

ENHANCING THE PERFECTION OF A SILICON CRYSTAL DOPED WITH NICKEL AND ZINC IMPURITIES

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This research paper presents the findings of an investigation into the interaction between zinc (Zn) and nickel (Ni) impurity atoms within a silicon (Si) matrix, which were doped sequentially in various combinations. The characterization techniques employed for this study encompass X-ray diffraction and IR-Fourier spectrometry. It is noteworthy that the degree of crystallinity exhibited by the silicon lattice, subject to the introduction of Zn and Ni impurities, is contingent upon the methodology employed for impurity incorporation. The results of this study reveal a distinctive trend in the optical properties of these doped silicon samples. Specifically, upon the introduction of Zn atoms into silicon that was pre-doped with Ni (Si<Ni, Zn>), there is a concomitant reduction in the concentration of optically active oxygen atoms. Remarkably, this alteration in the dopant composition leads to a marked enhancement in the transparency of the silicon crystal. In stark contrast, when the doping sequence is reversed (Si<Ni, Zn> Ni>), an opposing effect is observed, resulting in a diminishment of crystal transparency. These findings underscore the intricate interplay between the introduced impurity atoms, the dopant sequence, and their collective impact on the optical properties of the silicon matrix. Such insights contribute to our comprehension of the nuanced behavior of doped silicon and have implications for applications requiring tailored optical characteristics in semiconductor materials.

Keywords: *Silicon; Zinc; Nickel; Diffusion; X-ray diffraction spectrum; IR transmission*

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INTRODUCTION

Over the past few decades, extensive research has been conducted worldwide to investigate the behavior of defects in semiconductors and elucidate the mechanisms underlying their formation. Additionally, significant efforts have been directed towards the simultaneous mitigation of undesirable defects [1-9]. The scientific community has developed models to expound upon a diverse array of phenomena, encompassing topics such as the profile characteristics of dopants, conditions governing diffusion doping, non-equilibrium effects induced by chemical reactions or radiation-induced damage, diminishment in the electrical activation of dopant impurities due to the creation of impurity phases, clusters, and complexes involving other impurities, as documented in references [6-8]. Furthermore, research has probed the phenomenon of dopant accumulation at the interfaces and surfaces of semiconductor materials. The realm of transition metal impurities in silicon (Si) has been a subject of long-standing investigation, yielding a comprehensive understanding of the properties and electrophysical parameters of isolated atoms [9]. However, relatively limited attention has been directed towards the study of complexes involving atoms of multiple elements that facilitate the nucleation of precipitates [10, 11]. Transition element impurities, known for their ability to introduce deep energy levels within the band gap of silicon, exhibit remarkable mobility. Consequently, the mechanisms governing the motion of impurity atoms are contingent upon the doping methodology employed for their incorporation into the primary crystal matrix. The heightened mobility of these impurities engenders interactions with other uncontrolled impurities present in silicon, thereby giving rise to the formation of impurity pairs.

In light of these considerations, the investigation of defect formation processes in silicon doped with multiple impurity atoms of transition elements, specifically Ni and Zn, and their responses to various influencing factors, such as the interaction between technological and uncontrolled impurity defects in silicon [12], assumes paramount importance. Furthermore, understanding the impact of thermal and radiation-induced defects on the development of a defect structure in silicon when doped with Ni and Zn impurities emerges as a significant research challenge. These circumstances necessitate the exploration of novel theoretical and practical methodologies aimed at uncovering the mechanisms governing the formation and reconfiguration of structural defect complexes at the atomic level, thereby facilitating precise control over the properties of silicon doped with diverse impurities.

Consequently, the primary objective of this study was to delve into the defect structure and its interplay with technological impurities in the presence of rapidly diffusing transition elements, Ni and Zn, within the silicon lattice. To achieve this, we employed IR-Fourier spectroscopy and X-ray diffraction analysis.

