COOLING-REGIME-CONTROLLED STRUCTURAL EVOLUTION OF RHODIUM-DIFFUSED n-Si<P,Rh> MONOCRYSTALS: A WIDE ANGLE XRD STUDY

Z. M. Ibrohimov[3]
Andijan State Technical Institute, Andijan, Uzbekistan

Abstract:

This thesis presents a wide-angle X-ray diffraction study of the cooling-regime-controlled structural evolution of rhodium-diffused phosphorus-doped n-type silicon monocrystals. The main purpose of the work is to analyze how slow and rapid cooling after high-temperature treatment at 1300 °C influence the diffraction response of the silicon matrix. Special attention is focused on the dominant $(111)_{Si}$ reflection, which serves as a sensitive indicator of crystallographic orientation, coherent scattering intensity, and defect-related structural changes. The wide-angle XRD pattern shows that both slow-cooled and rapidly cooled n-Si<P,Rh> samples preserve the main monocrystalline silicon structure. However, the intensity and shape of the $(111)_{Si}$ peak differ significantly depending on the cooling regime. The slow-cooled sample demonstrates a higher $(111)_{Si}$ peak intensity and FWHM = 0.163°, indicating stronger coherent scattering from the silicon matrix and a more developed redistribution of Rh-related defect complexes. In contrast, the rapidly cooled sample exhibits a lower peak intensity and FWHM = 0.147°, which can be associated with the retention of nonequilibrium defects, frozen microstrain fields, and local impurity-defect configurations. The obtained results confirm that post-diffusion cooling is an important technological factor controlling the structural state of rhodium-diffused silicon. Slow cooling promotes partial relaxation and stabilization of Rh-related structural regions, whereas rapid cooling preserves a more nonequilibrium defect

state. These findings are relevant for optimizing silicon-based microelectronic, optoelectronic, and radiation-resistant semiconductor devices.

Keywords: rhodium-diffused silicon, n-Si<P,Rh>, wide-angle XRD, slow cooling, rapid cooling, $(111)_{Si}$ reflection, FWHM, microstrain, defect complexes.

Rhodium-diffused phosphorus-doped n-type silicon monocrystals are important objects for studying the relationship between high-temperature diffusion, impurity-defect interaction, cooling kinetics, and the final structural state of semiconductor materials. Silicon remains the basic material for microelectronic, optoelectronic, photovoltaic, and radiation-resistant devices. However, its functional properties strongly depend on the state of the crystal lattice, the distribution of dopant atoms, the presence of deep-level impurities, and the formation of local microstrain fields. In this respect, rhodium is a technologically interesting transition-metal impurity because it can interact with silicon, oxygen, phosphorus, and intrinsic point defects, thereby modifying both structural and electrophysical characteristics of the material [1].

The present thesis focuses on the wide-angle X-ray diffraction analysis of rhodium-diffused n-Si<P,Rh> monocrystals after high-temperature treatment at 1300 °C under two different cooling regimes. The main purpose is to clarify how slow cooling and rapid cooling affect the diffraction response of the silicon matrix. Special attention is paid to the dominant $(111)_{Si}$ reflection because this peak is highly sensitive to crystallographic orientation, coherent scattering intensity, internal stress, microstrain, and impurity-related structural changes. The comparison of the wide-angle XRD patterns allows one to evaluate not only the local shape of the $(111)_{Si}$ peak but also the general preservation of the monocrystalline silicon framework.

