DEFECT FORMATION IN IRON-DOPED SILICON SINGLE CRYSTALS

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Abstract: The effect of diffusion alloying with iron on the electrical properties of heat-treated silicon obtained by the Czochralski method has been studied. It is shown that the presence of iron reduces the concentration of nucleation centers for thermal donors of "growth" origin. The latter circumstance caused a decrease in their initial speed; on the other hand, the admixture of iron reduced the probability of decay of thermal donors, leading to their transformation into an electrically passive state, which led to an increase in the concentration of thermal donors during prolonged heating. Heat treatment at temperatures above 600°C caused the iron impurity to lose its electrical activity. Hardening of Si <Fe> crystals from 1100÷1200 °C for 10 hours returned the iron atoms to the electrically active substitution position.

Keywords: morphology, vacancy, mobility, temperature, diffusion, composition, surface, thermal donors.

ДЕФЕКТООБРАЗОВАНИЕ В МОНОКРИСТАЛЛАХ КРЕМНИЯ, ЛЕГИРОВАННОГО ЖЕЛЕЗОМ

Аннотация: Исследовано влияние диффузионного легирования железом на электрические свойства термообработанного кремния, полученного методом Чохральского. Показано, что присутствие железа снижает концентрацию зародышей термодоноров «ростового» происхождения. Последнее обстоятельство вызвало снижение их начальной скорости; с другой стороны, примесь железа снижала вероятность распада термодоноров, приводя к их переходу в электрически пассивное состояние, что приводило к увеличению концентрации термодоноров при длительном нагреве. Термическая обработка при температурах выше 600°C приводила к потере электрической активности примеси железа. Закалка кристаллов Si<Fe> от 1100÷1200 °C в течение 10 часов возвращала атомы железа в электрически активное положение замещения.

Ключевые слова: морфология, вакансия, подвижность, температура, диффузия, состав, поверхность, термодоноры.

INTRODUCTION

Silicon is the basic material of modern microelectronics. In addition, sensors, micro- and nanoelectromechanical systems, and other hybrid products of nanotechnology are manufactured on its basis. Doping of silicon with iron is widely used to reduce the lifetime of charge carriers and, accordingly, to increase the speed of semiconductor devices [1]. On the basis of silicon doped with iron, highly sensitive IR photodetectors are manufactured [2]. However, the effect of heat treatment on the properties of these materials has practically not been studied. It is known that among transition metals, the study of the properties of the interaction of iron (Fe) atoms in silicon is of great interest: after all, the iron (Fe) atom is one of the most common metals in technology, and it has a high probability of sudden deposition on its surface during silicon heat treatment. Due to the large diffusion coefficient of the iron atom (Fe), it spreads throughout the entire depth of the crystal, and due to the large transverse holding capacity of charge carriers on the surface of iron, even a very small concentration of iron atoms there can reduce the residence time of charge carriers in semiconductors. The relevance of such studies is due to the fact that at various stages of the technological process of manufacturing semiconductor devices (oxidation, diffusion, fit into a housing, etc.), silicon wafers are subjected to temperature effects, leading to the formation of various structural defects and impurity precipitates. These processes lead to a decrease in the yield of suitable devices.

EXPERIMENTAL TECHNIQUE

In this work, the effect of diffusion alloying of iron on the electrical properties of heat-treated silicon obtained by the Czochralski method was studied. In the experiments, we used plates without dislocation silicon of the KEF-50 brand with different oxygen concentrations.

The oxygen concentration in the interstitial position was measured by IR absorption in the 10^{-6} sm^{-1} band and varied within $(6.0\div10.5)\cdot10^{17}$ cm^{-3}. The concentration of carbon in the substitution position, measured in accordance with the procedure [3], was $6\cdot10^{16}$ cm^{-3} in all the studied samples. The density of dislocations detected by selective etching did not exceed 10^2 sm^{-2} in all the studied samples.

Single-crystal silicon samples 0.7x14x15 mm in size with ρ = 50 Om·sm n-type in the temperature range 900÷1200 °C were annealed in an electric muffle furnace brand KSI-1075-1 for 10-12 hours. As a source of diffusion, iron deposited with VUP-5 was used on the polished surface of a silicon sample with carborundum powder M-14, M-10, M-7.

Silicon samples coated with iron were placed in quartz ampoules, which were evacuated to 10^{-5}. The maximum cooling rate for samples immersed in oil after diffusion is $\upsilon_0 \approx 300$ K/s, the minimum cooling rate is $\upsilon_0 \approx 25$ K/s.

To remove the residual part of impurity atoms from the surface, the samples were washed in hydrofluoric acid HF and a boiling mixture of HNO_3. The iron distribution profile was determined with an MII-4 microinterferometer by removing thin layers of doped silicon 0.2–0.5 μm using a CP-4-HF: HNO_2:CH_3COOH solution followed by washing in a boiling HCI: HNO_3 mixture. The thickness of the removed layers was determined with a digital thickness gauge, before and after the removal of the layers.

The Fe impurity concentration in these samples practically did not change during heat treatment and was close to the iron concentration in the initial plates (less than $5\cdot10^{12}$ sm^{-3}). The concentration of iron in the electrically active state was controlled by measuring the Hall effect in the temperature range 78÷300 K according to the standard method in the mode of constant electric and magnetic fields [4]. Generation of generation thermal donors was carried out at temperatures of 450–650 °C in air.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The study of the electrical and optical properties of silicon single crystals doped with iron made it possible to establish the following main regularities. It was found that the diffusion of iron leads to an increase in the efficiency of oxygen precipitation. On the other hand, in samples with a high oxygen concentration, almost no conductivity compensation was observed after Fe diffusion, while the iron concentration determined by neutron activation analysis was almost an order of magnitude higher than in samples with a low oxygen concentration. This is due to the fact that, during diffusion, Fe atoms effectively interact with single oxygen atoms and growing small oxygen complexes, which leads to a decrease in the concentration of interstitial oxygen and prevents the transition of iron to an electrically active state. It has been shown that the oxygen precipitates formed during the preliminary high-temperature treatment (1100–1200 °C, 50–70 h) accelerate the diffusion of iron, while no capture of Fe atoms by the formed oxygen precipitates is observed. This is due to the fact that oxygen precipitates formed at high temperatures are sinks for their own interstitial atoms, which contributes to the transition of gold atoms to an electrically active substitution position.