MATERIAL AND METHOD

For the experiments we used samples of n-type silicon grown by the Czochralski method with a resistivity of 100 Ohm·cm. In these samples, the phosphorus concentration was about $\sim 10^{13}$ cm⁻³, the oxygen concentration

was $\sim 10^{17} \text{ cm}^{-3}$. During the diffusion of impurity atoms, metal Zn and Ni with a purity of 99.99% were deposited on the cleaned surface of the samples in vacuum. Doping of silicon samples with impurities was carried out by the thermal diffusion method in quartz ampoules evacuated to vacuum, in the temperature range from $T=1000^\circ\text{C}$ to 1100°C for $t = 1-5 \text{ h}$. As a result, 3 groups of silicon samples were obtained:

I) the first group was characterized by separate diffusions of impurities of nickel and zinc atoms into the initial silicon (samples $\text{Si}\langle\text{P},\text{Ni}\rangle$ and $\text{Si}\langle\text{P},\text{Zn}\rangle$);

II) the second group was obtained by diffusion of zinc atoms into silicon preliminarily doped with impurities of nickel atoms (samples $\text{Si}\langle\text{P},\text{Ni},\text{Zn}\rangle$);

III) the third group was obtained by diffusion of nickel atoms into silicon preliminarily doped with impurities of zinc atoms (samples $\text{Si}\langle\text{P},\text{Zn},\text{Ni}\rangle$).

Structural studies of the samples were carried out on a third-generation X-ray diffractometer of the Empyrean Malvern PANalytical L.T.D. type. ($\text{CuK}\alpha$ radiation, $\lambda = 0.15418 \text{ nm}$) according to the ω - 2θ scheme in the step-by-step scanning mode with a monochromator in the range $2\theta =$ from 15° to 140° continuously with a scanning speed of 0.33 deg/min and an angular step of 0.0200 (deg) . The IR absorption spectrum of the samples was recorded using an FSM-1202 IR-Fourier spectrometer at room temperature.

DESCRIPTION AND ANALYSIS OF RESULTS

After diffusion with Ni and Zn impurities, the values of the resistivity of the initial silicon changed significantly (Table 1). The table shows that in the overcompensated samples $\text{p-Si}\langle\text{P},\text{Ni},\text{Zn}\rangle$ ρ decreases, and in the samples $\text{p-Si}\langle\text{P},\text{Zn},\text{Ni}\rangle$ ρ increases. Such a difference in the value of ρ shows that the concentration of electroactive Ni atoms in $\text{p-Si}\langle\text{P},\text{Ni},\text{Zn}\rangle$ is higher than in $\text{p-Si}\langle\text{P},\text{Zn},\text{Ni}\rangle$ samples.

Table 1. The values of the resistivity of the samples

Samples	Technology of doping	Diffusion Mode	Conductivity type	ρ (Ohm·cm)
$\text{Si}\langle\text{P}\rangle$	–	–	N	100
$\text{Si}\langle\text{P}, \text{Ni}\rangle$	Spraying	T=1200°C, t=2 h	N	305
$\text{Si}\langle\text{P}, \text{Zn}\rangle$	Spraying		p	121
$\text{Si}\langle\text{P}, \text{Ni}, \text{Zn}\rangle$	Consistently: Ni - deposition, Zn - sputtering		p	64.3
$\text{Si}\langle\text{P}, \text{Zn}, \text{Ni}\rangle$	Consistently: Zn - sputtering, Ni - deposition		p	200

In our previous works [12, 13], using capacitive spectroscopy and the photoconductivity method, we identified the energy spectra of deep levels (DL) created by Ni and Zn atoms in Si upon their diffusion introduction and showed that in $\text{n-Si}\langle\text{P}, \text{Ni}\rangle$ DL $E_C - 0.42 \text{ eV}$, $E_V + 0.17 \text{ eV}$ are formed; in $\text{p-Si}\langle\text{Zn}\rangle$, the DL $E_V + 0.28 \text{ eV}$, $E_C - 0.55 \text{ eV}$ are formed, and in the simultaneous doping of $\text{p-Si}\langle\text{P}, \text{Ni}+\text{Zn}\rangle$, a new DL $E_C - 0.25 \text{ eV}$ is formed;

