Structural, electronic, and magneto-optical transformations in monocrystalline KDB-3 Silicon doped with manganese via high-temperature diffusion

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ABSTRACT

In the study, the influence of high-temperature manganese diffusion on the structural and electro-optical properties of monocrystalline KDB-3 silicon was analyzed. The surface morphology changes were investigated using atomic force microscopy, and Hall effect measurements were conducted. A sharp increase in the specific resistance of silicon, by more than three orders of magnitude, was identified after manganese diffusion at 1473 K. A significant decrease in charge carrier concentration and mobility was studied, indicating the formation of electrically active defect complexes involving Mn, B, and O atoms. A temperature-dependent conductivity type transition from p-type to n-type was determined within the range of 250–1250 °C, suggesting a Fermi level shift due to deep manganese states. Resonance-like effects observed in the impedance spectra were established and are presumably linked to localized plasmonic modes. A mechanism involving valence state transitions of manganese (Mn^{2+}, Mn^{+}, Mn^{0}) and the formation of neutral Mn–O complexes at elevated temperatures was formulated. It was proposed that the results enable targeted tuning of silicon's optical and electronic properties for potential applications in spintronic and plasmonic devices. A research direction was developed involving broadband impedance analysis and X-ray diffraction to clarify the nature of the observed effects.

Keywords: silicon, magneto-optical transformations, manganese, magneto-optical effects, doping, high-temperature diffusion, electro-optical properties, conductivity, charge states, nature of chemical bonding, magnetic properties of silicon, spintronics

1. INTRODUCTION

Silicon-containing semiconductor materials are one of the key components of modern electro-optics, photoelectronic, and microengineering. Control of their physical, chemical, and electrophysical properties, in particular by diffusion doping, plays an important role in the creation of highly efficient functional devices. Particular attention is currently paid to high-temperature doping processes, as they are capable of initiating the formation of complex nanoclusters, ion-covalent bonds of particles, as well as new phase structures in the silicon lattice. These structural rearrangements, in turn, can significantly affect the optical, electronic, and magnetic characteristics of the material, opening up opportunities for their targeted modification in the interests of photonics, spintronics, and plasmonics. In this context, the study of the mechanisms of formation of defect complexes and their influence on the functional properties of doped silicon is becoming relevant from both fundamental and applied points of view.

Let us briefly analyze previously published works devoted to the high-temperature diffusion method[1-4] and the electrophysical properties of silicon doped with manganese.

When comparing compensated (p-Si⟨B,Mn⟩) and overcompensated (n-Si⟨B,Mn⟩) samples with specific resistances at 300 K from 103 to 105 Ohm cm (samples of group I) with those doped with manganese and obtained by the method of loading and unloading at a high temperature, with similar specific resistances (samples of group II), it was experimentally established[1] that the structure of the nanocluster consists of a negatively charged boron atom, which is located in the center of four positively charged manganese atoms located in the nearest equivalent Intersolar positions,

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i.e. $[(Mn)_4^{n+}B^-]^{(n-1)+}$, and the charge state of the nanoclusters changes depending on the position of the Fermi level in the range from $[(Mn)_4^{8+}B^-]^{7+}$ to $[(Mn)_4^{4+}B^-]^{3+}$, i.e. nanoclusters act as multi-charged centers, with microscopic hole capture cross-sections. The authors attribute the discovered giant impurity photoconductivity and very low hole mobility to the presence of multi-charged centers.

In[2], the properties of KDB-5 silicon alloyed with manganese by diffusion in the 1100–1300°C temperature range were studied. It was found that with an increase in the diffusion temperature in the range of 1175–1300°C, the concentration of electroactive manganese atoms decreases, and at t = 1300°C their number becomes significantly less than the concentration of the initial boron impurity. According to the authors, this may be due to the formation of electrically neutral quasi-molecular complexes between oxygen and manganese atoms located in neighboring nodal states.

In the article[6-7], the authors state that manganese and oxygen atoms in silicon interact in diffusion annealing processes in the temperature range T=1160÷1330°C to form electrically neutral chemically bonded complexes (molecules). The effective temperatures at which almost all introduced manganese atoms participate in such complex formations are T=1320÷1330°C. and confirm that impurity manganese atoms form electrically neutral chemically bonded complexes with elements of group VI (O, S, Se), the effective temperatures of which are T=1320÷13300°C, T=1100÷1110°C, T=820÷830 °C, respectively.

