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STUDY OF THE ROLE OF THE TECHNOLOGICAL IMPURITIES STATES IN THE FORMATION OF A DEFECTIVE STRUCTURE OF Si DOPED WITH TRANSITION ELEMENTS

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Abstract. *In this paper, the effect of high-temperature treatments on the development of a defect structure of silicon with transition elements is studied by using capacitive and infrared spectroscopy. It was found that the presence of bound states of technological impurities - particles of* SiO_2 *and* SiO_4*, in Si doped with transition elements leads to a change in the efficiency of the formation of deep levels associated with the atoms of manganese, cobalt and chromium.*

It was found that the presence of bound states of technological impurities in silicon, for example, SiO_2 *particles in the Si lattice, increases the efficiency of the deep centers formation created in the semiconductor band gap, while the presence of a* SiO_2 *film, on the contrary, prevents the introduction of T-ion impurities into the bulk of silicon.*

Keywords: *T-ions, silicon, manganese, chromium, cobalt, diffusion, formation efficiency, high-temperature treatment, technological impurity, bound state.-*

ИЗУЧЕНИЕ РОЛИ СОСТОЯНИЯ ТЕХНОЛОГИЧЕСКИХ ПРИМЕСЕЙ В ФОРМИРОВАНИИ ДЕФЕКТНОЙ СТРУКТУРЫ Si, ЛЕГИРОВАННОГО ПЕРЕХОДНЫМИ ЭЛЕМЕНТАМИ

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Аннотация. *В данной работе методами емкостной и инфракрасной спектроскопии изучено влияние высокотемпературных обработок на развитие дефектной структуры кремния с примесями переходных элементов. Установлено, что присутствие связанных состояний технологических примесей – частиц* SiO_2 *и* SiO_4*, в Si, легированном переходными элементами приводит к изменению эффективности образования глубоких уровней, связанных с атомами марганца, кобальта и хрома.*

Обнаружено, что наличие связанных состояний технологических примесей в кремнии, например, частиц SiO_2 *в решетке Si увеличевает эффективность образования глубоких*

центров, создаваемых в запрещенной зоне полупроводника, присутствие же пленки SiO_2, напротив, препятствует введению в объем кремния примесей Т-ионов.

Ключевые слова: *Т-ионы, кремний, марганец, хром, кобальт, диффузия, эффективность образования, высокотемпературная обработка, технологическая примесь, связанное состояние.*

1. Introduction

In recent years, the so-called unconventional impurities — impurities of T-ions (transition elements), which create a number of deep levels in the forbidden zone of silicon, have been used for the controlled formation of a defect structure in silicon [1-5]. These specially introduced impurities interact with various uncontrolled impurities in the process of technological treatments. In addition, it was found that various high-temperature treatments lead to a change in the defect structure of monocrystalline silicon. This is accompanied by the formation of various associated states of technological impurities, for example, oxygen atoms in silicon. Depending on the processing temperature, new phase states of technological impurities are formed - particles of the SiO_2 or SiO_4 type [6-9].

In this work, the role of the state of technological impurities in the formation of the defect structure of silicon doped with transition elements and the interaction of T-ion impurities (in particular, Mn, Co, Cr impurities) with the bound states of oxygen atoms in Si using DLTS (deep level transient spectroscopy) and infrared spectroscopy is investigated [10-13].

2. Experimental technique

Samples of Si were fabricated by heat treatment at a temperature of 1100°C for 12 hours. Further, the diffusion of Mn, Co or Cr atoms was carried out into these samples in the temperature range 900 - 1200°C for 2 hours. From the surface of Si samples, preliminarily subjected to high-temperature treatment and then doped with one of the T-ions, mechanically damaged layers were removed by grinding. Then, the resistivity and infrared absorption spectra were measured in these samples. For comparison, control samples were investigated that underwent repeated heat treatment under the same conditions as the diffusion of T-ions (T = 900 - 1250°C for 20 hours), as well as samples doped with T-ions without preliminary high-temperature treatment.

3. Results and discussion

It is known [13] that oxygen atoms precipitate occurs during high-temperature treatment at T = 1100°C, that is, free interstitial oxygen passes into the second phase with the formation of SiO_2 particles. Impurities of T-ions, when introduced into preliminarily heat-treated silicon, most likely settle on SiO_2 accumulations, as a result of which they, probably, lose their electrical activity. This explains the difference in the change of the resistivity in p-Si samples with T-ion impurities with and without preliminary high-temperature treatment.

