INFLUENCE OF PALLADIUM ATOMS ON THE CRYSTAL STRUCTURE OF SILICON (n-Si)

Sharifa B. Utamuradova[1], Dilmurod A. Rakhmanov[1*], Afsun S. Abiyev[2]

[1] Institute of Semiconductor Physics and Microelectronics at the National University of Uzbekistan, 20 Yangi Almazar st., Tashkent, 100057, Uzbekistan;
[2] Western Caspian University, Baku, AZ1001, Azerbaijan

*Corresponding Author e-mail: dilmurod-1991@bk.ru

Abstract

The paper presents the results of a study of the effect of palladium atoms on the crystal structure and surface morphology of silicon single crystals. The study was carried out on n-type silicon doped with phosphorus during growth. X-ray diffraction and scanning electron microscopy were used for the study. When studying changes in the lattice parameters, it was found that doping at a temperature of 1100 ºC resulted in an expansion of 0.08%, while at 1200 ºC it was 0.22%. Using a scanning electron microscope, it was determined that doping silicon with palladium atoms at 1100 ºC leads to the formation of structural microdefects with a low concentration, while the introduction of palladium impurity into Si at 1200 ºC leads to the creation of smaller structural defects with a high concentration.

Key words: silicon, palladium, diffusion, doping, X-ray diffraction.

1. Introduction

In the process of diffusion doping of silicon single crystals with fast-diffusing elements, defective structures are formed at high temperatures, which in the sample volume can be both in thermodynamic equilibrium and nonequilibrium states [1,2]. The diffusion technology for obtaining compensated silicon with impurities that create deep energy levels is mainly associated with the values of solubility and diffusion parameters - the values of the diffusion coefficient, activation energy, charge state of diffusing impurity atoms in the lattice [3-5]. Of great importance is also the diffusion of individual elements, in addition to alloying additives, since it is difficult to completely exclude the ingress of many metals into the crystal, such as aluminum, iron, copper, titanium, etc., both during crystal growth and during technological processing of samples. It is known that silicon grown by the Czochralski method contains oxygen and carbon atoms in large quantities, which also have the ability to actively interact with the main impurity atoms [6,7]. As a result of such interactions, various complexes and complex chemical compounds can form in the volume of silicon single crystals.

The phenomenon of total external reflection of X-rays, in which X-rays do not enter the second medium and are almost completely reflected at the interface between media with different refractive indices [8-10], is observed at grazing angles less than a certain critical angle

α_c. If an X-ray beam falls on the interface between media and its angle of incidence is less than αc, the X-rays are specularly reflected, penetrating 1-2 nm deep into the substance. The critical angle α_c is extremely small and depends on the electron density of the material. The higher the angle of the incident X-ray beam relative to the critical angle, the greater the depth to which the X-rays penetrate into the material. For materials whose surface can be considered ideally flat, the reflectivity decreases sharply at angles greater than the critical angle. An increase in the roughness of the surface of the material leads to a sharp decrease in the reflectivity of this surface.

The aim of this work is to study the changes in the crystal structure and morphology of the near-surface region of n-Si single crystals after doping with palladium atoms using X-ray diffraction and scanning electron microscopy.

2. Experimental part

The experiments were performed on n-type silicon grown by the Czochralski method with a resistivity of 40 Ohm×cm. The concentration of the phosphorus dopant in the initial n-Si single crystals was $7.3\times10^{13}\div7.1\times10^{15}$ cm^{-3}. Silicon was doped with palladium by the diffusion method with the deposition of palladium atoms on the silicon surface in evacuated quartz ampoules at temperatures of 1100 and 1200 °C for 3÷5 hours.

The studies of doped silicon samples were carried out on an X-ray spectrometer with a Miniflex 300/600 goniometer and a D/teX Ultra2 detector. Cukα1 radiation (λ = 1.541 Å) was used at an accelerating voltage of 40 keV and a current of 15 mA on the X-ray tube. The measurements were carried out in the Bragg-Brentano beam geometry in the range of 2θ = from 5° to 60° continuously with a scanning rate of 10 degrees/min and an angular step of 0.02°. A scanning electron microscope “Tascan Vega3” was used to study the surface morphology of silicon single crystals.