Deep levels (DL) arising in silicon after its doping with manganese have been studied for many years by various methods; these studies were conducted mainly in two directions. The authors of the works related to the first of them[8-9] measured the energy position of the corresponding DL and its recombination characteristics. In the works related to the second direction[10-11], the structure of the introduced center, its nature, charge state, and local symmetry in the crystal lattice of the matrix were studied. These studies showed that manganese atoms can be in Si in various crystallographic positions and charge states Mn^{++}, Mn^{+}, Mn^{0}, Mn^{-}, Mn^{--}, $(Mn^{0})_4$, etc., depending on the initial material, heat treatment (HT) modes, and cooling after diffusion. Such a variety of manganese states, its ability to form complexes, and instability of some states even at room temperature significantly complicate the determination of the parameters of DL associated with Mn, and often lead to contradictions in the results and the interpretation of experimental data. It should be noted that the work in both directions was carried out almost independently of each other, and it is not always possible to identify with sufficient confidence any DL with a certain state of manganese atoms in the silicon lattice.

2. STATEMENT OF THE PROBLEM

This research addresses the complex physicochemical and structural transformations that occur in crystalline silicon doped with manganese (Mn) during high-temperature diffusion processes. Within the framework of materials science focusing on electronic, optical, and magnetic materials, the study aims to analyze and evaluate the mechanisms underlying the rearrangement of structural units and defect complexes in the Si<Mn, B, O> system. The problem is formulated through the following specific research objectives:

- To investigate the influence of stepwise thermal loading on the lattice parameters of the initial KDB-3 silicon crystal;
- To study the atomic/molecular oxygen redistribution mechanism during Mn diffusion and its role in the formation of defect structures;
- To determine the most probable thermodynamic and kinetic states of the material before and after high-temperature diffusion;
- To reliably assess the formation and configuration of structural defects involving Mn, B, and O atoms in the silicon matrix;
- To elucidate the mechanism of conductivity transformation of the host Si crystal upon Mn doping in the presence of oxygen;
- To identify the pathways and optimal temperature regimes for the complexation process in the Si<Mn, B, O> system;
- To evaluate the nature and energy levels of transitions within the defect complex, affecting the optical and electrophysical response;

- To perform comparative analysis of the known electrophysical parameters of the material before and after diffusion processing;
- To define the charge states of manganese (Mn^{2+} , Mn^{+} , Mn^{0} , Mn^{-} , Mn^{2-} , and potential molecular clusters such as $(Mn^{0})_4$) within the Si crystal;
- To assess the feasibility of employing high-temperature X-ray diffraction (XRD) analysis up to 3000 K for reliable structural characterization of the Si<Mn, B, O> complex.

This set of research questions is essential for the development of advanced silicon-based materials with tunable properties, relevant for optoelectronic, spintronic, and plasmonic applications.

3. EXPERIMENTAL PART

For the experiment, silicon of the KDB-3 grades (dimensions: 8:4:1 mm, chemical purity: 99.9%, resistivity: $\rho = 2.3\times10^3$ Ω·cm) was used. The sample was doped with manganese using the high-temperature diffusion method. The activation energy of diffusion was $E_a = 2.49$ eV, the diffusion temperature was $T_D = 1200 + 273.15^0$ K, and the diffusion time was t = 1×3600 s. The diffusion coefficient at infinite temperature was $D_0 = 0.65$ cm^2/s. The surface concentration of the diffusant was $C_0 = 2\times10^{16}$ cm^{-3}. The initial impurity concentrations in the silicon were $C_{01} = 7.0\times10^{15}$ cm^3 and $C_{02} = 1.1\times10^{15}$ cm^3. The Boltzmann constant used was $k = 8.625\times10^{-5}$ eV/K. Surface morphologies of the sample before and after high-temperature diffusion were examined using an atomic force microscope (FM-Nanoview 1000 AFM), and the electrophysical parameters were studied using the Ecopia Hall Effect Measurement System (HMS-7000).