As was previously established [5], conventional high-temperature treatments and diffusion of Fe stimulate the formation of oxygen precipitates in Si, which can affect the generation of thermal donors.

Kinetic curves for the accumulation of these defects are not presented, since their shape was similar to those described in the literature, for example, in [6]. We note the main regularities:

preliminary heat treatment at a temperature of 925°C suppresses the generation of thermal donors in Si with a high oxygen content. At a low concentration of this impurity ($<6\cdot10^{17}$ sm^{-3}), preliminary heat treatment could stimulate the generation of thermal donors.

1) their initial rate of introduction and the maximum achievable concentration could exceed the corresponding parameters measured for samples not subjected to preliminary annealing;

2) in the samples cut from the central part of the plates of the studied ingots, an acceleration of oxygen precipitation was observed, and the rate of its removal from the interstitial position increased with an increase in the concentration of interstitial oxygen (N_0). In samples cut from the peripheral parts of ingots and having a reduced oxygen concentration due to evaporation during crystal growth, this effect did not manifest itself.

A comparison of the experimental results for samples with different concentrations of oxygen precipitates [7] showed that the presence of precipitates plays a dominant role in the process of suppressing the generation of thermal donors, but it does not appear to be unambiguous to associate this effect with a specific process occurring in a silicon-based solid solution of oxygen. possible.

It is possible that the nucleation centers for both thermal donors and oxygen precipitates at the initial stages of the formation of these defects are the same. It should also not be ruled out that the effective capture radius of moving particles decreases during the generation of thermal donors and the influence of elastic stress fields created by oxygen precipitates in the Si lattice. In addition, mobile particles can be "recaptured" by oxygen precipitates, which will also lead to suppression of the generation of thermal donors.

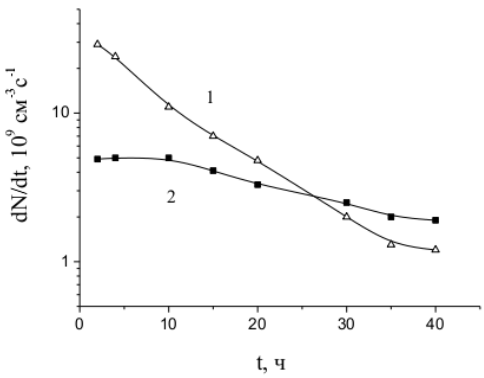

Fig. 1. Dependence of the rate of introduction of thermal donors 1 - control; 2 – Si<Fe>

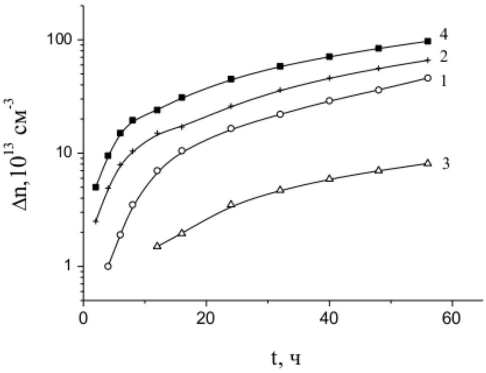

Fig. 2. Change in the electron concentration as a function of the duration of heating at 450°C: in silicon samples during heat treatment at 450°C. Pre-annealing modes: 1 - 880 °C, 24 h; 2 - 880 °C, 24 h (Fe diffusion); 3 - 1100°C, 70 h + 880°C, 24 h; 4 - 1100 °C, 70 h +880 °C, 24 h (Fe diffusion)

From the analysis of the presented figures, the following main conclusions can be drawn:

1) the admixture of Fe affects the kinetics of TD formation: at the initial stages of heating, a slowdown in the process of their formation was observed - the initial rate of introduction of thermal donors into Si <Fe> were less than in the control material;

2) as the duration of annealing increased, the thermal donors in the control material and Si <Fe> were compared in value; further heating led to a situation where the initial rate of introduction of thermal donors into Si <Fe> exceeded the corresponding parameter for control samples. As a result, the situation described in [8] and indicating the acceleration of the process of formation of thermal donors in silicon doped with iron was realized;

CONCLUSIONS

The results obtained indicate that the effect of iron on the processes of generation of thermal donors is manifested only when its concentration exceeds a certain threshold value, which in this case is ~ $5 \cdot 10^{13}$ sm^{-3} for all the crystals studied. With a decrease in N_{FE}, the noted effect weakened, and for samples cut from the upper part of the ingot, in which the iron content did not exceed ~ 10^{13} sm^{-3} [9-11].

Significant differences in the kinetics of accumulation of high-temperature thermal donors in the control silicon material, diffusion-doped iron, were not observed, since in this case the Fe atoms left the site position in the lattice and went to sinks. Hardening of Si<Fe> crystals from 1100÷1200°C returned gold atoms to the electrically active substitution position [12]. As for the increase in the efficiency of introducing thermal donors into Si <Fe> during prolonged annealing, the most probable mechanism is associated with a decrease in the probability of dissociation of thermal donors or with the transformation of these defects into associates that do not exhibit electrical activity.

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