3. Results and discussions

After doping at high temperatures with palladium, the diffraction pattern of the interaction of the Si single crystal with doping at different temperatures was analyzed. Based on the obtained results, the lattice parameter changes were theoretically determined using the Rietveld method supported by the Mag2pol software package [11,12]. As shown by various studies, the space group of the original material was determined as Fd-3m, which is consistent with our results after calculations.

In Fig. 1, the red line is the Rietveld diagram, the black dots correspond to the experimental scattering data, and the blue line indicates the difference between the theoretical and experimental results. The vertical green lines indicate the Bragg positions. The diffraction peak of the studied single crystal is designated as (111) [13-14]. The peak corresponding to this orientation is observed at 2θ = 28.54° for the initial state.

The absence of any phase transition suggests that substitution of Si atoms after interaction with the alloy at different temperatures is the more likely cause. The shift in scattering angles due to this expansion by 0.2 and 0.26, respectively, is shown in Figure 1.

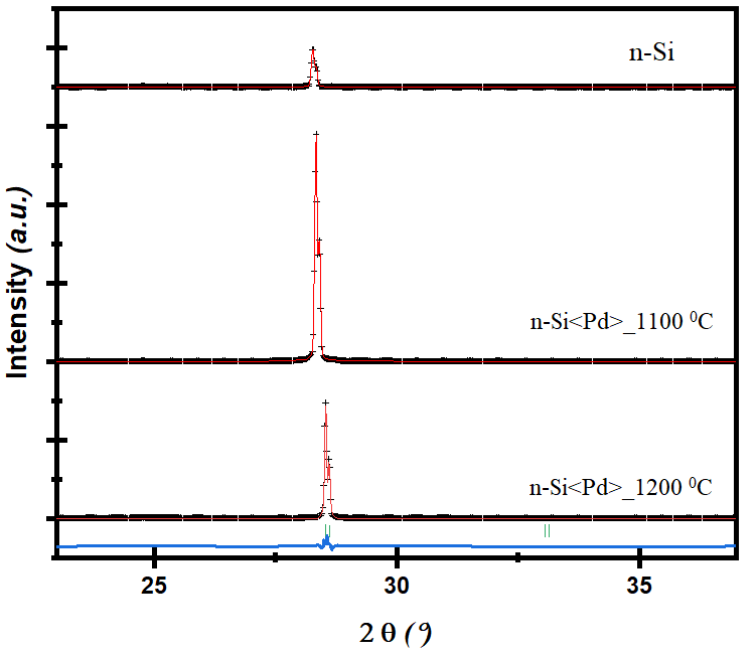

Figure 1. X-ray diffraction spectra of Si single crystals for each experimental condition

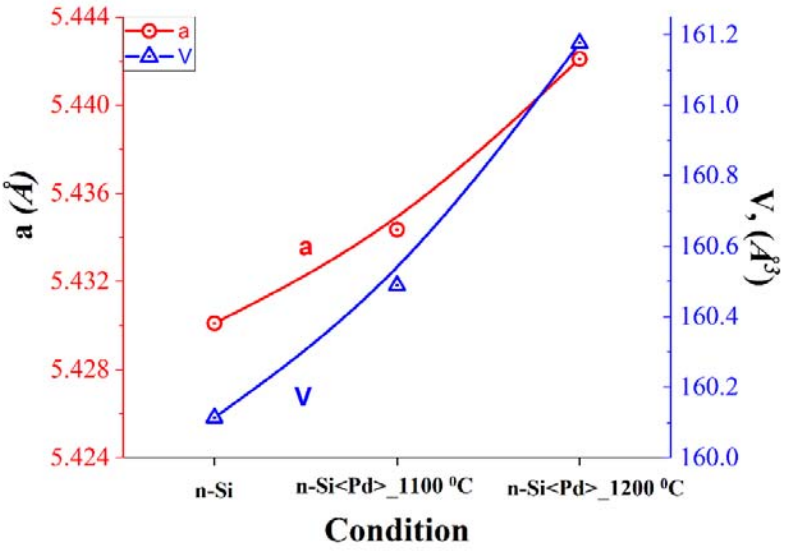

Figure 2. Changes in lattice parameters. The red line represents the change in the lattice constant a, the blue line shows the change in the volume parameter V

