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Research Article

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Spectroscopy of Defects in Semiconductors, Doped Nickel

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Abstract Methods of nonstationary capacitance spectroscopy of deep levels, photoelastic and infrared spectroscopy we studied the behavior of Nickel atoms introduced into the silicon by diffusion, and the crystal growing process. It is shown that in silicon, the diffusion–doped Nickel has two acceptor levels: the EU is 0.41 eV and Ev + 0.20 eV. The efficiency of formation of these defects depends on the temperature and duration of diffusion. Discovered that the Nickel atoms introduced into the silicon when growing electrically neutral. It was shown that prolonged high temperature processing of Si<Ni> ?at T?1000 ° C? translates a considerable part of Nickel atoms in the electrically active state throughout the volume of the silicon. It is shown that the introduction of Ni diffusion in Si with subsequent annealing leads to a noticeable reduction in the concentration of optically active kisloroda N0опт and deterioration of the optical transparency of the samples Si<Ni>.

Keywords spectroscopy, silicon, defect, doping of the impurity, Nickel

1. Introduction

In recent years intensified work on the preparation and study of properties of silicon doped with transitional elements (TE). This is primarily due to the fact that silicon with impurities of TE is used for a number of special semiconductor devices, for example, various types of photodetectors, solar cells and other devices with high photosensitivity, radiation resistance, thermal stability, etc.

The most studied among TE impurity in silicon is Nickel, but nevertheless no clear opinion about the deep centers, created in Si and Ni on the behavior of its atoms in the lattice of silicon. Thus, according to the authors of [1] with Nickel atoms in Si related deep levels (DL) E_V+0.18 eV, E_V+0.21 eV, E_V+0.33 eV, the authors of [2] give a different range for deep levels of Ni: E_C-0.41, E_V+0.21 eV. Note that the capture cross sections of the state E_V+0.21 eV in these works differ by more than two orders of magnitude. In other works values the ionization energy of the acceptor levels of Nickel in the upper half of the forbidden zone of silicon range in the range 0.35÷0.45 eV for levels in the lower half there is an even more mixed picture [3-5].

With the aim of obtaining more reliable information on the centers, created by the Nickel atoms in silicon, we investigated the physical processes in silicon, doped with Nickel, as by diffusion, and when grown from the melt by the methods of deep level transient spectroscopy (DLTS), photocapacitance (PC) and infrared spectroscopy (IR-absorption). Were conducted additional experiments using neutron activation analysis (NAA).

2. Experimental samples

Diffusion of Nickel atoms in the n - and p-Si was carried out from the deposited layer of metallic impurities in the temperature range 1000÷1250°C during 0.5÷30 hours, followed by cooling at different speeds ($\rho_{initial}$= 0.3÷40 Ohm·cm). After the diffusion of Nickel the resistivity ρ samples of n-Si was increased to $2{\cdot}10^4$ Ohm·cm, and p-Si, it is not appreciably varied.

For the experiments we used samples of silicon doped with Nickel at the growth (n-Si<Ni>$_{grown}$, p-Si<Ni>$_{grown}$), their the resistivity ρ was 40÷100 Ohm·cm.

For carrying out capacitive measurements were created Schottky barriers by evaporation in a vacuum of gold on n-Si and antimony - on p-Si. As the ohmic contact is a chemically deposited Nickel, sometimes deposited antimony or aluminum. DLTS spectra were measured in the regimes of constant capacitance [6] and direct current voltage [7], and measurements of the spectra of PC was carried out according to conventional techniques described in [8].

