Negative magnetoresistance in silicon doped with manganese

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Abstract. Based on the developed low-temperature step-by-step diffusion of impurity manganese atoms, magnetic nanoclusters of manganese atoms were formed in the crystal lattice of silicon with controllable concentration, with specified and reproducible electrophysical parameters. With the help of electron spin resonance, it was proved experimentally that magnetic nanoclusters are formed in p-Si<B,Mn> silicon and consist of four positively charged manganese atoms which are situated in the nearest equivalent inter-nodes around the negatively charged boron atom. Based on the study of electrophysical properties of the material obtained it is shown that in such materials an anomalous Hall effect is observed. Magnetoresistance in silicon p-Si<B,Mn> with magnetic nanoclusters at room temperature was studied and a giant negative magnetoresistance (NMR) $\Delta\rho/\rho \sim 300$ %, was found, it was shown that with increasing concentration of nanoclusters, NMR value essentially rate.

1 Introduction

The development of technology for obtaining new magnetic semiconductors and the study of their properties allows not only to further develop the scientific areas of spintronics, photomagnetism, magneto-optics and discover new physical phenomena associated with the magnetic properties of semiconductors, but also to significantly expand the scope of modern electronics, as well as to better understand what is happening in physical processes [1-7].

At the same time, the formation and study of magnetic nanoclusters in a crystalline silicon matrix without disturbing its phase and chemical composition is of particular scientific and practical interest. This interest is important because, on the one hand, the base material used, silicon, is the main material for modern electronics, and this significantly speeds up the practical application of the results obtained based on this material. On the other hand, the creation of magnetic nanoclusters with controlled parameters and concentration makes it possible to reveal new yet unexplored facets of the magnetic properties of silicon with nanostructures and the possibility of their use in the development and creation of a fundamentally new generation of electromagnetic and photomagnetic devices.

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2 Objects and methods of research

Most atoms in solids do not have a magnetic moment, but there are a number of transition elements in which the internal d inhabited only partially filled, and therefore, these atoms have a non-zero magnetic moment. If clusters are formed on the basis of such atoms, then the magnetic moment of each atom interacts with the magnetic moments of other atoms in such a way that it can align all atoms in one direction along a certain symmetry axis of the cluster. Such a cluster has a sufficiently large total magnetic moment [8–10]. Therefore, it is of great interest to study the formation of clusters based on elements of the transition group in the crystal lattice of a semiconductor.

Choosing of manganese as impurity atom, was dictated by the fact that, firstly, manganese is a unique paramagnetic atom that has the electronic structure … 3d5 4s2 with the spin, and secondly, the manganese atom has the Mn++(3d5) state with a small ionic radius (0.96 Å), which is smaller than the Si bond ling's (1.77 Å). Therefore, manganese atoms in silicon are located mainly in interstitial-site state and have the largest diffusion coefficient. These mentioned parameters of manganese atoms in the silicon lattice seem to stimulate the formation of clusters [11]. Indeed, as was shown in [12-14] using the electron spin resonance (ESR) method, nanoclusters consisting of 4 neutral manganese atoms were found in manganese-doped silicon during slow cooling after diffusion. However, controlling the cooling rate did not make it possible to obtain samples with reproducible parameters. The composition, structure, size, magnetic moment, and magnetic properties of silicon with such nanostructures have also not been practically studied.

Although the modern diffusion technology used in electronics does not require impurity diffusion according to a given mechanism, the development of nanotechnology and especially the development of technology for the formation of nanoclusters of impurity atoms with a controlled structure, composition, and their distribution in the crystal volume suggests the need for diffusion of impurity atoms mainly along the interstitial mechanism. Since only diffusion through interstices allows one to control the state of impurity atoms in the lattice and their interaction with each other and defects, and most importantly, under certain thermodynamic conditions, it allows the formation of nanoclusters with different structures and compositions [15].

One of the real ways to perform inter-nodal diffusion is to perform low-temperature and step diffusion. By low-temperature diffusion one must understand such diffusion process, in which thermally equilibrium concentration of vacancies (Nv) in lattice must be essentially less than concentration of introduced impurity atoms (N) in lattice.

