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Physical mechanism of gettering of impurity Ni atom clusters in Si lattice

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Abstract. This article presents the gettering mechanism and the physical model of impurity Ni atom clusters in the Si crystal lattice. The study finds out that the formed Ni atom clusters lead to gettering various rapidly diffusing impurities, both present in the Si lattice and introduced, as well as oxygen atoms, by stimulating generation of recombination centers of thermal and radiation defects.

Keywords: silicon, cluster, gettering, nickel, thermal donors, lattice, physical mechanism, impurity.

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1. Introduction

Semiconductor materials used in electronic industry always contain sufficient concentrations of uncontrolled oxygen as well as rapidly diffusing impurities such as copper, chromium, iron, cobalt, *etc*. During manufacturing semiconductor devices, the initial Si undergoes various thermal impacts that lead to formation of thermal defects. In their turn, these defects change electrical and recombination properties of the material, hence, deteriorating the thermal stability of the parameters of the manufactured devices [1–3]. In this regard, neutralizing the influence of oxygen and other impurities on the electrophysical parameters of Si is one of the key challenges for modern electronics. Gettering of uncontrolled impurities from Si is mainly realized by introducing various metals (Au, Gd, Sm) and rare earth elements [4–6]. Gettering can be also performed using irradiation and laser treatment [7], or creation of a porous or amorphous layer on the Si surface by ion implantation [8]. Use of the methods mentioned above not only significantly affects the electrophysical parameters, but also induces structural changes to the source material. Therefore, the effectiveness of these methods is low that prevents their wide application in the electronics industry.

In this work, we propose a new original method that allows gettering of many uncontrolled impurities, including residual oxygen, which are activated by various thermal impacts or generate thermal defects, from the monocrystalline Si bulk. The study finds out that formation of electroneutral clusters of impurity Ni atoms in a Si crystal lattice leads to gettering of uncontrolled defects [9]. As is known [10, 11], Ni has a sufficiently high solubility ($N \sim 10^{18}$ cm^{-3}) and a high diffusion coefficient ($D_{Ni} \sim 10^{-5}$ cm^2/s at T = 1200 °C) in Si. The main part of the introduced Ni in the Si lattice is in the electroneutral state (99.99%). Ni atoms form electroneutral clusters that do not affect the electrophysical properties of the starting material [12]. The results of the study show that introduction of Ni at concentrations $N < 10^{14}$ cm^{-3} practically does not affect the electrical parameters of the initial *p*-type Si with a resistivity of $\rho < 100$ Ohm·cm and *n*-type Si with $\rho < 40$ Ohm·cm. In general, electroneutral clusters of Ni atoms in Si act as powerful and efficient gettering centers.

2. Experimental results

The starting material was single-crystalline (111) *p*-type Si with a resistivity ρ = 40, 10, 5, 3, and 1 Ohm·cm and a dislocation density $S \le 10^3$ cm^2. The initial Si samples were doped during t = 30…60 min from a sprayed Ni layer in a vacuum both in evacuated ampoules and in open furnace. The doping temperature was T = 1200 °C. The state of the Ni clusters was studied using a scanning electron microscope. The cluster composition was confirmed by energy-dispersive X-ray spectroscopy (EDS).

Fig. 1 shows scanning electron microscopy images of the formation process of Ni atom clusters in Si. The Ni clusters were formed as a result of diffusion annealing with subsequent cooling down at a rate of ~ 20 °C/s. The images were obtained using a MIRA 3 TESCAN scanning electron microscope. The obtained results demonstrated that formation of Ni clusters did not depend on the type and initial concentration of impurity atoms in the Si wafer. The cluster size, shape and concentration were mainly determined by the temperature, diffusion time and cooling rate of the Si samples after the diffusion.