3. Results and Discussion

In Fig.1 shows typical DLTS spectra of samples of silicon diffusion-doped with Nickel (Si<Ni>$_{diff.}$), followed by a sharp hardening. Processing of these spectra and the calculations show that the introduction of diffusion of Nickel atoms in n-Si and p-Si leads to the formation of several deep levels with fixed energy of ionization. In samples n-Si<Ni>$_{diff.}$ deep levels discovered with parameters E_C – 0.19 eV, $\sigma_n = 2\cdot10^{-15}$ cm^2 and E_C – 0.41 eV, $\sigma_n = 6\cdot10^{-16}$ cm^2 (Fig.1, curve 1) and the samples p-Si<Ni>$_{diff.}$ observed deep levels E_V + 0.20 eV, $\sigma_p = 7\cdot10^{-15}$ cm^2 and E_V + 0.41 eV, $\sigma_p = 3\cdot10^{-15}$ cm^2 (Fig. 1, curve 2).

A comparison of the DLTS spectra in doped and control samples showed that deep levels E_C – 0.19 eV and E_V + 0.41 eV are observed in heat-treated samples (without Ni), and their concentration in Si<Ni>$_{diff.}$ are much lower. From a study of the kinetics of the formation of deep centers associated with Nickel in silicon, are installed what technological regimes (temperature of diffusion $T_{diff.}$ and the cooling rate after diffusion $\vartheta_{cool.}$) depends on the effectiveness of education only levels of E_C – 0.41 eV and E_V + 0.20 eV: with the growth of $T_{diff.}$ and $\vartheta_{cool.}$ their concentration increase.

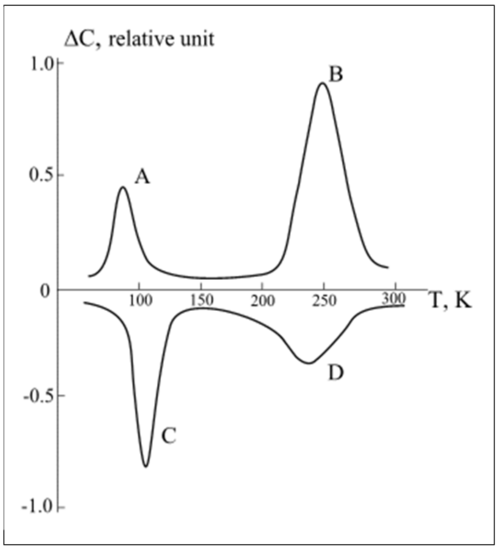

Figure 1: Typical DLTS spectra of the samples n-Si<Ni>$_{diff.}$ (curve 1) and p- Si<Ni>$_{diff.}$ (curve 2) peaks A: E_C-0.19 eV, B: E_C-0.41 eV, C: E_V+0.20 eV, D: E_V+0.41 eV, $T_{diff.}$ = 1150^{o}C, $t_{diff.}$ = 4 hours.

The results of the measurements of the PC spectra of the samples n- Si<Ni>$_{diff.}$ showed that there is a relaxation of the capacity associated with the recharging of the two deep levels: E_C – 0.20 eV and E_C – 0.40 eV. Spectra induced by PC are detected in two steps near hν ~ 0.20 eV and 0.40 eV (Fig. 2, curves 1 and 2). Note that the comparison of the DLTS spectra and PC shows that the energy is thermal and the optical activation of the detected levels in samples of Si<Ni>$_{diff.}$ is almost the same.

Measurement of DLTS spectra and of PC in Si doped Ni at growing showed that any deep levels in sufficient concentration in the bandgap of the samples is not observed. At the same time, the NAA data indicate the presence of Nickel atoms in the bulk of silicon at high enough concentrations, total concentration of Ni atoms in such samples is $(6\div8)\cdot10^{17}$ cm^{-3}. From these data it follows that the Ni atoms introduced into the lattice of silicon in the growing process, is electrically neutral.

With the aim of establishing the possibility of activation of Nickel atoms at thermal influences, we carried out high-temperature treatment (HTT) in the temperature range 1000÷1250 ^{o}C during 0.5÷30 hours followed by quenching in oil. As a result of comprehensive research discovered that after the HTT when 1100^{o}C for 3 hours on the PC spectra of the samples n- Si<Ni>$_{grown}$ appears weak relaxation capacity near hν ~ 0.40 eV, and the spectra induced by PC near the hν ~ 0.20 eV.