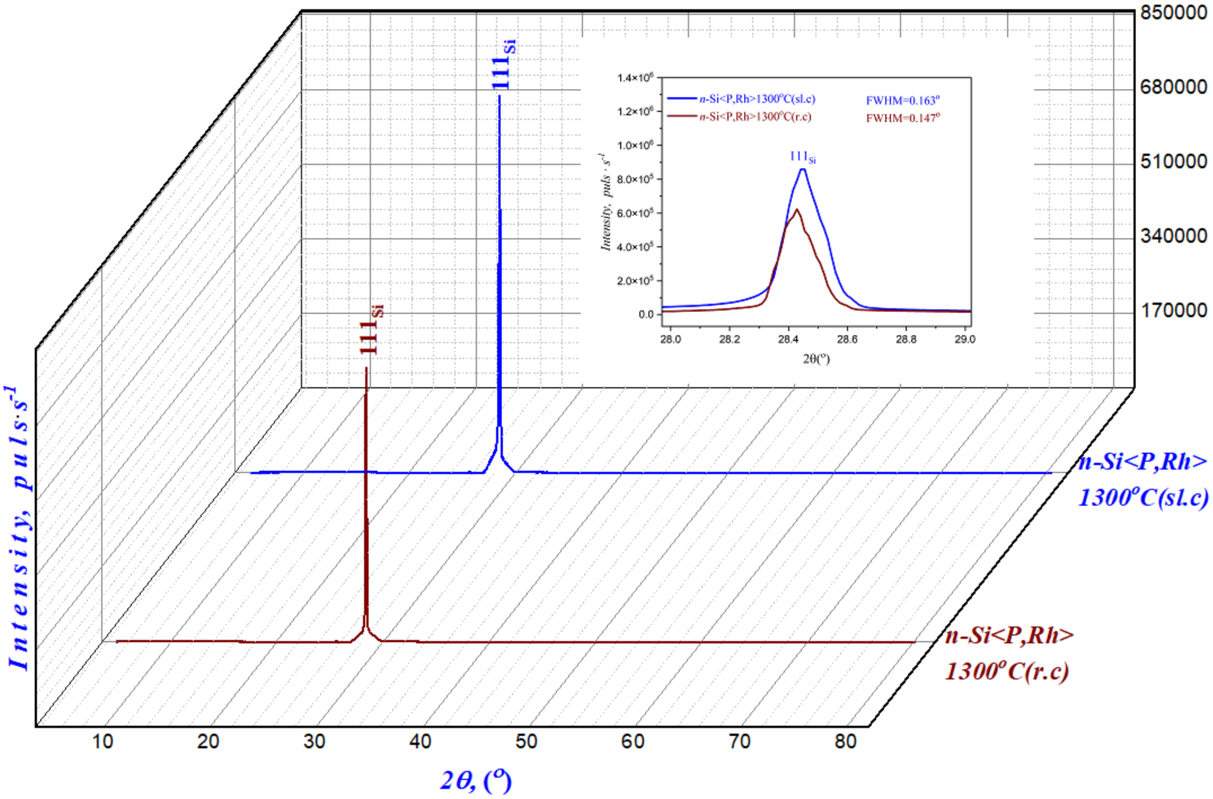

Figure 1. *Wide-angle three-dimensional XRD patterns of rhodium-diffused n-Si<P,Rh> monocrystals after high-temperature treatment at 1300 °C under slow cooling and rapid cooling regimes. The inset shows the enlarged (111)$_{Si}$ diffraction peak, where the slow-cooled sample demonstrates higher intensity and FWHM = 0.163°, while the rapidly cooled sample shows lower intensity and FWHM = 0.147°.*

As shown in Figure 1, both investigated samples exhibit a clearly defined diffraction maximum corresponding to the (111)$_{Si}$ crystallographic plane. This indicates that the main monocrystalline orientation of the silicon matrix is preserved after rhodium diffusion and subsequent cooling. The preservation of the (111)$_{Si}$ peak confirms that the applied high-temperature diffusion process does not destroy the basic diamond-type lattice of silicon. At the same time, the difference in peak height, shape, and FWHM demonstrates that the cooling regime significantly affects the internal structural state of the material. The slow-cooled n-Si<P,Rh> sample is characterized by a higher $(111)_{\mathrm{Si}}$ peak intensity than the rapidly cooled sample. This means that a larger fraction of the silicon matrix contributes coherently to the main Bragg reflection after slow cooling. Such behavior can be explained by the longer time available for defect recombination, impurity redistribution, and partial relaxation of internal stresses during gradual cooling. Rhodium atoms introduced at 1300 °C can migrate toward energetically favorable sites, interact with vacancy-type defects, and participate in the formation of Rh-related structural complexes. Slow cooling allows these processes to proceed more completely, resulting in a stronger diffraction response from the silicon matrix [2].

In contrast, the rapidly cooled sample shows a noticeably lower $(111)_{\mathrm{Si}}$ peak intensity. Rapid cooling limits the time available for atomic redistribution and freezes a larger part of the high-temperature nonequilibrium defect configuration. As a result, vacancies, interstitials, rhodium-related complexes, and oxygen-associated defects may remain distributed in the silicon lattice in a less relaxed state. These frozen defects and local strain fields reduce the effective coherently diffracting volume of the silicon matrix and may increase diffuse scattering. Therefore, the lower peak intensity of the rapidly cooled sample indicates a higher degree of nonequilibrium structural disorder compared with the slow-cooled sample [3]. The FWHM values provide additional information about the microstructural state of the samples. The slow-cooled sample has FWHM = 0.163°, whereas the rapidly cooled sample has FWHM = 0.147°. At first glance, the smaller FWHM of the rapidly cooled sample may seem to indicate a more perfect crystalline structure. However, in thermally processed and impuritydoped monocrystalline silicon, FWHM must be interpreted carefully. Peak width is affected not only by coherent scattering domain size, but also by microstrain, mosaicity, local lattice distortions, impurity redistribution, and instrumental broadening. Therefore, FWHM should not be analyzed separately from peak intensity and peak shape.

The combination of higher intensity and larger FWHM in the slow-cooled sample suggests a structurally more relaxed but microstructurally redistributed state. In this case, the silicon matrix remains highly diffracting, while the broader peak may reflect the presence of several local lattice environments caused by rhodium redistribution, Rh–Si interaction, and impurity-defect complex formation. Thus, the larger FWHM of the slow-cooled sample does not necessarily mean poorer crystallinity. It may indicate that slow cooling promotes a wider distribution of stable local structural states while preserving strong coherent scattering from the silicon matrix [4].