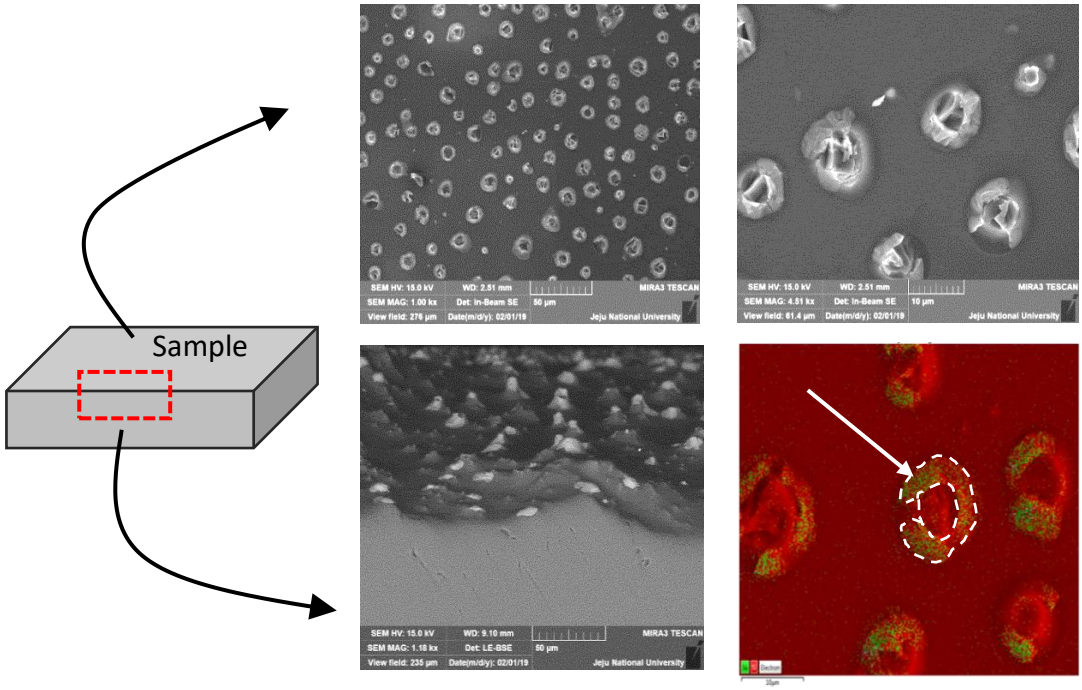

Fig. 1. Distribution of Ni atom clusters in Si doped at T = 1200 °C, obtained using a MIRA 3 TESCAN scanning electron microscope (field-emission scanning electron microscope, FE-SEM).

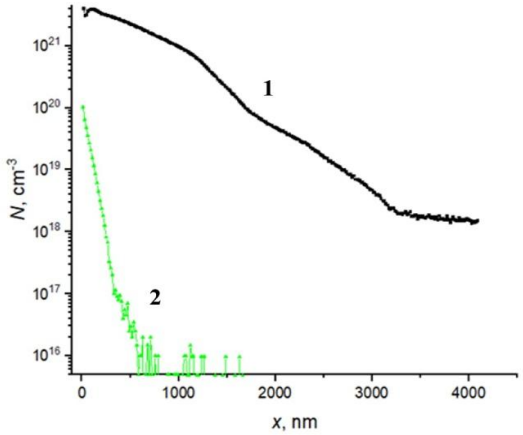

Fig. 2. Distribution of Ni atoms in the front (*1*) and back (*2*) layers of Si after diffusion from a Ni film deposited on one Si surface.

Analysis of the obtained results made it possible to conclude that decrease in the cooling rate induced increase of the cluster size to several hundred nanometers [13].

It was found out that Ni atoms not only had a fairly high volumetric solubility in the Si samples (N_{Ni} ~ 10^{17} cm^{-3}), but also a very high solubility in the near-surface region (d = 2…3 μm), where their concentration could reach N_{Ni} ~ 10^{20}…10^{21} cm^{-3} (Fig. 2) [14, 15].

It was observed that, depending on the conditions of diffusion and thermal annealing, Ni atom clusters were formed both on the surface and in the bulk of silicon. Based on the IR microscopy, SEM and SIMS results, the surface density of the formed Ni atom clusters was determined to be ~ 10^{6}…10^{7} cm^{-2}. The number of Ni atoms in a cluster was about 10^{5}…10^{7}, and the cluster concentration in the Si bulk was ~ 10^{12}…10^{15} cm^{-3}. The composition of the Ni clusters after diffusion and additional thermal annealing was determined. After the additional thermal annealing, the concentration of Ni atoms in the clusters increased by ~ 30…40%, the concentration of oxygen by ~ 10…20%, and the concentration of other uncontrolled impurities by ~ 20…40%. It was found out that Ni atom clusters getter rapidly diffusing impurities, which act as recombination centers in Si (Fig. 3).

3. Discussion

During diffusion annealing and cooling down, electrically neutral Ni atoms in Si form nuclei for cluster formation. Additional thermal annealing activates the processes of cluster formation and growth. Electrically neutral Ni atoms in the clusters are located in the nearest

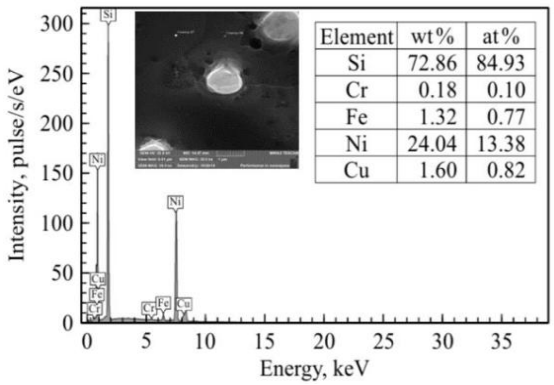

Fig. 3. Spectrum and composition of Ni clusters obtained using the SEM elemental analysis tool.

