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Sh. Utamuradova
Institute of Semiconductor Physics and Microelectronics at NUUz,

A. Uteniyazova
Institute of Semiconductor Physics and Microelectronics at NUUz,

K. Fayzullaev
Institute of Semiconductor Physics and Microelectronics at NUUz,

E. Naurzalieva
Institute of Semiconductor Physics and Microelectronics at NUUz,

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Sh. Utamuradova, A. Uteniyazova, K. Fayzullaev, E. Naurzalieva

Institute of Semiconductor Physics and Microelectronics at NUUz, Tashkent, 100057, Tashkent, Uzbekistan

Abstract. *The processes of defect formation in Si with T-ion admixtures have been studied using IR absorption and capacitive spectroscopy. The kinetics of deep level annealing was studied. The activation energies of deep level annealing of T-ions were determined. It was found that the efficiency of formation and the kinetics of deep level annealing depends on the content of oxygen and carbon in silicon.*

Keywords: *silicon, alloying, impurities, manganese, chromium, cobalt, defect formation, annealing, activation energy of annealing.*

Impurities that create deep energy states in the band gap of silicon, as a rule, have a high migration ability and therefore they are often responsible for the observed instability of solid semiconductor solutions [1-2].

In addition, it is known that in the bulk of Si, besides especially introduced impurities, uncontrollable impurities are always present, the so-called technological impurities [3]. Such impurities in Si are oxygen and carbon atoms, which are always present in its crystal lattice in high concentrations up to $10^{17} \div 10^{18}$ cm $^{-3}$. Note that their characteristic feature is their tendency to various interactions.

In this regard, the purpose of this work was to study the interaction of T-ion atoms with atoms of technological impurities and the kinetics of low-temperature annealing of deep levels in Si using infrared (IR) and capacitive spectroscopy (DLTS). For the experiments, we used Si samples doped with T-ions (Mn, Cr, and Co) during diffusion. The IR absorption spectra in the initial Si and Si samples doped with Mn, Cr, and Co were measured using a Specord-IR-75 spectrophotometer operating in a two-beam scheme.

The concentrations of optically active oxygen and carbon in the initial samples of n-Si and p-Si were, respectively, $N_O^{opt} \sim 10^{16}$ and $(6.2 \div 13) \cdot 10^{17} cm^{-3}$ and carbon $N_C^{opt} = (2 \div 20) \cdot 10^{15}$ cm^{-3}, specific resistance $\rho \sim 5$ Ohm·cm. The content of oxygen N_0^{opt} and carbon N_C^{opt} was estimated from the IR absorption spectra in the range of wave numbers k = 1100 cm^{-1} (oxygen band at 9.1 μm) and k = 610 cm^{-1} (carbon band at 16.4 μm), measured on a Specord - IR-75 spectrophotometer at 300 K. As a control sample, we used polished oxygen-free silicon of the same thickness as the sample under study with $N_0^{opt} \leq 10^{16}$ cm^{-3}, $N_C^{opt} = 5.10^{15}$ cm^{-3}.

Measurements of the IR absorption spectra showed that the presence of atoms, for example, Mn, in the Si lattice leads to a significant decrease in the concentration of N_0^{opt} in comparison with the initial control Si samples with close values of the resistivity ρ. It follows from the calculations that the concentration of N_0^{opt} in samples n - Si <Mn> is 10 - 20% less than in control samples of

initial Si (see Fig. 1, curves 1 and 2). In this case, the higher the content of Mn atoms in the bulk of Si, the lower the concentration of N_0^{opt} (curves 2 and 3).