In the process of high-temperature diffusion on silicon surface up to 20 μm depth [16] intensive silicide formation occurs in the temperature range T=1030÷1120 ºC as well as essential erosion of material surface. During silicide formation (Mn4Si7) practically all interstitial atoms are captured and also diffusion rate of impurity manganese atoms in silicon decreases. Therefore, these facts significantly limit the possibility of using high-temperature doping to form clusters of impurity atoms in the lattice, which requires a more detailed study of this process. At the same time it is necessary to obtain an answer about the possibility of using the obtained diffusion parameters of impurity atoms during high-temperature diffusion under conditions of low-temperature and step diffusion process. In order to obtain compensated silicon with specified and reproducible electrophysical parameters the low-temperature stepwise doping method was used.

The essence of our developed low-temperature stepwise diffusion is as follows. The samples under study and the diffusant - pure metallic manganese of a certain mass (determined by the ampoule volume) are in evacuated quartz ampoules (ampoule pressure ~10-6 mmHg.), which are introduced into the diffusion furnace at T=300 K. It has been determined in advance that the temperature of the furnace at the location of the ampoule is gradually increased at a rate of 5 deg/min [17]. The samples are heated to a temperature of T=550÷700 ºC and held at this temperature for t=10÷20 min, then the temperature is raised at a rate of 15÷16 ºC/min to a value of T=960÷1100 ºC (Figure 1). The samples are held at this temperature for 5÷10 min, then the ampoules are removed from the oven and cooled at a rate of 200 ºC/sec.

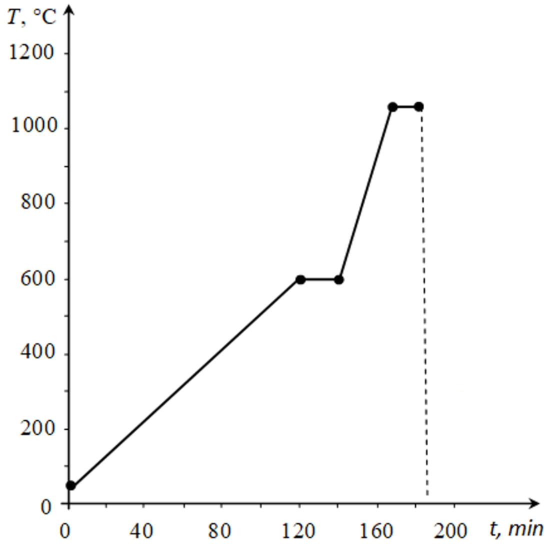

Fig. 1. Technology of low-temperature step-by-step method of silicon doping with manganese atoms

It is known from the literature [18-20] that the ESR method is often used to investigate the state of manganese atoms in the silicon crystal lattice.

Manganese atoms are paramagnetic centres with spin S=5/2 (3d5 4s0) and depending on the doping condition can be found in the crystal lattice of silicon in the states Mn0 (3d5 4s2), Mn+ (3d5 4s1), Mn++ (3d5 4s0) or [MnB]+.

If we consider that manganese atoms in silicon create two donor energy levels E1=EC-0.27 eV and E2=EC-0.5 eV [19] then in compensated samples p-Si<B,Mn> with ρ=(5÷10)·103 Ohm·cm, in which the Fermium energy equals EF=EV+(0.38÷0.45) eV, all injected manganese atoms are mainly in double positively ionized state Mn++. As the Fermi level shifts towards conduction zone the concentration of atoms in [Mn]++ state decreases and correspondingly the concentration of atoms in Mn+ and Mn0 states increases, and in overcompensated samples manganese atoms are mainly in Mn0 and Mn+ states.

The following samples were made to investigate the state of manganese atoms by ESR.

I-party. Compensated silicon samples p-Si<B,Mn> and overcompensated silicon samples n-Si<B,Mn> doped with manganese atoms by low-temperature technology [21];

II-party. Compensated and overcompensated silicon samples with similar resistivities doped with manganese atoms by conventional high-temperature diffusion technology.

To clarify the nature of the state of manganese atoms in the silicon lattice they were also investigated by means of ESR spectra on Broker at T=77 K. To record the ESR spectra a spectrometer operating in the 3 cm wavelength range was used. Integral sensitivity of the device was ~5·1010 spin/Gs and the accuracy of detection was up to 0,001%. The precise determination of the g-factor of the observed spectrum was carried out using a marker line with g=2.0024.

