Formation of iron impurity clusters in silicon

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Abstract: This article discusses the formation of impurity clusters in the bulk of single-crystal silicon doped with iron using high-temperature (T = 1300 °C) diffusion. Schematic models of the formation sequence of spherical, needle-shaped, and lenticular impurity clusters in the bulk of iron-doped n-type silicon samples are also presented. It was revealed that the quantitative fraction of iron atoms (by mass) in the volume of single-layer impurity clusters reaches ~50%, which corresponds to iron silicide FeSi2. In contrast, in the bulk of bilayer clusters, this value in the inner layer reaches ~66.5%, and it corresponds to iron silicide FeSi. And in the outer layer of such impurity clusters, the quantitative fraction of iron atoms is ~50%.

Keywords: impurity, clusters, silicon, iron, cooling rate

Introduction

Controlling the electrical properties of semiconductor materials by doping them with various impurities is widely used in the modern electronics industry. The introduction of donor or acceptor impurities into the bulk of a semiconductor material allows for targeted modification of the concentration and type of charge carriers, resistivity, Fermi level position, and other important electrical parameters of the material. By controlling the impurity concentration, the material's conductivity can be varied over a very wide range - from a lightly doped semiconductor to a degenerate state similar in properties to a metal. Increasing the concentration of impurity atoms leads to an increase in the number of free charge carriers, but can also reduce their mobility due to increased scattering by impurity ions. Furthermore, bulk clusters of impurity atoms, which arise when impurity atoms are introduced into a semiconductor material, also significantly affect the electrical, mechanical, optical, and recombination properties of the material [1-5]. The nature of the formation of impurity defects during diffusion doping of semiconductors is determined by the nature of the crystal lattice, the diffusion mechanism and the interaction of the impurity with the intrinsic defects of the crystal.

Materials and methods

To study the formation of impurity clusters, n-Si<Fe> samples were prepared using initial single-crystal silicon grown by the Czochralski method with a resistivity of ρ= 20 Ω·cm. Iron atoms with a thickness of ~100 μm were deposited onto pre-prepared parallelepiped-shaped silicon samples with corresponding dimensions of 1x4x8 mm by sputtering. Iron diffusion in silicon was carried out at a temperature of T = 1300 °C for 2 hours in a SOUL-4 furnace. The samples were placed in closed ampoules where the vacuum was ~10^{-3} Torr. After diffusion annealing, the samples were cooled slowly (υ_{cool} = 0.05 °C/s) and then rapidly (υ_{cool} = 200 °C/s). Structural studies were conducted using a state-of-the-art JSM-IT200 scanning electron microscope and a Superprobe JXA-8800R electron probe microanalyzer. These devices enable highly accurate study of the morphological parameters of impurity clusters forming in the near-surface regions and within the bulk of silicon samples.

Results and discussion

Comprehensive electron microscopy studies of the structure of n-Si<Fe> samples obtained by slow and rapid cooling after diffusion annealing have enabled us to identify the key morphological parameters of the forming iron impurity clusters within the bulk of silicon. Figure 1 shows a photograph of an n-Si<Ni,Fe> sample obtained by rapid cooling. Needle- and lens-shaped iron impurity clusters, reaching sizes up to ~200 nm, are observed within the sample. These impurity clusters have a single-layer structure. Structural analyses have shown that, unlike the fast-cooled n-Si<Ni,Fe> samples, the slow-cooled samples, in addition to needle- and lens-shaped clusters, also contain larger (up to ~400 nm) impurity clusters, which are mostly spherical (Fig. 2). Similar, relatively large clusters with spherical shapes have a two-layer structure.