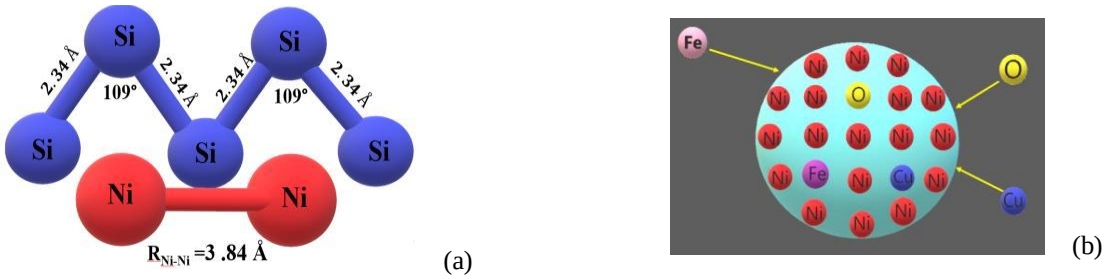

Fig. 4. a) Structure of a Ni atom cluster and b) model of the process of gettering of uncontrolled defects by Ni atom clusters. (Color online)

equivalent interstitial positions in the Si crystal lattice forming a partially or completely filled cubic Ni sublattice. The chemical bonds between the Ni atoms in Si are predominantly metallic in nature.

According to the proposed structure, the Ni atom clusters in Si were simulated by the Avogadro and Chem3Dvisualiser softwares. The 3D structure of a cluster formed in the Si lattice was studied. Based on the calculation results, the following interatomic distances in the clusters were determined: oxygen-nickel – $R_{O\text{-}Ni}$ ~ 4 Å, oxygen-oxygen – $R_{O\text{-}O}$ ~ 3.84 Å, nickel-nickel – $R_{Ni\text{-}Ni}$ ~ 3.84 Å, silicon-silicon – $R_{Si\text{-}Si}$ ~ 2.34 Å, and nickel-silicon – $R_{Ni\text{-}Si}$ ~ 4.5 Å. Such model of a Ni atom cluster in Si not only agrees quite well with the obtained experimental results, but also explains the physical mechanism of cluster migration in the Si lattice.

The obtained experimental results and the proposed physical model of the Ni cluster structure not only point to a discovery of a new physical phenomenon, namely migration of impurity clusters in Si, but also makes it possible to control the clusters state. This enables creation of Ni atom clusters in Si, which may be considered as a creation of a new class of photonic materials with bulk superlattices. The obtained research results may be summarized as follows: Si samples doped with Ni atoms by diffusion have unique functionality for creating optoelectronic, nanoelectronic and photoelectric devices as well as sensors of a new generation. A more comprehensive study of the physical properties of Si with Ni atom clusters has revealed new physical phenomena absent not only in doped semiconductor materials, but also in Si with clusters of different impurities.

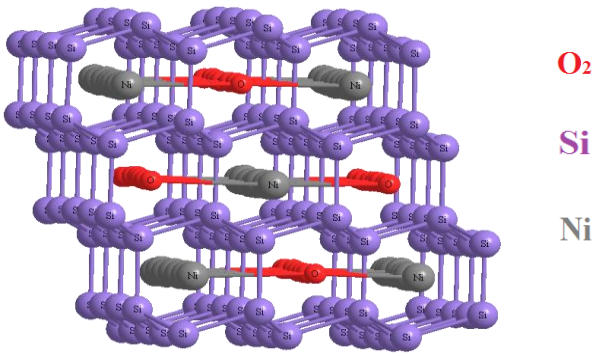

Fig. 5. Sublattice of a Ni atom cluster in Si lattice. (Color online)

4. Conclusions

- Electroneutral Ni atoms have gettering properties. They reduce the concentration of recombination centers by capturing uncontrolled impurity atoms and increase the lifetime of minority charge carriers in Si.
- During diffusion in the Si bulk, a number of complex types with Ni atoms form: interstitial nickel – interstitial silicon (Ni-Si), nickel-oxygen (Ni-O), nickel-uncontrolled impurities (Ni-Cu, Ni-Fe, *etc*.), and nickel-nickel. Moreover, a deposited metal Ni layer getters uncontrolled impurities from the Si bulk.
- During cooling down, atomic complexes interact with each other and form clusters that accumulate near defective regions of the crystal lattice.
- During annealing, defect clustering process (including interstitial Ni atoms) is activated. The Ni clusters grow and getter (dissolve) uncontrolled recombination-active impurities thus reducing their bulk concentration.

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Фізичний механізм гетерування кластерів домішкових атомів нікелю в ґратці кремнію

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Анотація. У статті наведено механізм гетерування та фізичну модель кластерів домішкових атомів нікелю в кристалічній ґратці кремнію. Дослідженнями встановлено, що утворені кластери атомів нікелю приводять до гетерування різноманітних швидкодифундуючих домішок, як присутніх у ґратці кремнію, так і введених, а також атомів кисню, стимулюючи генерацію центрів рекомбінації теплових і радіаційних дефектів.

Ключові слова: кремній, кластер, гетерінг, нікель, термодонори, ґратка, фізичний механізм, домішка.