After recording the IR absorption spectra in polished samples in the range from 1000 to 1100 cm^{-1} , the concentrations of optically active oxygen atoms N_O^{Opt} and carbon N_C^{Opt} were calculated. To calculate the concentration of optically active oxygen atoms N_O^{Opt} and carbon N_C^{Opt} , formulas (1, 2) were used.

$$N_O^{Opt} = 3,3 \cdot 10^{17} \cdot \frac{1}{d} \ln \frac{I_0}{I}, \quad (1)$$

$$N_C^{Opt} = 1,1 \cdot 10^{17} \cdot \frac{1}{d} \ln \frac{I_0}{I}, \quad (2)$$

where I_0 – is the intensity of the incident light; I – the intensity of the transmitted light; d – is the sample thickness.

On Fig. 1 shows typical IR absorption spectra of optically active oxygen in samples: $\text{Si}\langle\text{P}\rangle$; $\text{n-Si}\langle\text{P}, \text{Ni}\rangle$; $\text{p-Si}\langle\text{P}, \text{Zn}\rangle$; $\text{p-Si}\langle\text{P}, \text{Zn}, \text{Ni}\rangle$; $\text{p-Si}\langle\text{P}, \text{Ni}, \text{Zn}\rangle$, from which it can be seen that the oxygen band and the carbon band are visible in the region of wave numbers $k = 1100 \text{ cm}^{-1}$ ($9.1 \mu\text{m}$). Analysis of IR absorption in the region of 1100 cm^{-1} showed that in all silicon samples doped with nickel and zinc, there is a decrease in optically active oxygen N_O^{Opt} and carbon N_C^{Opt} within 20-40%. This can be explained by the difference between the limiting solubility of nickel and zinc in silicon at 1200°C , which, according to the data of [12,15,16], is $N_{prev}^{Ni} \sim 10^{17} \text{ cm}^{-3}$ and $N_{prev}^{Zn} \sim 10^{16} \text{ cm}^{-3}$ electrically active nickel and zinc $N_{e.a.}^{Ni} \sim 10^{14} \text{ cm}^{-3}$ and $N_{e.a.}^{Zn} \sim 10^{15} \text{ cm}^{-3}$, respectively. This difference between N_{prev} and $N_{e.a}$ is apparently due to the precipitation of some part of the dissolved nickel and zinc atoms on some sinks or the binding of Ni and Zn into neutral complexes, for example, such as Ni-O, Ni-C, Zn-O and Zn-C.

If we pay attention to the $\text{Si}\langle\text{Ni}\rangle$ samples, the IR band at 1100 cm^{-1} is shifted down, which indicates a loss of transparency of the crystal itself. According to the authors of [17], the opacity of $\text{Si}\langle\text{Ni}\rangle$ samples is associated with the arrangement of interstitial inactive nickel atoms: during quenching, clusters form and the sample becomes opaque.

It is also assumed that the temperature interval and time at which diffusion of nickel atoms into silicon is carried out leads to the dissolution of any kind of defective associations, precipitates of the second phase, accumulations of impurities, including nickel atoms and their uniform distribution in the silicon lattice, and rapid quenching Si<Ni> samples after diffusion leads to freezing of such a finely dispersed state of Ni atoms in the Si lattice [18–20].

In the case of Si<Zn> samples, a decrease in optically active oxygen of ~10-15% is observed, but without loss of transparency. This is most likely due to site substitutions of zinc atoms in the silicon crystal.

Interesting phenomena occur when Zn atoms are introduced into Si with pre-doped nickel atoms (Si<Ni, Zn>). Along with a decrease in the concentration of optically active oxygen atoms, the transparency of the crystal also improves, while in samples with the reverse combination of doping (Si<Zn, Ni>), the opposite effect is observed (Fig. 1, curves 4 and 5).