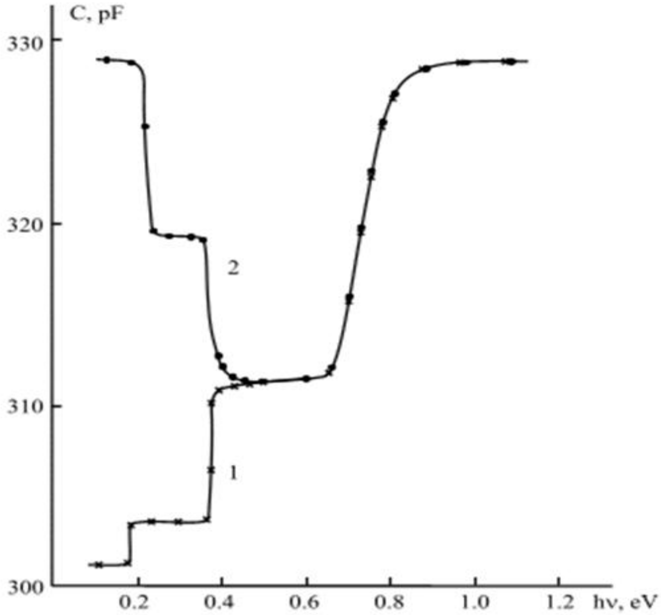

Figure 2: Photocapacitance spectra of (curve 1) and induced photocapacitance (curve 2) samples n-Si<Ni>$_{diff.}$

The increase of temperature and duration of the HTT (at 1250°C, 10 hours) allowed to identify the distinct steps in the spectra of photocapacitance at the above hν. Spectra measurements DLTS carried out on samples n-Si<Ni>$_{grown}$ peak detected at T = 240 K, and the samples p- Si<Ni>$_{grown}$ – at T =107 K; the slopes of the dependencies lg θ =f (1/ T) obtained from the conversion DLTS peaks, give the ionization energy of deep levels E_C – 0.41 eV and E_V + 0.20 eV, their concentra-tion of about $5{\cdot}10^{13}$ cm^3 and $3{\cdot}10^{13}$cm^{-3}, respectively.

The above was shown to be deep levels with the same parameters are observed in silicon, Nickel doped diffusion method (see Fig.1). It should be noted that the efficiency of formation of these levels in samples of Si<Ni>$_{diff.}$ is significantly higher than in samples Si<Ni>$_{grown}$.

So in the samples of Si diffusion doped Ni at 1100°C for 3 hours concentration deep levels E_C – 0.41 eV and E_V + 0.20 eV is $6{\cdot}10^{14}$cm^{-3} and $2{\cdot}10^{14}$cm^{-3}, respectively, and in samples of Si<Ni>$_{grown}$ heat-treated under the same conditions as the diffusion introduction of Ni concentration is similar to deep levels make $4{\cdot}10^{13}$см$^{-3}$ and $8{\cdot}10^{12}$см$^{-3}$, respectively.

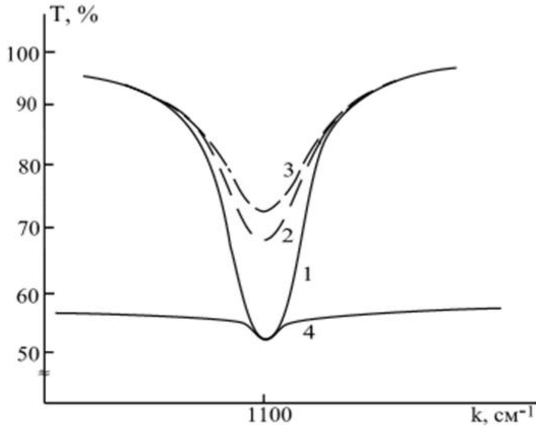

Figure 3: Spectra of infrared absorption in samples of Si diffusion alloyed Ni. $T_{diff.}$: 2 - 1000°C, 3 - 1100°C, 4 - 1200°C. 1 - the initial (control) silicon

Were also conducted experiments with profiling by layer-by-layer etching of the surface samples Si<Ni>$_{grown}$. Profiles of the concentration distribution deep levels E_C – 0.41 eV and E_V + 0.20 eV in samples Si<Ni>$_{grown}$ subjected to HTT with 1250°C for 10 hours suggests that prolonged heat treatment converts a substantial part of the Nickel atoms in the electrically active state throughout the volume of the silicon.