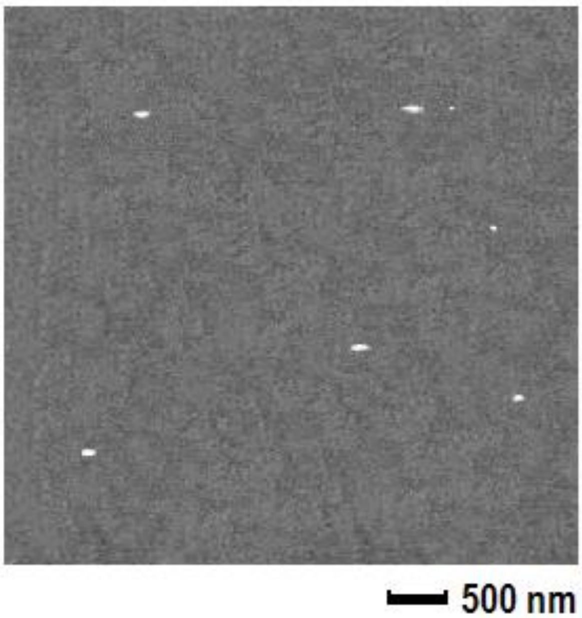

Fig. 1. Photograph of impurity clusters in n-Si<Fe> samples obtained with υ_{cool}=200 °C/s

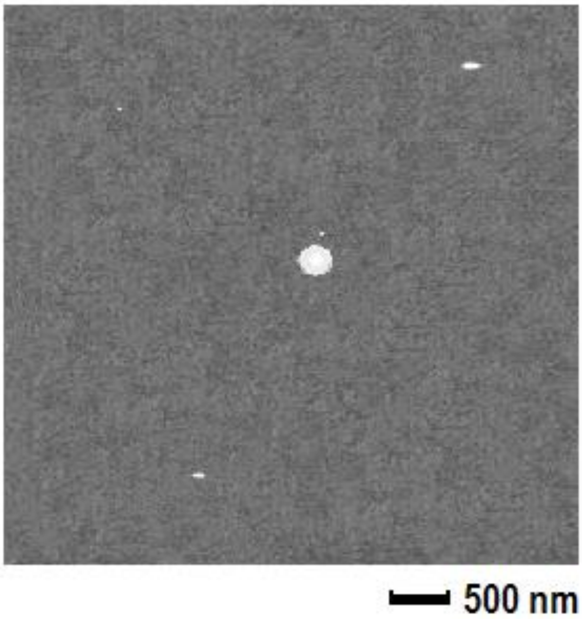

Fig. 2. Photograph of impurity clusters in n-Si<Fe> samples obtained with υ_{cool}=0.05 °C/s

The results of the analysis of the initial stages of the formation of micro- and nanoclusters of iron impurity atoms in silicon during diffusion doping at high temperatures (T = 1300 °C) and the processes of their growth showed that the presence of a strong influx of iron impurity atoms into the reaction zone around vacancy pores, dislocations, and microcracks formed in the crystal structure of Si [6-8] leads to the formation of $FeSi_2$ silicide as an independent phase. As the diffusion process continues, the influx of Fe impurity atoms into this zone continues, and, due to the instability of this phase, the formation of a relatively stable FeSi silicide layer in the inner region is observed. It should be noted that the main factor influencing this formation of iron impurity clusters is the cooling rate of the samples after diffusion. The higher its value ($\upsilon_{cool} \geq 200$ °C/s), the smaller the size of the resulting impurity clusters, which primarily have a single-layer structure, i.e., consist of $FeSi_2$ silicide. The size of such impurity atom clusters can reach several hundred nanometers, and therefore they can be called impurity nanoclusters.

Analysis of the elemental composition of impurity clusters revealed that the proportion of iron atoms (by mass) in the volume of single-layer impurity clusters does not exceed ~50%. Within the volume of two-layer clusters, the proportion of iron impurity atoms in each layer has a specific value. In the central part, i.e., in the inner layer of the two-layer cluster, this value reaches ~66.5%, and in the outer layer, it is ~50%.

Figure 3 shows a schematic model of the formation sequence of spherical silicide phases of impurity clusters in the bulk of n-Si<Fe> samples during diffusion alloying. According to the results of these studies, in slowly cooled (υ_{cool} = 0.05 °C/s) samples, at the initial stage of spherical cluster formation, an outer layer of the impurity cluster containing the silicide $FeSi_2$ forms, while within this layer, another type of silicide, FeSi, forms, which constitutes the inner layer of this cluster.

