seen, up to diffusion temperature T=1050 °C, the samples doped with manganese remain p-type, but their resistivity increased from 12 to $2 \cdot 10^3 \Omega \cdot \text{cm}$, and at T>1050 °C, the samples acquired n-type conductivity and further as the diffusion temperature increased, their resistivity decreased. These data show that manganese in silicon is indeed a donor impurity atom and the concentration of electroactive atoms in the studied temperature range varies from $3 \cdot 10^{14}$ to $3,5 \cdot 10^{15} \text{ cm}^{-3}$, which confirms the results of [3]. Samples doped only with nickel in the studied temperature range remain p-type, but their resistivity decreases slightly with increasing temperature. This means that the nickel atoms in silicon act as an acceptor impurity, but the maximum concentration of atoms is $N=(4\div 6) \cdot 10^{14} \text{ cm}^{-3}$.

Thus, it was found that in all studied temperature ranges, the concentration of electroactive manganese atoms is almost 8÷10 times higher than the concentration of electroactive nickel atoms, which allows us to conclude that in samples simultaneously alloyed with nickel and manganese, the material properties should be determined only by manganese atoms. However, as can be seen from the table, interesting phenomena are observed in samples simultaneously alloyed with nickel and manganese. Up to diffusion temperature T=1025 °C, although the samples Si <B,Ni,Mn> remain p-type, their resistivity decreases, and at diffusion temperature T=1050 °C, the samples acquire their initial parameters, p-type with $\rho \sim 9 \div 11 \Omega \cdot \text{cm}$, i.e. as if there were no impurity atoms of manganese and nickel in these samples. At T>1070 °C, the resistivity increases again, and then the type of conductivity changes, i.e. the samples become n-type, the resistivity increases and becomes greater than the resistivity of silicon samples doped only with manganese at this temperature. Such behavior of samples simultaneously doped with Ni and Mn cannot be explained by compensating donor energy levels of Mn with acceptor energy levels created by Ni atoms in silicon, since at a temperature T=1050 °C the concentration of electroactive manganese atoms is almost 1.5 orders of magnitude greater than the concentration of electroactive nickel atoms in silicon.

Figure 1 shows the spectral dependences of the photoconductivity of samples Si <B,Mn>, Si <B,Ni>, Si <B,Ni,Mn> doped at a temperature of T=1050 °C.

As can be seen from the figure, in the samples Si <B,Mn> the photo response begins at $h\nu = 0.2 \text{ eV}$, and with increasing photon energy it continuously and significantly increases, i.e. the samples have a fairly high photosensitivity,

which coincides with the results of [4]. In samples Si <B,Ni>, weak photoconductivity is observed at $h\nu = 0.2$ eV, which is associated with the transition of electrons from the valence band to the level of nickel atoms. At the same time, any impurity photoconductivity in the studied spectral region is absent in the samples Si <B,Ni,Mn>, and the photoresponse is observed only for $h\nu > E_g$.

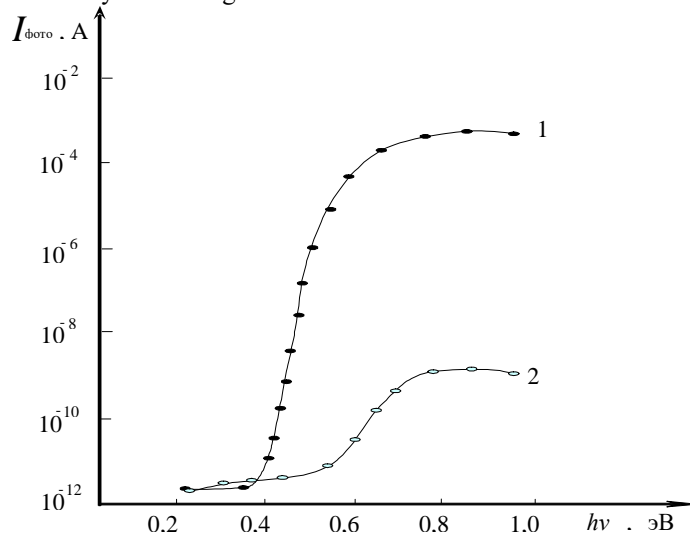


Figure 1. Spectral dependence of the photocurrent in samples of Si<B,Mn> с $\rho = (6-8) \cdot 10^3 \Omega \cdot \text{cm}$ p-type
1). Samples I group, 2). Samples II) group.