Figure 1 shows the infrared absorption spectra of the initial control samples of n-Si (curve 1), n-Si subjected to high-temperature treatment (curve 3), n-Si doped with manganese (curve 2), n-Si, preliminarily subjected to heat treatment at 1100°C and then doped with manganese (curve 4).

Measurements of infrared absorption spectra in heat-treated silicon samples showed that heat treatment at 1100°C, accompanied by the precipitation of oxygen atoms, leads to a significant decrease in N_O^{opt} - by 45-50% (Fig. 1, curve 4). Earlier [9], we showed that the introduction of impurities of T-ions into Si leads to a decrease in the concentration of optically active oxygen N_O^{opt}. A similar effect was not observed in samples previously subjected to high-temperature treatment and then doped with T-ions. This is probably due to the peculiarities of the interaction of T-ion impurities with the bound states of oxygen atoms.

The effect of preliminary heat treatments on the defect structure of the initial silicon, as well as on the development of the defect structure of silicon with T-ions impurities, has been studied. It was found that various high-temperature treatments lead to a change in the defect structure of single-crystal silicon. It is shown that this is accompanied by the formation of various associated (bound) states of technological impurities, for example, oxygen atoms in silicon. In order to study the role of the state of technological impurities in the processes of defect formation and their effect on the energy spectrum of deep levels, samples of initial silicon containing diffusion layers of atomic oxygen O, SiO_2 films on the Si surface, and SiO_2 particles in the bulk of Si were prepared by special heat treatments. Then, under certain conditions, such samples were doped with cobalt, manganese or chromium. The effect of various precipitates of technological impurities on the energy spectrum of deep centers in silicon has been studied.

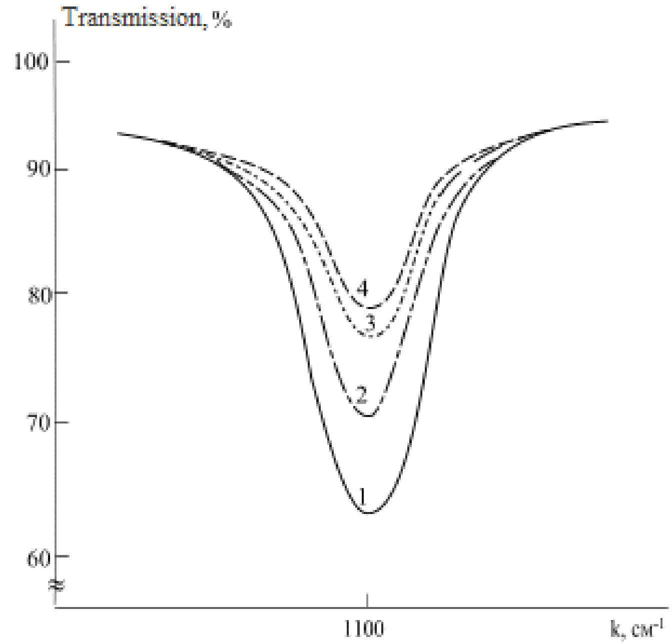

Fig. 1 Typical infrared absorption spectra of control samples n-Si (curve 1), n-Si <Mn> (curve 2), n-Si + heat treatment (curve 3), n-Si <Mn> with preliminary heat treatment at 1100°C (curve 4).

By capacitive spectroscopy, it was found that preliminary heat treatment of monocrystalline silicon in the temperature range 450 ÷ 550°C and 900 ÷ 1200°C with different durations lead to intense precipitation of oxygen and the formation of various accumulations and precipitates of the 2nd phase (SiO_2 and SiO_4 particles), the size of which is 10 ÷ 100 μm. Measurements and analysis of the DLTS spectra of samples with a developed defect structure (Fig. 2, curves 1 - 3, curve 4 is a control sample) showed that the presence of various bound states of oxygen and carbon - particles of SiO_2, SiO_4, COn and others differently affects the efficiency formation of deep levels by atoms of manganese, cobalt and chromium. It was found that the presence of bound states of technological impurities in silicon, for example, SiO_2 particles in Si lattice, increases the efficiency of the formation of deep centers created in the semiconductor band gap (Fig. 2, curve 2). While the presence of SiO_2 film, on the contrary, prevents the introduction of silicon impurities of T-ions (Fig. 2, curve 3).