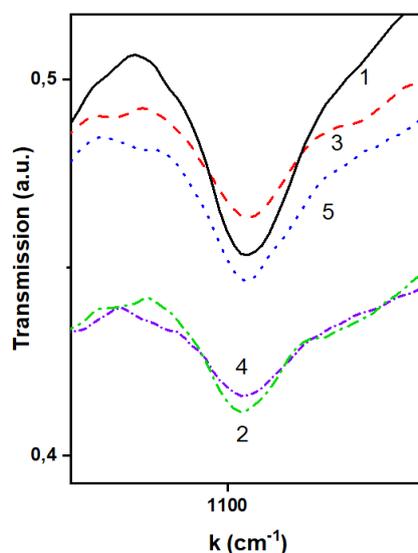


Figure 1. IR transmission spectrum of optically active oxygen in silicon:
 1-Si<P>; 2-Si<Ni>; 3-Si<Zn>; 4-Si<Zn, Ni>; 5-Si<Ni, Zn>

To elucidate the cause of this phenomenon, an additional structural analysis of the samples was carried out. Fig. 2 shows the X-ray diffraction spectra of the main reflection Si (111) of samples Si<P>, n-Si<Ni>, n-Si<Zn>, n-Si<Zn, Ni>, n-Si<Ni, Zn>.

The maximum intensity of the Si (111) reflection and the small width (FWHM) testify to the high perfection of the silicon crystal structure, since the intensity of the main reflection indicates the number of atoms in the lattice site of the crystal. It can be seen from Fig. 2 that the intensity in the X-ray diffraction spectrum of silicon after doping with Ni atoms decreased by a factor of 10. This indicates that the periodicity of the crystal lattice is destroyed and the Ni atoms are in the interstitial position, which also underlies the results of IR absorption. But in the p-Si<P, Zn> single crystal, the intensity of the Si(111) reflection decreased insignificantly. It is known from the literature that Zn atoms mainly diffuse into crystal lattice sites.

After indexing the X-ray diffraction pattern of a substance with a cubic lattice, the crystal period is easily determined by formula (3)

$$a_{Si} = \frac{\lambda}{2\sin\theta} \sqrt{h^2 + k^2 + l^2}, \quad (3)$$

The average crystallite size was estimated using the Scherrer formula [21]

$$D = \frac{k\lambda}{\beta\cos\theta}, \quad (4)$$

where k- is the Scherrer coefficient (equal to 0.9), λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the crystalline peaks in radians, θ is the Bragg angle of the diffraction peak, D is the grain size (in nm). The size of subcrystallites estimated from the width of this peak was $D_{Si} \approx 24.55$ nm.

It can be seen from the Fig. 2 that the samples of the II-group (n-Si<Ni, Zn>) show the highest intensity, while the samples of the III-group (n-Si<Zn, Ni>) give the lowest intensity. This indicates that silicon sequentially doped with Ni and Zn impurities has a high degree of crystallinity, which depends on the intensity. The shift of the intensity of X-rays towards smaller scattering angles shows the microdistortion of the silicon crystal with an increase in the lattice constant d. If the position of the breakline is shifted without loss of intensity, then this indicates a uniform distortion of the crystal lattice [14].

The table lists the positions of the Si(111) peak and the average subcrystallite size of a silicon single crystal. Table 2 shows that the samples n-Si<Ni>, n-Si<Ni, Zn> and n-Si<Zn> cause inhomogeneous microdistortion, which reduces the

size of the silicon subcrystallite. In the case of n-Si<Ni, Zn> samples, the silicon crystal lattice is distorted uniformly, but the crystallite size increases by 30 nm relative to the original sample.