The results of the lattice determination after the Rietveld refinement are clearly shown in Figure 2. The errors of the fitting results in the graph indicate the accuracy of the refinement. Certain results show that the expansion of the lattice size became inevitable after alloying at high temperatures. This can be explained by the substitution of Pd atoms with large ionic radius for Si atoms and the effect of temperature, leading to expansion. The left shift in the X-ray spectrum indicates an increase in the lattice parameters, which can be the result of thermal expansion, alloying, or chemical interactions. Comparison of the spectra presented in Figure 1

shows that after the initial doping effect, the sample not only retained the long-range order, but also strengthened it. This may be due to the fact that at 1100 ºC, the Pd atoms cannot penetrate sufficiently, and the annealing effect of temperature increases the crystallinity of the single crystal.

In contrast, the interaction with the alloy at 1200 ºC shows completely opposite results. The decrease in intensity thus indicates that the substitution of Si atoms in the lattice after the interaction with new atoms, as well as the substitution with atoms with a larger atomic radius, led to the creation of distortions in the crystal lattice.

As stated in many studies, Si exhibits anisotropic properties [15,16]. In the W-H plot of the sample, the negative intercept does not directly indicate anisotropy; however, the expansion of FWHM actually indicates an increase in microstrain. This indirectly confirms that the negative intercept result is related to anisotropy.

Table 1. Changes in lattice parameters under the influence of high temperature and Pd ions.

Space Group	Condition	a (Å)	V (Å^3)
F d -3m (227)	300 *K*	5.4301	160.114
F d -3m (227)	1373 *K* + Pd	5.43436	160.489
F d -3m (227)	1473 *K* + Pd	5.4421	161.176

Table 1 clearly shows how the parameters changed after the alloying process. Alloying with Pd atoms caused a noticeable increase in the lattice parameters. When studying the changes in the lattice parameters, it was found that when alloying at 1100 ºC, the expansion was 0.08%, and at 1200 ºC, 0.22%.

The presence of palladium in single crystals is confirmed by X-ray spectral microanalysis, according to which the palladium content in the samples is 0.57 at.% or 2.82 wt.%. Energy dispersive spectra (Fig. 3) indicate the presence of oxygen and carbon atoms in the composition of the studied samples in addition to palladium atoms. The content of oxygen atoms in the samples is 1.03 at.% or 1.32 wt.%, carbon atoms 2.3 at.%, respectively.

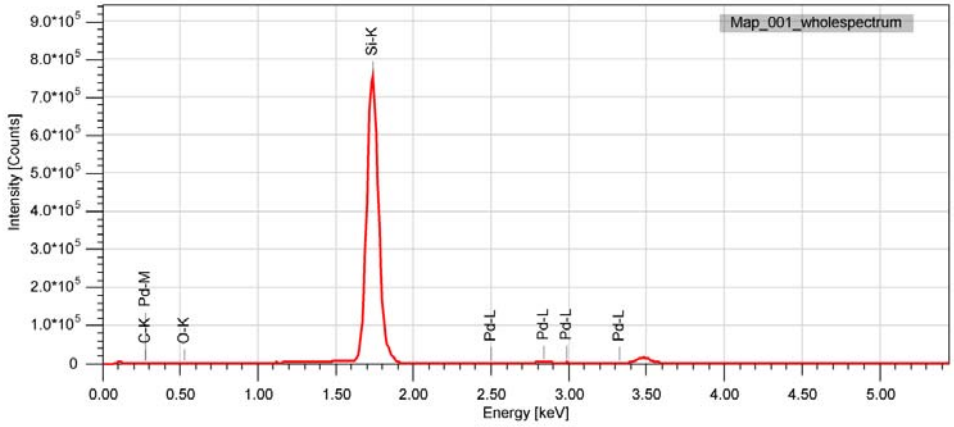

Fig. 3. Energy dispersive spectra of silicon samples doped with palladium

We also further studied the morphology and formation of microstructures on the surface

of the doped samples. Fig. 4 shows micrographs of the original and doped samples. Micrographs of the Pd-doped Si samples (Fig. 4b, 4c) show that after diffusion doping with Pd atoms, microstructures are formed on the silicon surface.