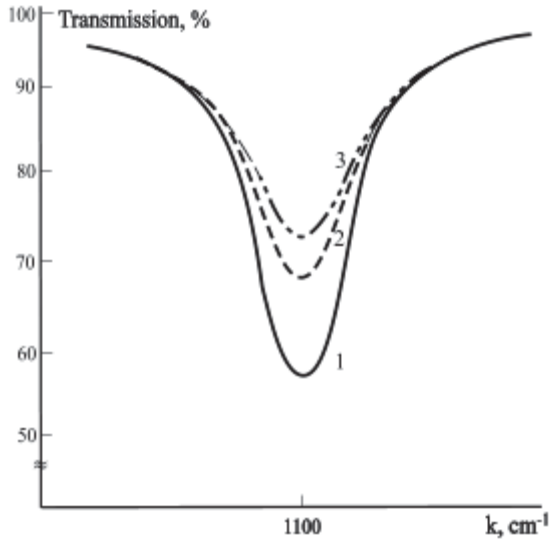

Fig. 1. IR absorption spectra in Si <Mn>$_{diff}$ samples: 1 - control sample T_{diff}: 2 - 1000ºC, 3 - 1200ºC

Earlier [4], we have shown that in the upper half of the band gap n - Si <Mn>, four deep levels with fixed ionization energies are formed: E_c-0.13 eV, E_c-0.20 eV, E_c-0.42 eV and E_c-0.54 eV, in the lower one is one level with E_v + 0.50 eV.

Measurements of DLTS spectra showed that the efficiency of the formation of deep levels associated with manganese atoms in the states Mn° and $(Mn°)_4$ in n-Si (E_c-0.42 and E_c-0.54 eV with $\sigma_n \sim 8\cdot10^{-15}$ and $2\cdot10^{-14}$ cm^2, respectively), depends on the content of oxygen and carbon in the samples. The efficiency of formation of deep level E_c-0.13 eV ($\sigma_n \sim 8\cdot10^{-14}$cm^2) associated with the paramagnetic center Mn^- does not correlate with the content of O and C. It turned out that an increase in N_O^{opt} in initial Si stimulates an increase in the concentration of electroactive Mn at diffusion.

Estimation of the carbon content N_C^{opt} before and after the introduction of Mn and comparison of the data with N_{Mn}^{ea} showed that the role of carbon is opposite: the more carbon in the sample, the lower the amount of introduced electroactive Mn. It was found that both for oxygen and carbon after the introduction of Mn, a decrease in N_O^{opt} and N_C^{opt} is observed. In contrast to oxygen, where ΔN_O^{opt} was 10–50% [4], for carbon the effect was stronger and the decrease in N_C^{opt} value exceeded 1–1.5 orders of magnitude. It should be noted that a decrease in N_C^{opt} is accompanied by a shift of the absorption band from 607 to 620 cm^{-1}. No additional bands were observed in the IR absorption spectra in the range 400–4000 cm^{-1}. Such a strong decrease in N_O^{opt} and N_C^{opt} is due precisely to the diffusion of Mn, since in the control samples (without Mn) such a decrease in the concentration of O and C was not observed.

A decrease in N_O^{opt} and N_C^{opt} can explain the existing difference between the value of the limiting solubility of Mn in Si N_{Mn} total and the concentration of electroactive manganese N_{Mn}^{ea} [3]. This difference between N_{Mn} total and N_{Mn}^{ea} can be associated with the deposition of some part of the dissolved Mn atoms on some sinks or the binding of manganese into neutral complexes of the

Mn-O or Mn-C type. To clarify the correlation between the behavior of the electroactive fraction of Mn and interstitial oxygen, low-temperature anneling (LTA) was carried out at 100–300°C (see Fig. 2). It can be seen that in samples with a high oxygen concentration ($N_O^{opt} \sim 10^{18}cm^{-3}$), the annealing of deep level occurs 3-4 times slower than in Si with $N_O^{opt} < 10^{16}cm^{-3}$.