Thus, heat treatment of the samples Si<Ni>$_{grown}$ leads to the activation of Nickel atoms and formation of two deep levels E_C – 0.41 eV and E_V + 0.20 eV, which are formed and with the introduction of Ni diffusion in Si.

Measurement of spectra the infra red (IR) absorption of samples Si, diffusion - doped Ni (Fig.3, curves 2-4) showed that the presence of Ni atoms in the volume of Si leads to a noticeable decrease in the intensity of oxygen absorption peaks, that is, to reduce N^O_{opt}.

Discovered that the observed effect depends on the concentration of Ni introduced: the more the N_{Ni}, the greater the reduction in N^O_{opt}. Reduce the size of the N^C_{opt}. or formation of new peaks associated with C is not detected. Note that the introduction of Ni diffusion in Si with subsequent annealing leads to a deterioration of the optical transparency of the samples Si<Ni> (Fig.3, curve 4), which was not observed in samples with slow cooling (Fig.3, curves 2-4). The analysis of these data leads to the conclusion that the introduction of Ni in Si is probably formed electrically neutral and optically inactive complexes with the participation of atoms of Ni and O.

From the analysis of the results of the conducted research it can be concluded that Nickel in the silicon (if diffusion introduction) associated levels of E_C – 0.41 eV and E_V + 0.20 eV. In addition, discovered two deep levels that are observed in doped and control samples: E_C – 0.19 eV and E_V + 0.41 eV. The first of these last two levels is most likely a thermal defect, as the same deep levels is formed without introducing impurities. The parameters of the second level correspond to the parameters of deep levels E_V + 0.41 eV, associated with the interstitial atoms in iron as Fe^o [11]. Note that the presence of Ni atoms in the amount of Si reduces the effectiveness of education in those levels. Moreover, the higher the concentration of the Nickel, the lower the concentration of deep levels E_V + 0.41 eV. The reduction in the concentration of this level in the presence of Nickel atoms, due, apparently, extraction of iron atoms from the bulk to the surface Si atoms of Nickel, which was observed by us in [12] by the method of autoradiography. There is also the possibility of education in the amount of silicon in any of the neutral complexes with the participation of atoms of Nickel and iron.

From the results of measurement of samples of Si<Ni>$_{grown}$ it follows that when the silicon doped with Nickel in the process of growing, the Ni atoms do not show electrical activity. According to the authors [13], the electroneutrality is typical of many fast diffusing impurities are inserted into the lattice of silicon under growing. The absence of deep levels in samples Si<Ni>$_{grown}$ is probably due to the fact that at slow cooling process after growing the silicon, the Nickel atoms have time to form precipitates or other inclusions of the second phase, or to achieve a neutral effluent, where they lose electrical activity. Note that the tendency to precipitation is one of the characteristic features of the behavior of Ni in Si as observed by the diffusive introduction of it in silicon [14-17].

4. Conclusions

Thus, from the analysis of the obtained results it can be concluded that the high-temperature treatment can lead to the activation of atoms of Nickel in samples of Si<Ni>$_{grown}$, moreover, the concentration of deep levels associated with Ni is much smaller than in the diffusive introduction of Ni into Si at the same temperature, and heat treatment. This is explained, apparently, by some peculiarities in the formation of the defect structure by diffusion of Nickel atoms in silicon and their introduction into the process of growing. In addition, the diffusive introduction of Ni in Si with subsequent annealing also leads to a marked reduction in the concentration of optically active oxygen N^O_{opt} and deterioration of the optical transparency of the samples Si<Ni>.

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