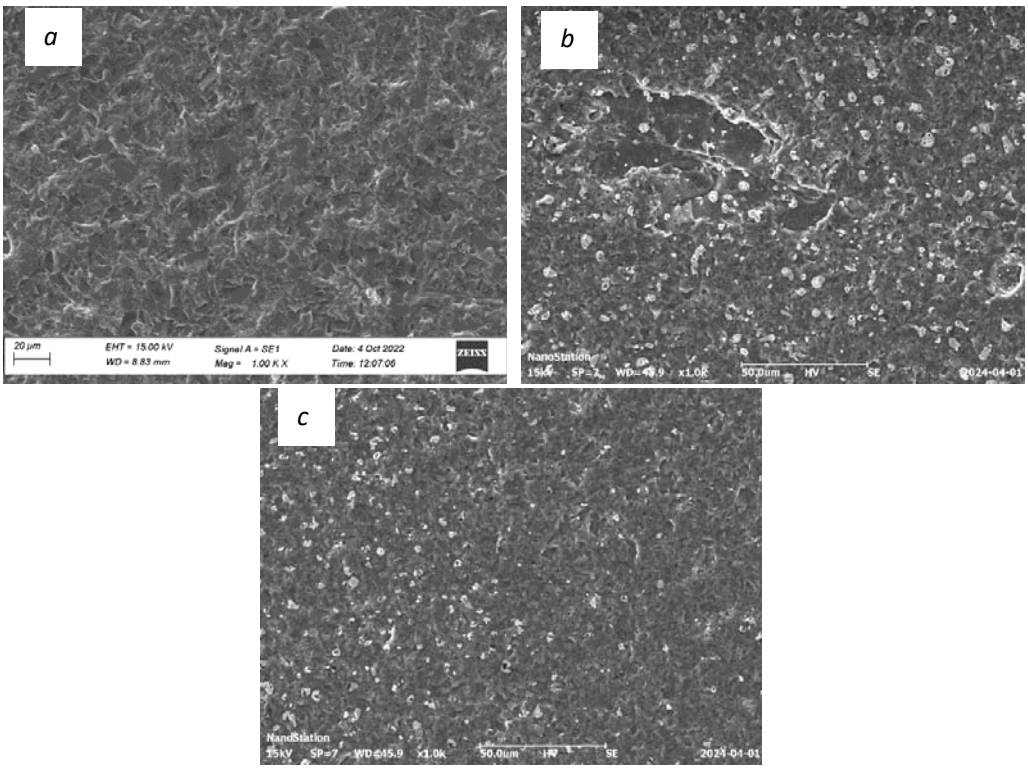

Fig. 4. – Micrographs of the surface of single-crystal silicon plates before (a) and after doping with palladium (at 1100 ^{o}C (b) and at 1200 ^{o}C (c))

From the obtained results we can conclude that doping silicon with palladium atoms at 1100 ^{o}C (Fig. 4b) leads to the formation of structural microdefects with a low concentration, and the introduction of palladium impurity into Si at 1200 ^{o}C (Fig. 4c) leads to the creation of smaller structural defects with a high concentration [17,18]. Apparently, when doping silicon in the process of diffusion, the atoms interact with technological impurities with the formation of some complexes of the type (Pd-O), as a result of which the concentration of interstitial optically active oxygen N_O^{opt} decreases.

4. Conclusion

Based on the X-ray structural analysis carried out after alloying Si atoms with Pd atoms, the following main indicators of the effect of temperature on this process were identified: at a temperature of 1100 ^{o}C, the main effect on the single crystal is exerted by temperature, leading only to an increase in crystallinity; at 1100 ^{o}C, the ability of Pd atoms to penetrate into the Si single crystal is limited, which leads to substitution, increasing the microstrain in the lattice. At 1200 ^{o}C, doping leads to substitution of atoms in the lattice, which disrupts the long-range order; the crystal lattice expanded by 0.08% and 0.22%, respectively, under two experimental conditions.

Micrographs of Pd-doped Si samples show that doping silicon with palladium atoms at 1100 ºC leads to the formation of structural microdefects with a low concentration, and the introduction of palladium impurity into Si at 1200 ºC leads to the creation of smaller structural defects with a high concentration.

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