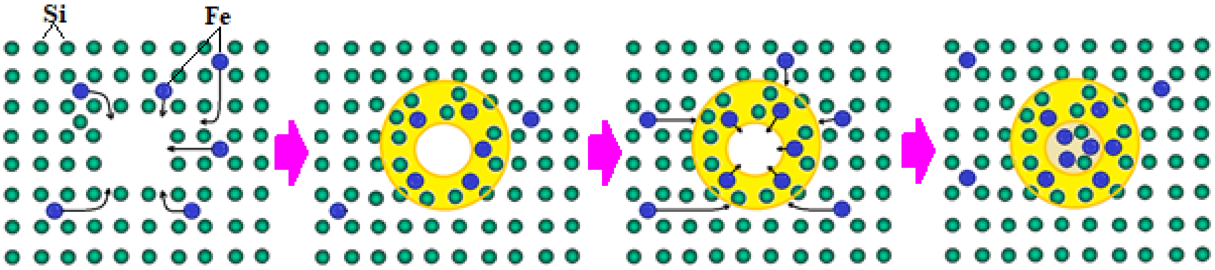

Fig. 3. Schematic model of the sequence of formation of spherical silicide phases of impurity clusters in n-Si<Fe> samples

Figure 4 shows a schematic model of the formation of needle-shaped (a) and lens-shaped (b) nanoclusters in the volume of rapidly cooled (υ_{cool} = 200 °C/s) n-Si<Fe> samples. As you can see, such impurity accumulations are formed mainly in dislocation lines of the crystalline structure of silicon, which are formed under the influence of high diffusion temperatures.

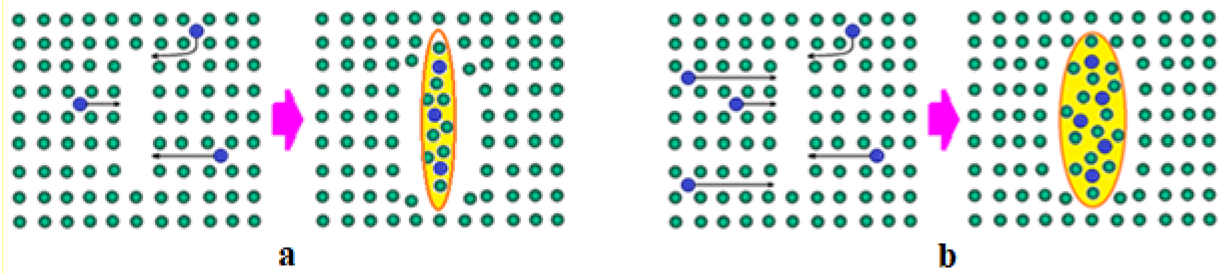

Fig.4. Schematic model of the formation of needle-shaped (a) and lens-shaped (b) impurity nanoclusters in n-Si<Fe> samples

In silicon, the formation of silicides in the crystal lattice due to the interaction of metal and silicon leads to a sharp decrease in volume. This may be the primary cause of internal stress in clusters. The simplest method for calculating the volume change resulting from the reaction between metal and silicon is based on the atomic volume of the reacting elements and the molecular volume of the resulting compound. For the following compound formation process:

$$xM + ySi \rightarrow M_xSi_y$$

where: x is the number of metal atoms, y is the number of silicon atoms.

The change in volume ΔV(%) can be calculated using the following expression [9]:

$$\Delta V = \frac{(xV_M + yV_{Si}) - V(M_x\,Si_y)}{(xV_M + yV_{Si})} \cdot 100\%$$

where: V is the molecular volume, x and y are the number of metal and silicon atoms in the silicide M_xSi_y, respectively.

This volume change during the formation of metal silicide within micro- and nanoclusters formed within the bulk of a silicon single crystal leads to a pressure difference at the boundary between the Si single crystal and the impurity cluster. Specifically, during the formation of iron clusters in silicon, the volume reduction of the iron silicide region is ~22%, creating a pressure difference at the boundary between the impurity cluster and the base Si crystal.

Conclusions

Thus, based on the obtained results, it was revealed that the main factor influencing the formation of iron impurity clusters in silicon is the cooling rate of the samples after diffusion. The higher its value ($\upsilon_{cool} \geq 200$ °C/s), the smaller the size of the impurity clusters formed. It was found that in the samples, at the initial stage of spherical cluster formation, a silicide layer with the smallest proportion of iron atoms forms, while in the inner region of this layer, silicide layers with an increasing proportion of iron atoms form. During the formation of iron impurity clusters in silicon, the reduction in the volume of the iron silicide region leads to the emergence of a pressure difference at the boundary of the impurity cluster and the silicon matrix element.

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