The rapidly cooled sample, on the other hand, exhibits lower peak intensity together with smaller FWHM. This combination indicates that only a smaller part of the crystal volume contributes efficiently to the central $(111)_{Si}$ reflection, while defect-rich or distorted regions contribute weakly to the main Bragg peak or appear as diffuse scattering. Therefore, the smaller FWHM of the rapidly cooled sample should not be interpreted as direct evidence of better overall structural quality. The reduced peak intensity shows that the coherent diffraction contribution of the silicon matrix is weakened by the retention of nonequilibrium defects and frozen microstrain fields.

The role of background oxygen in Czochralski-grown silicon should also be considered. Oxygen is commonly present in such silicon crystals and can form oxygen-related complexes, oxide precipitates, or local strain centers during high-temperature treatment. When rhodium is introduced into the silicon matrix, Rh atoms may interact not only with silicon but also with oxygen. Under slow cooling, Rh–Si interaction and partial structural stabilization may be more favorable, whereas rapid cooling can preserve Rh–O-related local configurations or oxide-like nanophases. Therefore, the final diffraction behavior of n-Si<P,Rh> is determined by the combined influence of rhodium diffusion, phosphorus doping, oxygen background, defect migration, and post-diffusion cooling kinetics [5].

The wide-angle three-dimensional XRD representation is especially useful because it shows that the dominant structural response in both samples remains associated with the silicon matrix. The inset provides a detailed comparison of the $(111)_{Si}$ peak, while the full wide-angle pattern confirms that the observed changes are not isolated graphical features but part of the general diffraction behavior of the material. This combined representation strengthens the interpretation because it connects local peak-shape analysis with broader phase and structural context.

From a technological point of view, the obtained results show that post-diffusion cooling is an important parameter for controlling the structural state of rhodium-diffused silicon. Slow cooling may be preferable when stronger coherent scattering, partial stress relaxation, and more stable Rh-related structural configurations are required. Rapid cooling may be useful when nonequilibrium impurity-defect states need to be preserved, although this regime can reduce the effective coherent diffraction intensity and increase local structural disorder. Thus, the selection of cooling regime should depend on the intended application of the material. These results are relevant for the development of silicon-based microelectronic, optoelectronic, and radiation-resistant devices. Rhodium-related centers can influence carrier lifetime, recombination processes, conductivity relaxation, and radiation-induced defect behavior. Therefore, the ability to control

the defect state and microstructural organization of n-Si<P,Rh> monocrystals by changing the cooling regime may provide a useful technological route for optimizing semiconductor device performance.

In conclusion, the wide-angle XRD analysis demonstrates that slow and rapid cooling regimes lead to different structural states in rhodium-diffused n-Si<P,Rh> monocrystals. Both samples preserve the dominant $(111)_{\text{Si}}$ orientation, confirming that the monocrystalline silicon matrix remains stable after high-temperature treatment. However, slow cooling results in a higher $(111)_{\text{Si}}$ peak intensity and FWHM = 0.163°, indicating stronger coherent scattering and developed impurity-defect redistribution. Rapid cooling leads to lower peak intensity and FWHM = 0.147°, which is associated with frozen nonequilibrium defects and reduced coherent scattering from the silicon matrix. These findings confirm that cooling regime is a key technological factor for controlling the structural evolution of rhodium-diffused n-type silicon monocrystals.

References

[1] Li J., Wang J., Zhong Z., Li Z., Wen Y., Wang L., Liu L. Pathway and control of oxygen transport in the melt during single crystal silicon growth by continuous-feeding Czochralski method. Journal of Crystal Growth, 2025, Vol. 662, Article 128183. https://doi.org/10.1016/j.jcrysgro.2025.128183

[2] Newman R. Oxygen diffusion and precipitation in Czochralski silicon. Journal of Physics: Condensed Matter, 2000, Vol. 12, No. 25, pp. R335–R365. https://doi.org/10.1088/0953-8984/12/25/201

[3] Wang Q., Zhang M., Peng M. Effect of annealing conditions on phosphorus inward diffusion from N+ Poly-Si layer in N-type TOPCon solar cells. Materials Science in Semiconductor Processing, 2024, Vol. 176, Article 108282. https://doi.org/10.1016/j.mssp.2024.108282

[4] Schellenberg L., Jorda J. L., Muller J. The rhodium-silicon phase diagram. Journal of the Less Common Metals, 1985, Vol. 109, No. 2, pp. 261–274. https://doi.org/10.1016/0022-5088(85)90058-X

[5] Turano M. E., Jamka E. A., Gillum M. Z., Gibson K. D. Emergence of subsurface oxygen on Rh(111). The Journal of Physical Chemistry Letters, 2021, Vol. 12, No. 25, pp. 5844–5849. https://doi.org/10.1021/acs.jpclett.1c01820