As was shown in [5], in samples Si <B,Mn>, with $\rho \sim (3-5) \cdot 10^3 \Omega \cdot \text{cm}$ at room temperature, a rather high negative magnetoresistance (NMR) is observed associated with magnetic nanoclusters of manganese atoms in the lattice. Therefore, the authors also investigated the magnetoresistance of three types of samples by doping at $T = 1050^\circ \text{C}$ (Figure 2). Indeed, in the samples Si <B,Mn>, NMR is observed, the value of which increases with increasing magnetic field (curve 1). In the magnetoresistance characteristic of samples Si <B,Ni>, there is a small positive magnetoresistance (PMR), the value of which weakly depends on H (curve 2). In samples Si <B,Ni,Mn>, for a small value of H, a weak PMR occurs, and with an increase in the magnetic field, the sign of the magnetoresistance occurs, i.e. a small NMR is observed (curve 3).

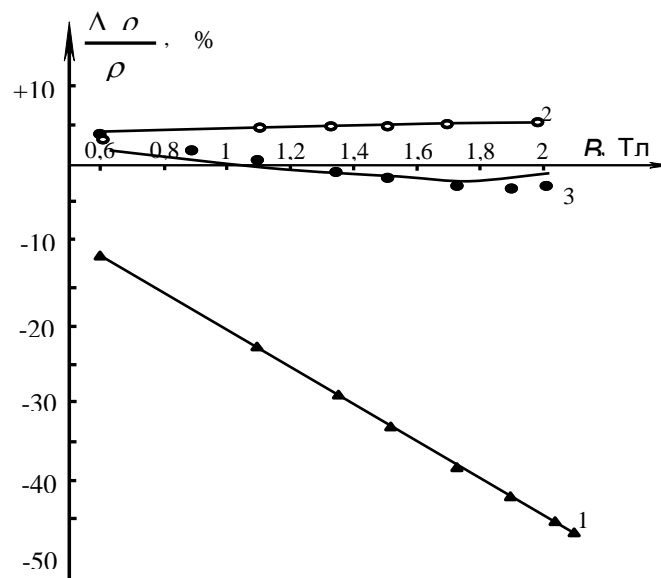


Figure 2. Dependence of the magnetoresistance in Si<B,Mn>, Si<B,Ni> and Si<B,Ni,Mn> samples on magnetic field at $T=300\text{K}$ and $E=100 \text{ V/cm}$: 1- Si<B,Mn>, $\rho=5,07 \cdot 10^3 \Omega \cdot \text{cm}$, with nanoclusters; 2-Si<B,Ni>, $\rho=9,22 \cdot 10^2 \Omega \cdot \text{cm}$; 3-Si<B,Ni,Mn>, $\rho=7,9 \Omega \cdot \text{cm}$.

As can be seen, the NMR value in Si <B,Mn> is 12÷15 times greater than in Si <B,Ni,Mn>. These data indicate that the presence of nickel atoms substantially affects the concentration of nanoclusters of manganese atoms in silicon. To confirm this assumption, the authors studied the state of manganese atoms in Si <B,Ni,Mn> by the EPR method, which showed that they do not observe a hyperfine spectrum of 21 lines associated with clusters of four manganese atoms, but instead there is a usual spectrum of 6 lines associated with the atomic state of manganese atoms [3,4,5]. The state of nickel atom clusters in the samples Si <B,Ni> and Si <B,Ni,Mn> was studied using an MIK-5 IR microscope (Figure 3. a,b).

As can be seen, although the clusters of nickel atoms are clearly visible in both samples, a decrease in their size and concentration is observed in the samples Si <B,Ni,Mn> (Figure 3.b). These results show that in samples Si <B,Ni,Mn>, the concentration of nickel and manganese atoms has the same value as in samples Si <B,Mn> and Si <B,Ni>, respectively.

