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About Thermal Stability of Clusters of Manganese Atoms in Silicon

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ABSTRACT: In silicon samples with nanoclusters of manganese atoms we have been able to observe some very interesting physical phenomena. In the course of study of magnetic properties of these materials, we have been able to discover anomalously large negative magneto-resistance (NMR) at $T = 300\ K$, i.e. the ferromagnetic state of silicon. Magnetic properties can be varied over a wide range by means of temperature, electric field, and irradiation. We have also been able to reveal double inversion of the value of the magneto-resistance (MR). The authors show that silicon with magnetic nanoclusters is a promising novel material for modern spintronics and optoelectronics, i.e. one can use this material to create sensitive magnetic and photomagnetic devices.

I. INTRODUCTION

In silicon samples with nanoclusters of manganese atoms we have been able to observe some very interesting physical phenomena. In the course of study of magnetic properties of these materials, we have been able to discover anomalously large negative magneto-resistance (NMR) at $T = 300\ K$ [1,2], i.e. the ferromagnetic state of silicon [3]. Magnetic properties can be varied over a wide range by means of temperature, electric field, and irradiation [4,5]. We have also been able to reveal double inversion of the value of the magneto-resistance (MR) [4,5]. Meanwhile, in the course of study of photovoltaic properties, we had revealed bias of the photo-response edge towards $\lambda = 10$ micron, an anomalously high impurity photoconductivity in the diapason $\lambda = 10 \div 1{,}5$ *micron* [6,7], as well as the effect of the stimulated impurity photoconductivity in the presence of background light.

II. METHODOLOGY

The obtained experimental results evidence of unique, functional properties of silicon with nanoclusters of manganese atoms that could be availed of for the development and design of innovative electronic devices in the field of spintronics and optoelectronics, as well as for the development of highly sensitive sensors of various physical properties. Therefore, of particular scientific interest is the study of how properties of silicon with nano-scale clusters of manganese atoms change in dependence of various heat treatment processes and how could these features be utilized for manufacturing of a certain row of devices.

Thermal stability of silicon doped with manganese, without the formation of nanoclusters has been studied in [8], According to the results of this work, annealing at $T \geq 125$ °C for 30 ÷ 40 minutes, changes the material properties significantly, while annealing for $t = 1{,}5 \div 2$ hours brings forward total dissociation of clusters, i.e. the material acquires its original properties. Based on these results, one could conclude that the atomic state of manganese atoms in the silicon lattice is not thermally stable, whereas at $T \geq 100$ ° C that causes a change in electrical properties of manganese-doped silicon samples. The question is: how does thermal annealing affect the state of the cluster and at the same time influences electrical properties of silicon nanoclusters with manganese atoms.

Samples with nanoclusters of manganese atoms were prepared based on our "low-temperature" diffusion technique [9]. The sample was a *p-type* single- crystalline silicon with a resistivity of 3 Ω·cm. Samples after doping with manganese atoms turned out to be *p- type* with $\rho \sim (4 \div 5)10^3 \Omega \cdot cm$ at $T = 300\ K$. The presence of manganese atoms in the nanoclusters in the samples was confirmed by electro-paramagnetic resonance (EPR) and atomic-force microscopy (AFM) techniques.

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The obtained samples at room temperature manifest anomalously large negative magneto-resistance and high impurity photoconductivity in the range of $\lambda = 10 \div 1,5$ *micron* symbolic of samples with nanoclusters of manganese atoms [1,4,6,7]. At the same time, based on p-type silicon with a ρ= 3 Ω·cm, samples doped with manganese by using high-temperature doping technique were prepared, the same parameters, however without nanoclusters. Lack of nanoclusters in these samples was confirmed by EPR.

Thermal annealing was carried out in special furnaces, during certain duration. After each step of thermal annealing, the samples were chemically treated to remove SiO_2 layers and to study electrical and magnetic, and photoelectric properties were studied under identical conditions. The Fig 1 shows the relative change of holes' concentration in samples as a function of annealing time at T = 125 °C. As you can see, the holes' concentration in the samples withe nanoclusters in the test range does not virtually depend on duration (Curve 1).

Studies have shown that, the magnetic and photoelectric properties of these samples also retained their values precedent to annealing process. At the same time in the samples doped with manganese (without the formation of nanoclusters) electrical parameters change significantly as annealing time drags longer, whereas annealing for t = 300 minutes, brings forward complete dissociation of manganese atoms (Curve 2).