3 Results and their discussion

As demonstrated by the results of investigations in samples of I-party at T=300 K obtained by new technology p-Si<B,Mn> with Fermi level position in EF=EV+(0.38÷0.45) eV, the superfine ESR spectra consisting of 21 lines (Fig. 2.a) characteristic for nanoclusters containing four manganese atoms [22] are clearly observed. With shift of Fermi level from EF=EV+(0.38÷0.45) to the middle of forbidden zone F=EV+(0.52÷0.55) eV the ESR spectra are observed which intensity decreases due to decrease of atoms concentration in [Mn]++ state and corresponding increase of atoms concentration in Mn+ state.

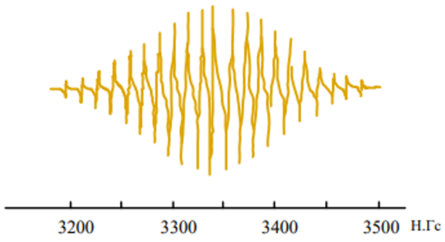

Fig. 2a. ESR spectrum of [Mn]4 in silicon

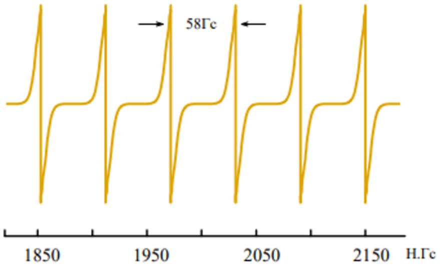

Fig. 2b. ESR spectrum of manganese Mn++ atoms in silicon

In samples of II party alloyed on usual technology were obtained samples Si<B,Mn> of p-type conductivity with similar parameters (resistivity), the same as in samples obtained on new technology, where nanoclusters of manganese atoms were observed, However in these samples Si<B,Mn> irrespective of their parameters ESR has not shown presence of nanoclusters of manganese atoms and also in overcompensated Si<B,Mn> n-type samples obtained by new technology not depending on position of Fermi level in them. The ESR spectra observed in these cases are associated with a single state of manganese atoms (Fig. 2.b).

As a result of a creative collaboration with the Seoul University Semiconductor Research Centre team from South Korea, we have been greatly assisted by the structural analysis of Mn-doped Si samples by our colleagues using an X-ray diffractometer (XRD, Rigaku mini flex).

Figure 3 shows Si (111) diffraction peaks showing manganese boride (Mn4B) complexes. These results are direct evidence for the formation of magnetic clusters of impurity atoms in the silicon lattice.

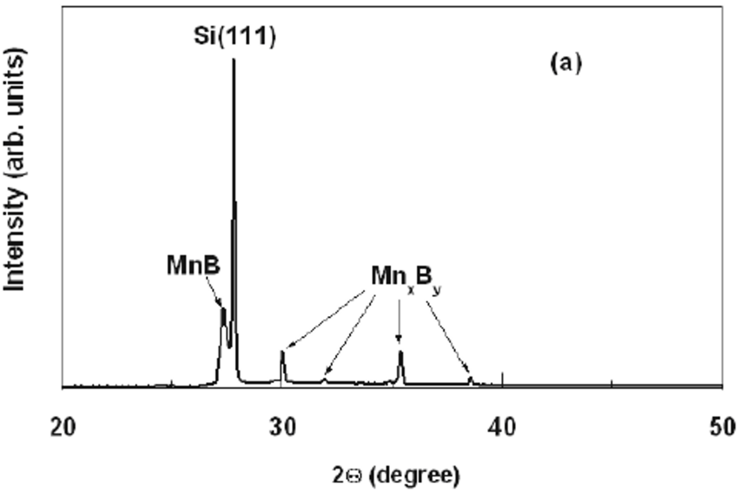

Fig. 3. X-ray spectra of magnetic clusters.

It should be noted that in n-type silicon samples doped with manganese as well as in overcompensated samples no spectra associated with nanoclusters of manganese atoms are observed. Therefore, we can say with certainty that low-temperature doping is a new technological solution for the formation of nanoclusters of impurity atoms in the silicon lattice. This is a fundamentally new approach to the formation of nanoscale structures in the semiconductor lattice, which does not require expensive technological equipment. As shown by ESR studies, in samples where nanoclusters of manganese atoms are observed spectra, nanoclusters are observed throughout the entire sample volume. We stepwise grinded 30÷50 μm from the sample surface to half of the sample thickness and after each grinding step the ESR spectra were taken, which were the same each time without significant changes. These results clearly show that nanoclusters and nanoscale structures can form throughout the entire crystal volume.