4. RESULTS AND DISCUSSION

It was found that in the temperature range of 250 – 350 °C the original Si sample exhibits p-type conductivity, and in the range of 1000 - 1250 °C it exhibits n-type conductivity. Let us present the main experimental results obtained:

(a) (b)

Figure 1. KDB-3 silicon sample in its initial state (a) and placed inside the ampoule (b).

Table 1. Electrophysical parameters of silicon samples before and after manganese doping.

Samples	Specific resistance, ρ, ohm·cm	Mobility μ, $cm^2/V\cdot s$	Charge carrier concentration N, cm^{-3}
Si<B> (KDB-3, before doping)	3	300	$7\cdot10^{15}$
Si<B,Mn>	$2.3\cdot10^3$	60	$4.5\cdot10^{13}$

Table 1 compares the electrophysical properties of Silicon samples before and after their legalization with manganese. These experimental studies have shown significant changes in the electro-physical properties of samples of Silicon (Si<B,Mn>), which are legitimized at high temperatures with manganese atoms. After manganese diffusion:

- Specific resistance increased significantly (3 ohm·cm → 2.3×103 ohm·cm).
- Charge carrier mobility decreased (300 cm^2/V·s → 60 cm^2 / V·s.
- While the concentration of charge carriers decreased dramatically ($7×10^{15}$ cm^{-3} → 4.5×1013 cm^{-3}).

These changes are associated with binding centers, defects, and structural disturbances that occur in the crystal lattice, confirming the important role of manganese in controlling the semiconductor properties of the material. These results will serve as an important basis for the development of silicon materials, the properties of which will be controlled for electronic devices in the future.

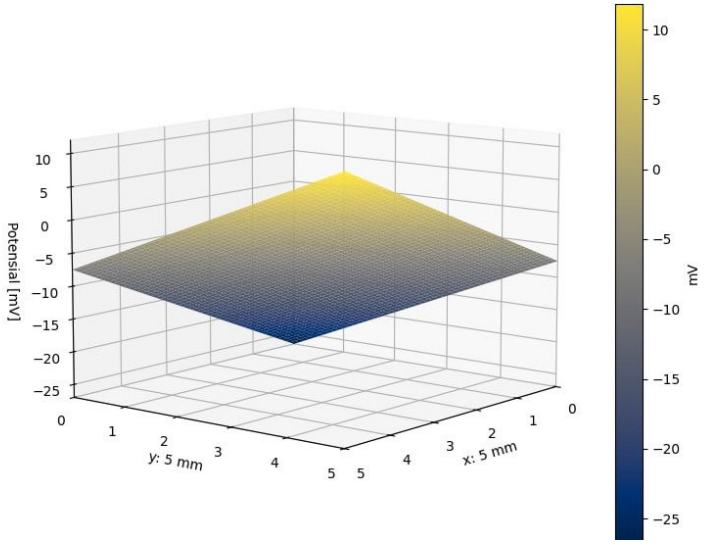

Figure 2. Surface relief of the original sample before high-temperature diffusion.

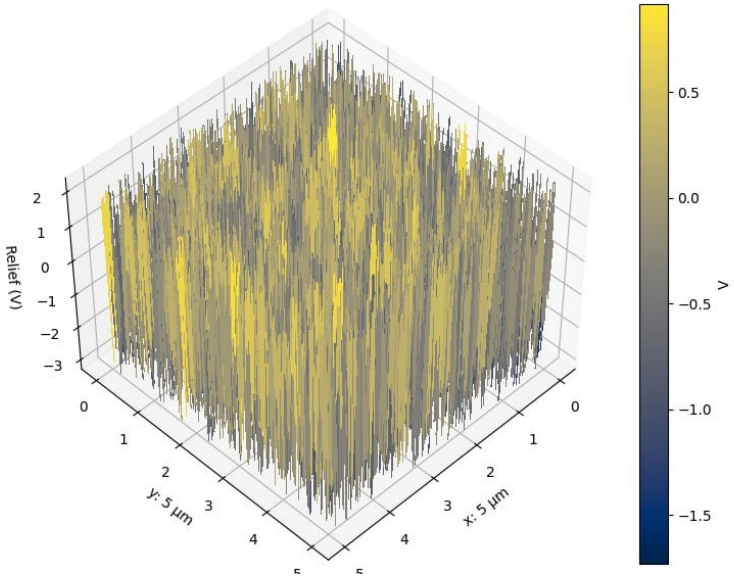

Figure 3. The surface relief of the sample after high-temperature diffusion.