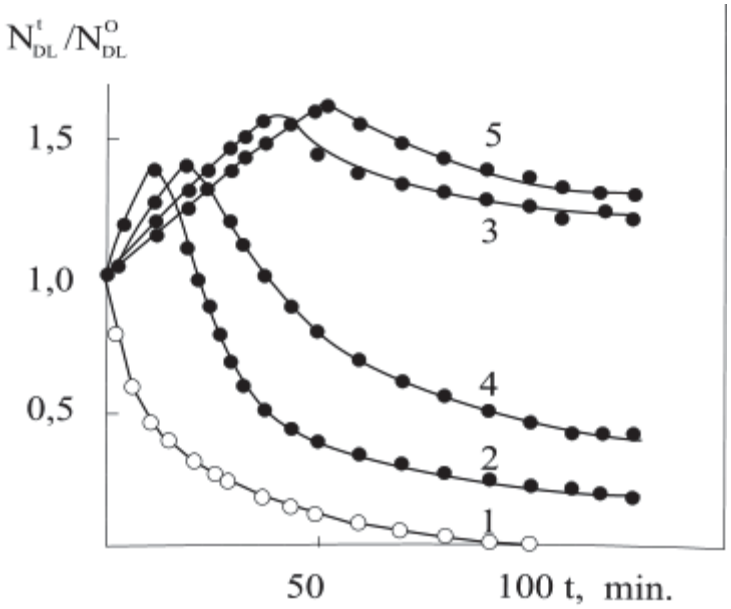

Fig. 2. Kinetics of LTA of n-Si <Mn> samples at 200°C

Comparison of the DLTS spectra of Si samples doped with Cr before and after HTT at 100 – 200°C for 12 hours showed that isothermal annealing in this temperature range does not lead to noticeable changes in the concentration and parameters of deep level. The measurement results showed that with an increase in the annealing temperature, starting from 300°C, there is a noticeable change in the concentration of all DLs with time and temperature of HT. The kinetics of annealing of Cr levels in Si is also nonmonotonic (Fig. 3).

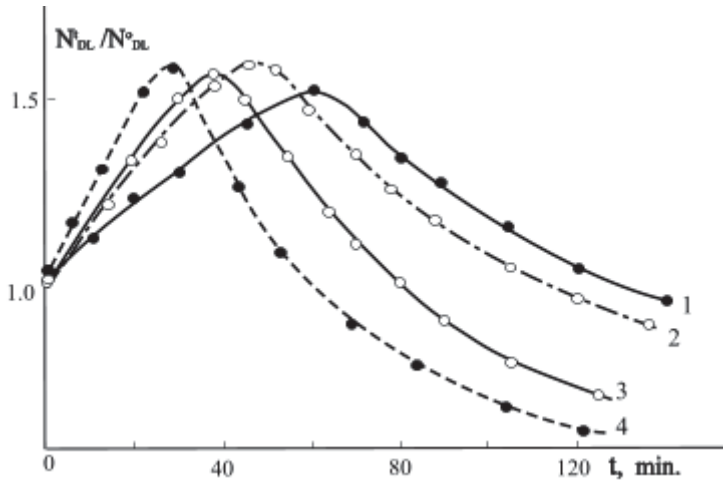

Fig. 3. Kinetics of low-temperature annealing of chromium levels in n-Si <Cr> at 350°C

The results of studying the kinetics of LTA of Si samples doped with impurities of manganese, chromium, cobalt and showed that impurities of T-ions have a high migration ability and therefore the parameters of the deep centers (DC) created by them are unstable.

Isothermal annealing of deep centers of nearly all the T-ion impurities studied by us nonmonotonically occurs with the annealing time. The known cross-sectional method was used to estimate the activation energy of the annealing of deep levels of T-ions and it was found that the activation energy of the annealing for deep level of manganese in silicon, E_c-0.42 eV, is 0.50±0.02 eV, and for the level E_c-0.54 eV, 1.8±0.02 eV, and for levels chromium E_c-0.41 eV it is 0.55±0.02 eV, for E_c-0.51 eV it is 1.7±0.02 eV. Other T-ion impurities have similar meanings.

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