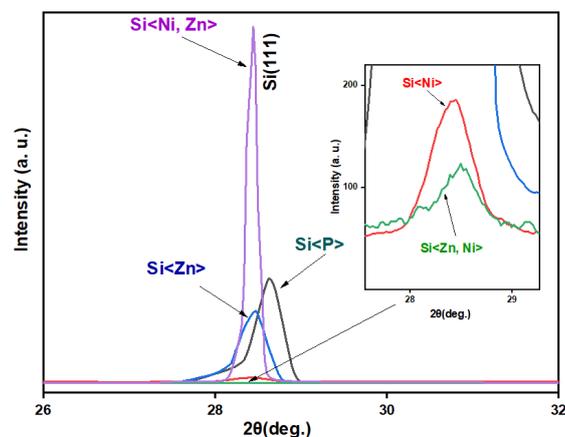


Figure 2. X-ray diffraction spectrum of silicon doped with nickel and zinc at various doping technologies

Table 2. Main parameters of X-ray diffraction pattern

Samples	Peak position 2θ, deg.	Average size of Si subcrystallite, nm
Si<P>	28.62±0.05	24.55±0.01
Si<P, Ni>	28.40±0.03	15.56±0.01
p-Si<P, Zn>	28.43±0.02	22.53±0.01
p-Si<P, Ni, Zn>	28.43±0.01	54.89±0.01
p-Si<P, Zn, Ni>	28.47±0.02	20.59±0.01

Comparing the obtained experimental data on IR absorption with the results of X-ray diffraction analysis of Si<Ni, Zn> samples, the increase in intensity can be explained by two circumstances: 1) high-temperature diffusion of zinc atoms serves as annealing for Si<Ni> samples, in which various kinds of defect states formed begin to decompose and redistribute, gathering on some sinks 2) Zn atoms, being located at the nodes of the silicon crystal, fill the vacant places by the mechanism $V + Zn = Zn_{int}$, thereby improving the periodicity of the crystal lattice.

CONCLUSION

The findings obtained through IR-Fourier spectrometry and X-ray diffraction analysis reveal the strong influence of the silicon doping process with nickel and zinc impurities on the initial silicon structure. Specifically, it is evident that silicon subjected to sequential doping with Ni and Zn impurities exhibits a notably enhanced crystal perfection. A noteworthy observation is the reduction in the concentration of optically active oxygen atoms, which ranges from 15% to 30%, contingent on the concentration levels of nickel and zinc atoms during the high-temperature diffusion process. Moreover, across all samples, a consistent decrease in the concentration of optically active oxygen and carbon atoms has been observed. This phenomenon is attributed to the formation of electrically neutral complexes, namely Ni-O, Ni-C, Zn-O, and Zn-C.

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ПІДВИЩЕННЯ ДОСКОНАЛОСТІ КРИСТАЛУ КРЕМНІЮ, ЛЕГОВАНОГО ДОМІШКАМИ НІКЕЛЮ ТА ЦИНКУ

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Ця дослідницька стаття представляє результати дослідження взаємодії між домішковими атомами цинку (Zn) і нікелю (Ni) у кремнієвій (Si) матриці, які були леговані послідовно в різних комбінаціях. Методи визначення характеристик, використані для цього дослідження, охоплюють рентгенівську дифракцію та ІЧ-Фур'є-спектрометрію. Слід зазначити, що ступінь кристалічності, який демонструє решітка кремнію, за умови введення домішок Zn і Ni, залежить від методології, яка використовується для включення домішок. Результати цього дослідження показують відмінну тенденцію в оптичних властивостях цих легованих зразків кремнію. Зокрема, при введенні атомів Zn в кремній, попередньо легований Ni (Si<Ni, Zn>), відбувається супутнє зниження концентрації оптично активних атомів кисню. Примітно, що ця зміна складу допantu призводить до помітного підвищення прозорості кристала кремнію. На відміну від цього, коли послідовність легування змінюється (Si<Ni, Zn> Ni>), спостерігається протилежний ефект, що призводить до зменшення прозорості кристала. Ці висновки підкреслюють складну взаємодію між введеними атомами домішок, послідовністю допantів та їхнім сукупним впливом на оптичні властивості кремнієвої матриці. Такі ідеї сприяють нашому розумінню нюансів поведінки легованого кремнію та мають наслідки для застосувань, які вимагають індивідуальних оптичних характеристик у напівпровідникових матеріалах.

Ключові слова: кремній; цинк; нікель; дифузія; рентгенівський дифракційний спектр; ІЧ-пропускання