Therefore, we assume that the structure of a magnetic nanocluster consists of four positively charged manganese atoms, which are in the nearest equivalent inter-nodes around a negatively charged boron atom. The nanoclusters of manganese atoms can act as magnetic centres because the clusters consist of four manganese atoms with spins S=5/2 and total spin 4S=10, i.e. they should act as a powerful magnetic moment and lead to a significant change in the anomalous Hall effect.

Results of researches of electro-physical properties of the received material have shown, that in samples from I party the new galvanomagnetic phenomenon which essence consists that the Hall voltage drop in these samples considerably differs in comparison with samples of II party is observed. With a change of 2-3 times the polarity of the magnetic field, the Hall voltage drop of the electric field is observed. This difference is more clearly seen in those samples where there are magnetic nanoclusters of manganese atoms. In the compensated samples from batch II, as well as in the overcompensated samples, regardless of their resistivity, the usual Hall mobility of charge carriers is observed, practically comparable to the mobility of charge carriers without impurity atoms.

Results of research of anomalous Hall effect in samples of I party depending on resistivity of samples showed that effect has the maximum value in samples of p-type with $\rho=7\cdot103$ Ом·см, in range $5\cdot10^3$ Ohm·cm>ρ>10^4 Ohm·cm it weakens, and in samples with resistivity $3\cdot10^2$ Ohm·cm>ρ>$1{,}2\cdot10^5$ Ohm·cm and in n-type samples with a wide range of resistivity the usual Hall effect is observed, i.e. the anomalous Hall effect is canceled (Table 1).

Table 1. Characteristics of samples obtained by different diffusion methods and anomalous Hall effect in silicon

Method diffusion	No	The resulting samples	Type	ρ, Ohm·cm	Usual R_X, cm³/Cl	Anomalous $R_I \chi_{Mn}$, cm³/Cl	μ, cm²/V·s
I party	1	Si<B,Mn>	p	$2\cdot10^2$	$4.26\cdot10^4$	-	213
	2	Si<B,Mn>	p	$3\cdot10^2$	$7.5\cdot10^4$	$2{,}5\cdot10^4$	167
	3	Si<B,Mn>	p	$8\cdot10^2$	$2\cdot10^5$	$1.28\cdot10^5$	90
	4	Si<B,Mn>	p	$8\cdot10^3$	$2\cdot10^6$	$1.49\cdot10^6$	63
	5	Si<B,Mn>	p	$1.2\cdot10^4$	$3\cdot10^6$	$2.06\cdot10^6$	78
	6	Si<B,Mn>	p	$2\cdot10^4$	$5\cdot10^6$	$3.4\cdot10^6$	80
	7	Si<B,Mn>	p	$4\cdot10^4$	10^7	$7\cdot10^6$	75
	8	Si<B,Mn>	p	$1.2\cdot10^5$	$3\cdot10^7$	$1.11\cdot10^7$	158
	9	Si<B,Mn>	p	$2\cdot10^5$	$7.5\cdot10^7$	-	250
	10	Si<B,Mn>	n	$3\cdot10^3$	$3.64\cdot10^6$	-	1214
	11	Si<B,Mn>	n	$5\cdot10^4$	$6\cdot10^7$	-	1192
	12	Si<B,Mn>	n	$1.2\cdot10^5$	$1.4\cdot10^8$	-	1160
II party	1	Si<B,Mn>	p	$3\cdot10^2$	$7.5\cdot10^4$	-	240
	2	Si<B,Mn>	p	$6\cdot10^3$	$1.5\cdot10^6$	-	268
	3	Si<B,Mn>	p	$7\cdot10^4$	$1.75\cdot10^7$	-	236
	4	Si<B,Mn>	n	$4.5\cdot10^3$	$5.4\cdot10^7$	-	1240
	5	Si<B,Mn>	n	$6\cdot10^4$	$7.2\cdot10^7$	-	1208

Magnetoresistance (MR) in p-Si<B,Mn> samples with magnetic [Mn]4 nanoclusters was investigated at room temperature in transverse (B I) direction of magnetic field. The magnetic field strength varied in the range B=0÷2 Tl, i.e. the condition of weak magnetic field was fulfilled. The results of magnetoresistance in silicon with magnetic nanoclusters of manganese atoms are shown in Fig. 4.