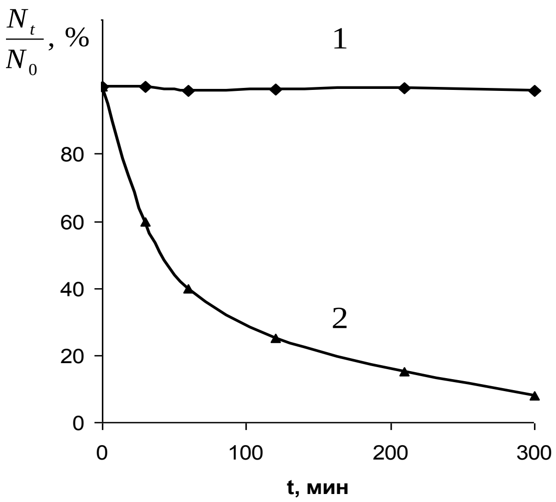

Fig. 1 Relative change in the concentration of the majority charge carriers in silicon doped with manganese: 1) images with nanoclusters, 2) images without nanoclusters

Since the basic feature of silicon with nanoclusters of manganese atoms is the large value of NMR and high photosensitivity in the range of λ=1,5micron, so we carried out the study of influence of the duration of thermal annealing at T = 150 ° C on relative change in NMR (Fig.2, curve 1), and photosensitivity at λ = 1,5 micron (Curve 2). As the results show, annealing for 30 minutes had reduced NMR by 15%, while photosensitivity practically does not change significantly. In the range of 30 to 60 minutes of annealing, NMR value decreases by 40%, while photosensitivity deteriorates by 12 ÷ 15%.

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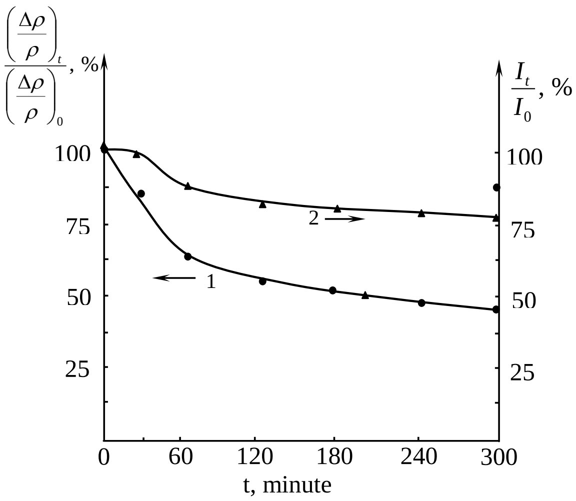

Fig.2. Relative change in NMR (1) and photosensitivity at λ = 1,5 micron (2) in silicon samples with nanoclusters as a function of thermal annealing duration at T = 150 ° C.

Further increase in the annealing duration deteriorates NMR and photosensitivity parameters, however deterioration continues but its speed slows down considerably. Fig. 3 shows the relative change in NMR and photosensitivity at λ = 1,5 micron at various temperature and the same annealing duration (t = 30 minutes).

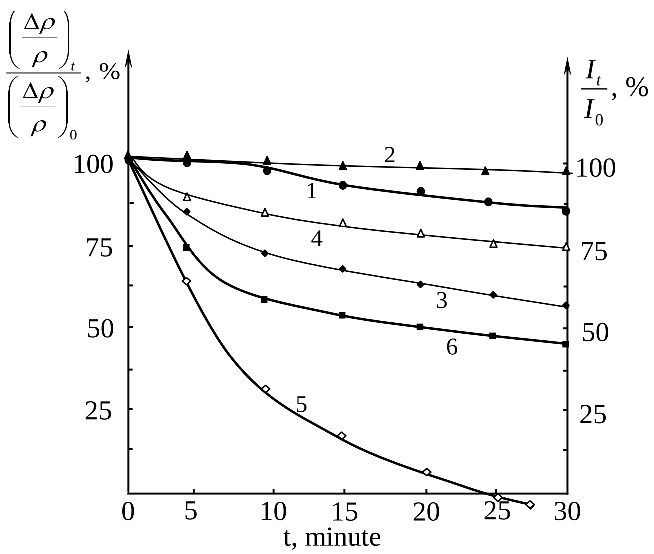

Fig. 3. Relative change in NMR (1,3,5) and photosensitivity at λ = 1,5 micron (2,4,6) in silicon samples with nanoclusters as a function of thermal annealing duration at various temperatures. 1, 2 -T = 150 ° C, 3, 4 -T= 180 ° C T 5, 6 - T= 200 ° C.

III. CONCLUSION

Results of the study show that increase in thermal annealing temperature in samples with nanoclusters, brings forward accelerated change in the value of NMR and photosensitivity at λ = 1,5 micron. After t = 25 minutes at temperature of thermal annealing of T = 200°C, MR changes its value from negative to positive MR (PMR).
The results show that Si <B, Mn> samples with nanoclusters, thermal stability could be explained by strongly conservation in nanoclusters of the Coulomb balancing, repulsion of manganese atoms and mutual attraction of manganese and boron atoms.

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Thus, these results show that silicon with magnetic nanoclusters is a promising novel material for modern spintronics and optoelectronics, i.e. one can use this material to create sensitive magnetic and photomagnetic devices.

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