Measurements of DLTS and IR absorption spectra have shown that doping of silicon with T-ion impurities leads to a decrease in the concentration of optically active oxygen N_O^{opt} by 10-30%, depending on the concentration of the introduced impurity. This indicates the interaction of T-ion impurities with oxygen atoms. It was also found that preliminary high-temperature treatment of silicon samples at 1100°C for 12 hours leads to the precipitation of oxygen with the formation of SiO_2 particles. In this case, N_O^{opt} decreases by 45 - 50%.

Additional introduction of manganese, cobalt or chromium atoms into silicon, preliminarily heat-treated at 1100°C for 12 hours, leads to a decrease in N_O^{opt} by 8-10%. This is due to the peculiarities of the interaction of T-ion atoms with SiO_2 particles. Preliminary experiments on structural studies have shown that in silicon samples with impurities of T-ions that have undergone preliminary heat treatment, large clusters are observed, consisting of atoms of specially introduced and technological impurities.

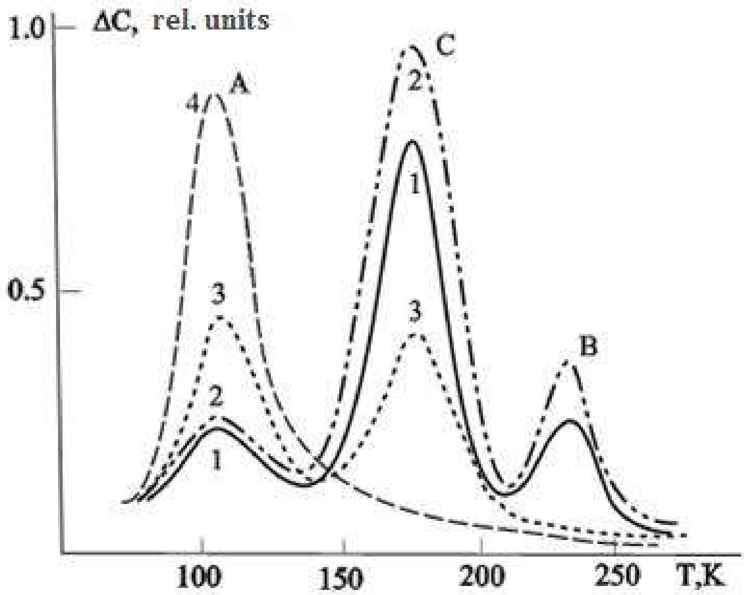

Fig. 2. DLTS spectra of n-Si <Mn> samples with bonded oxygen states

Earlier, by X-ray topography and electron microscopy, we found an additional phase in these Si samples, which, in a typical mode of Mn addition, is particles of an indefinite shape (~ 500 Å in size), high density (~ 1010 cm^{-3}) [14].

Preliminary experiments were carried out to determine the phase composition of these particles by X-ray structural analysis (DRON-1M). The diffraction patterns revealed a peak whose parameters according to ASTM tables coincide with manganese silicate (presumably $MnSiO_3$). In addition, a peak was found in these spectra, which has not yet been identified; possibly, it is associated with carbon manganese complexes.

4. Conclusion

Thus, it has been shown that doping of silicon with T-ion impurities leads to a decrease in the concentration of optically active oxygen N_O^{opt} by 10–30%, depending on the concentration of the introduced impurity. This indicates the interaction of T-ion impurities with oxygen atoms. It was also found that preliminary HTT of Si samples at 1100°C for 12 hours leads to the precipitation of oxygen with the formation of SiO_2 particles. In this case, N_O^{opt} decreases by 45-50%. Additional introduction of manganese, cobalt or chromium atoms into silicon, preliminarily heat-treated at 1100°C for 12 hours, leads to a decrease in N_O^{opt} by 8-10%. This is due to the peculiarities of the interaction of T-ions with SiO_2 particles. Preliminary structural investigates have shown that in silicon samples with T-ions impurities that have undergone preliminary HTT, large clusters are observed, apparently consisting of atoms of specially introduced impurities and technological impurities.

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