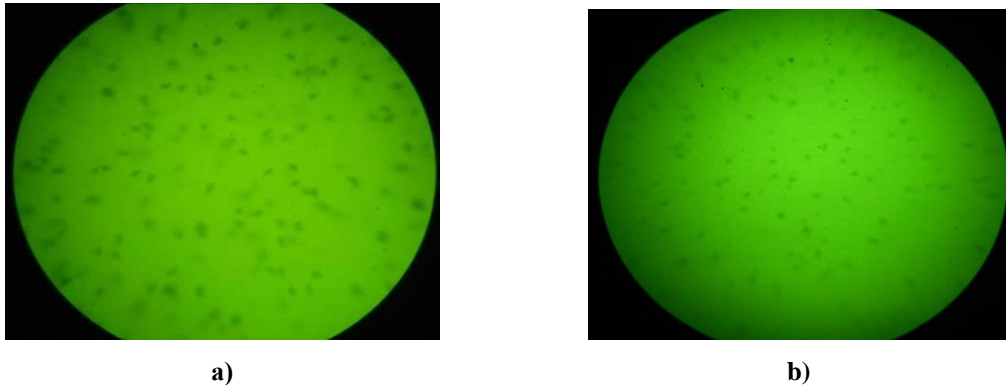


Figure 3) a,b Clusters of nickel atoms in Si<B,Ni> and Si<B,Ni,Mn> samples were investigated using an MIK -5 IR microscope.

As is known [6,7], nickel atoms and manganese atoms in silicon mainly diffuse along interstitial sites. Moreover, the diffusion coefficient of Ni is almost an order of magnitude larger than the diffusion coefficient of Mn [7,8] and the solubility of nickel in silicon is also 1.5 orders of magnitude greater than the solubility of manganese. Therefore, it can be assumed that a sufficiently high concentration of interstitial nickel atoms and their high diffusion coefficient simply do not allow the formation of nanoclusters consisting of four manganese atoms located in blissful interstices around boron atoms.

But then the question arises: why do the manganese atoms in the samples Si <B,Ni,Mn> not show electroactivity?

This can be explained as follows. It is known that nickel atoms in the sites of the silicon lattice act as an acceptor, creating two acceptor levels. In p-type materials, these levels are mostly unfilled. At the same time, the main manganese atoms that are in the internodes act as a double donor. Manganese atoms can give their outer ($4S^2$) two electrons to Ni atoms, which are located in the lattice sites with the formation of electron-neutral complexes. The formation of such complexes virtually eliminates the compensation of holes in the valence band by electrons of manganese atoms, as well as the increase in holes due to the transition of electrons from the valence band to nickel energy levels with an ionization energy $E_1 = E_v + 0.2$ eV. In this case, the samples should retain their initial parameters, which is observed experimentally. To fulfill this condition, the concentration of Ni atoms in the lattice sites should be two times higher than the concentration of electroactive manganese atoms in the interstices. Therefore, it can be assumed that the formation of such electroneutral complexes stimulates the presence of Ni atoms in the sites.

This assumption explains the decrease in the size and concentration of nickel atom clusters in such samples (Figure 3). Change in the conductivity type of samples Si<B,Ni,Mn>. At $T > 1070^\circ\text{C}$, it can be explained by the destruction of such complexes and the compensation of holes due to manganese electrons. This can be proved by the fact that the samples Si <B,Ni,Mn>, which acquired the n-type conductivity upon diffusion. $T = 1100^\circ\text{C}$, repeatedly annealed at $T = 1050^\circ\text{C}$, again became the p-type with the initial electrical parameters $p \sim 10 \Omega\cdot\text{cm}$.

V. CONCLUSION

The presence of impurity nickel atoms in the interstices of the silicon lattice does not allow the formation of clusters of manganese atoms. This is explained by the formation of binary complexes consisting of nodal nickel atoms and interstitial manganese atoms in the form of $\text{Ni}^- \text{Mn}^{++}$. The formation of such electrically neutral complexes is



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stimulated by the substitution of nickel atoms in the sites. In this case, the photoelectric and magnetic properties of the material change significantly.

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