$$T := 1000..1600; \quad D(T) := Do \cdot \exp\left(\frac{-Ea}{k \cdot T}\right); \quad D(T) := 2.004 \times 10^{-9} cm^2 / s.$$

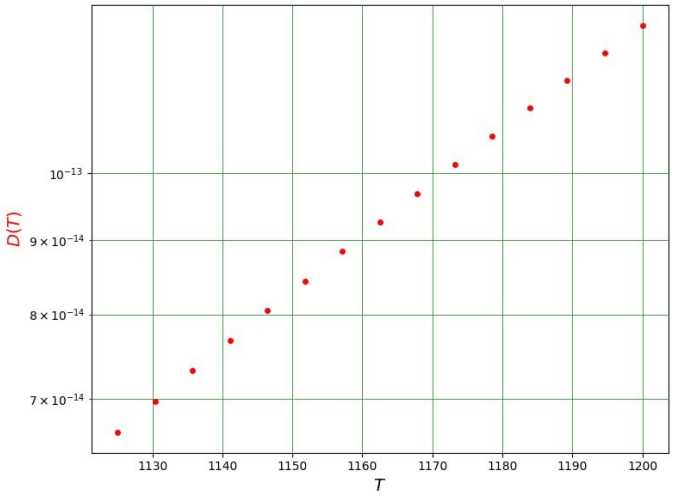

Figure 4. Temperature dependence of the diffusion coefficient.

Within the framework of this study[12-13], a software and toolkit were developed using modern, most widely used technologies, such as the Python programming language, Django frameworks, sets of visualization libraries, numpy, pandas, scipy, matplotlib, requests, etc.

The experimental studies showed that the KDB-3 crystalline silicon sample has p-type conductivity in the temperature range of 250-350 °C and n-type conductivity in the range of 1000-1250 °C. This is due to the electronic changes that occur when silicon is doped by manganese diffusion. Analysis of the electrophysical parameters showed that in the manganese-doped sample, the specific electrical resistance increased from 3 ohm cm to 2.3 × 10^3 ohm cm, and the mobility decreased from 300 cm^2/V·s to 60 cm^2/V·s, indicating that the binding centers and barriers arose as a result of doping. At the same time, the concentration of charge carriers decreased significantly (from 7 ·10^{15} cm^{-3} to 4.5·10^{15} cm^{-3}), indicating a sharp change in the electrical properties of the material.

The results of 3D scanning of the surface relief (Figures 2 and 3) show that after high-temperature diffusion in the sample, significant irregularities and structural changes were formed on the surface. This condition is explained by disturbances and atomic redistributions occurring in the crystal lattice during the diffusion process. The diffusion coefficient of manganese atoms was determined to be approximately $D(T) \approx 2.004 \times 10^{-8} cm^2 / s$, evaluated using the Arrhenius equation. These results indicate that the diffusion process of manganese in silicon occurs intensively at high temperatures, suggesting that the electrical and structural properties of silicon can be purposefully controlled through this method.

5. CONCLUSION

Thus, the conducted studies show the relevance of studying the structural and physicochemical transformations in manganese-doped single-crystal silicon for promising optical, magnetic, and electronic materials. It was revealed that in the temperature range of 250 - 350 °C, the original Si sample exhibits p-type conductivity, and in the range of 1000 - 1250 °C, n-type conductivity. Such temperature-dependent behavior indicates a shift in the Fermi level due to the activation of deep states of manganese and the formation of complex defect structures.

The results show that the formation of stable Si<Mn, B, O> complexes significantly affects the electrophysical and potentially magneto-optical properties of the material. However, the exact mechanism of such complex formation

remains unresolved. The final determination of the structural nature and distribution of the charge state of manganese in the silicon matrix requires further study. Additional high-temperature X-ray diffraction (XRD) analysis and broadband impedance spectroscopy are proposed. These methods will allow reliable characterization of the defect landscape and electronic transitions in the Si<Mn, B, O> system before and after thermal treatment. Such studies are crucial for the development of tunable semiconductor materials with individual functions for spintronic, plasmonic, and optoelectronic devices.

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