As can be seen from the figure, with increasing concentration of nanoclusters, the negative magnetoresistance (NMR) value increases significantly. In the samples with nanoclusters concentration N=1015 cm-3 at room temperature, at E=100 V/cm a giant NMR Δρ/ρ~300 % is obtained, and magnetic field sensitivity is α=150 %/Tl. These results, not only clearly demonstrate that the occurrence of NMR and its nature in such samples is directly related to the presence of nanoclusters of manganese atoms in the lattice, but also to the possibility of controlling the value of NMR in a wide range by changing the concentration of nanoclusters.

It was found that with increasing concentration of nanoclusters in the range of 2·1013 ÷ 1015 cm-3, under the same experimental conditions, the value of OMC increases by 8÷10 times, and the sensitivity of the magnetic field increases from α=28 %/Tl to α=150 %/Tl.

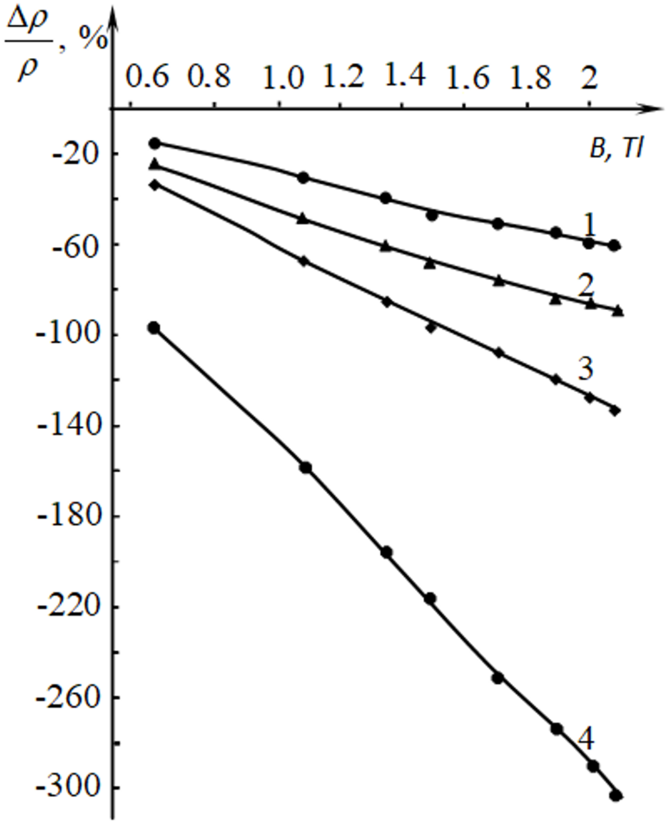

Fig. 4. MR dependence on magnetic field in samples with different concentration of magnetic nanoclusters at T=300 K, E=100 V/cm: 1 – N(Mn)4 = 2·1013 cm-3, 2 – N(Mn)4=2·1014 cm-3, 3 – N(Mn)4 = 5·1014 cm-3, 4 – N(Mn)4 =1015 cm^{-3}

4 Conclusions

To summarize the results of the research presented in this paper, the following conclusions can be drawn from the individual results, which have an important value in their own right:

1. The technology of formation of nanoclusters of impurity manganese atoms with controlled structure and properties in the silicon lattice has been developed, which is one of the most actual and perspective solved problems of modern nanoelectronics, as the creation of magnetic nanoclusters - magnetic quantum dots in the silicon lattice not only allows to manage the fundamental parameters of silicon, its magnetic properties, but also reveals a number of new physical phenomena still unknown to us.
2. The electrophysical and magnetic properties of silicon with nanoclusters of manganese atoms are investigated and anomalously high NMR ( ) is found at room temperature.
3. The regularity of NMR value change from nanoclusters concentration and electrophysical parameters of samples with nanoclusters were determined. It is shown that with increasing concentration of nanoclusters NMR value significantly increases, and for detection of maximum NMR it is necessary to use silicon of p-type with ρ=(3÷10)·103 Ohm·cm at room temperature.

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