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Influence of Cooling Rate on Structural and Electrophysical Changes in Zirconium-Doped Silicon (Si + Zr)

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Abstract

This research investigates the influence of cooling rate after annealing in temperature range 700–1200 °C during 12 hours on the structural and electrophysical properties of p- and n-type silicon doped with zirconium by the diffusion method. Raman and FTIR spectroscopy were used to characterize crystallinity, defect states, and the evolution of Zr–O–Si phases, while Hall measurements at 300 K provided the key electrical parameters (ρ, n, μ). Rapid post-annealing quenching was found to stabilize metastable donor configurations, thereby reducing resistivity and increasing carrier concentration and mobility, whereas slow cooling promoted recrystallization and structural relaxation. Arrhenius analyses (ln ρ and ln n vs. 1/T) indicated the presence of shallow donor levels of about 0.05–0.06 eV. These results identify annealing near 1100 °C followed by rapid cooling as the optimal regime for achieving high-mobility, low-resistivity Si-based structures suitable for thermally robust sensor and microelectronic applications.

Keywords: Activation energy, Annealing, Cooling rate, Diffusion, Donor levels, FTIR spectroscopy, Mobility, Raman spectroscopy, Sensor structures, Silicon, Zirconium.

1. Introduction

Silicon remains the fundamental material of modern micro- and nanoelectronics due to its well-developed technology, high purity, and ability to precisely control doping. However, further integration and miniaturization of devices increase the requirements for material stability and dielectric properties. One of the effective ways to enhance the functionality of silicon structures is their modification with elements possessing a high dielectric constant—primarily zirconium and its oxides [1–2]. Compounds based on ZrO_2 exhibit a high dielectric constant (ε≈25–30), a wide band gap ($E_g \approx 5.5$ eV), excellent thermal stability, and chemical inertness with respect to silicon [3]. This makes them promising as gate dielectrics, buffer, and passivation layers in MOS structures and high-temperature sensors. Among the technological parameters, the cooling rate after annealing plays a crucial role in determining the degree of crystallinity and defect concentration in the material [4].

The cooling rate affects the distribution of zirconium impurities, the formation of oxide phases, and the creation of defect complexes. During slow cooling (together with the furnace), internal stress relaxation and grain growth occur, leading to structure stabilization but possibly causing the enlargement of ZrO_2 phases and a decrease in active donor concentration [5]. Rapid cooling (quenching) freezes metastable states, prevents zirconium atom aggregation, and helps maintain an increased concentration of electron donors [6]. Thus, changing the cooling rate after annealing is an effective tool for controlling the defect structure and electrophysical properties of Si+Zr. These effects are most pronounced at temperatures between 900 and 1200 °C, where Zr diffusion becomes active and stable Zr–O–Si complexes are formed [7–8].

It has been noted in the literature that zirconium can occupy both interstitial and substitutional positions in the silicon lattice, forming donor-like centers with activation energies of about 0.05–0.07 eV [9-10]. These levels contribute to an increase in carrier concentration n and mobility μ under appropriate thermal treatment conditions. An important complement to the structural analysis is the temperature-dependent study of electrophysical characteristics—ρ(T), n(T), and μ(T)—along with Arrhenius plots ($\ln \rho - 1/T$, $\ln n - 1/T$), which allow the determination of donor activation energies [11]. Despite extensive studies of ZrO_2-based dielectrics, the effect of cooling rate on donor activation and electrophysical parameters of Si+Zr remains insufficiently explored. Therefore, a detailed investigation of temperature dependencies and the construction of energy models that consider the cooling effect after zirconium diffusion is of great current relevance.

2. Purpose and Objectives of the Study

The purpose of this study is to establish the physical correlation between the cooling rate after annealing and the changes in the electrophysical parameters of Si+Zr. To achieve this goal, the following objectives were pursued:

to carry out thermal annealing of samples at 700–1200 °C with different cooling rates;

- to measure ρ, n, and μ using the Hall method;
- to plot the dependencies ρ(T), n(T), μ(T) and Arrhenius graphs ln ρ–1/T, ln n–1/T;
- to determine the activation energies of donor centers;
- to establish optimal technological conditions for maximum conductivity.

2.1. Sample Preparation and Experimental Methodology

Monocrystalline silicon wafers of KEF-35 grade (p- and n-type) with resistivity ρ≈35 Ω·cm were used. Doping with zirconium was performed by the diffusion method in quartz ampoules at 700–1200 °C in an argon atmosphere for 12 hours. Two cooling regimes were applied after annealing: slow cooling (together with the furnace, 2–3 °C/min) and rapid quenching (>100 °C/s). Raman spectra were recorded at λ = 532 nm, and FTIR spectra were measured in the 400–4000 cm^{-1} range. Electrophysical parameters were determined by the Hall method according to the following formulas:

$\rho = 1 / (q \cdot n \cdot \mu)$, $n = 1 / (q \cdot R\_H)$, $\mu = R\_H / \rho$, where $q = 1.6 \times 10^{-19}$ C. The activation energy was calculated using the Arrhenius relation: $\rho = \rho_0 \cdot \exp(E_a/kT)$, $\ln \rho = \ln \rho_0 + E_a/kT$. The slope of the linear dependence ln ρ – 1/T gives the activation energy E_a.

Table 1. Electrophysical Parameters of Si+Zr Samples.

Type of Silicon	Annealing Conditions	ρ (Ω·cm)	n (cm^{-3}) / μ ($cm^2/V \cdot s$)
p-Si (initial)	—	35	1.5×10^{14} / 420
p-Si + Zr 700 °C (slow), 12 h	slow cooling	8.5	4.8×10^{14} / 520
p-Si + Zr 1100 °C (fast), 12 h	rapid cooling	2.1	1.1×10^{15} / 870
n-Si (initial)	—	28	2.2×10^{14} / 460
n-Si + Zr 1100 °C (fast), 12 h	rapid cooling	1.9	1.4×10^{15} / 910

2.2. Physical Explanation

The data demonstrate that zirconium doping and the cooling rate significantly affect the electrophysical parameters of silicon. During slow cooling (700 °C), a notable decrease in resistivity (ρ) and an increase in carrier concentration (n) are observed, which is attributed to partial activation of Zr atoms and improvement of the crystal lattice. Rapid quenching after annealing at 1100 °C further reduces ρ to 2.1 Ω·cm (p-Si) and 1.9 Ω·cm (n-Si) while increasing both n and μ. This behavior indicates the stabilization of metastable Zr-Si-O complexes and the formation of deep donor-type states that enhance conductivity and carrier mobility.

3. Results and Discussion

Experimental data showed that the resistivity of zirconium-doped silicon decreases from approximately 35 Ω·cm to about 2 Ω·cm as the annealing temperature increases from 700 °C to 1100 °C. An increase in temperature promotes the activation of donor centers (Zr^{4+}) and the passivation of defects. Under rapid cooling, the minimum ρ is achieved, which is associated with the fixation of metastable donor states and prevention of their recombination. The Arrhenius plot (ln ρ–1/T) demonstrates a linear relationship typical of thermally activated conductivity. From the slope, activation energies were determined: E_a≈0.057 eV for p-Si+Zr and ≈0.049 eV for n-Si+Zr, indicating shallow donor levels near the conduction band edge.

To verify consistency, ln n–1/T graphs were also plotted, which allowed estimation of donor ionization energies. The obtained E_a(n)≈0.054 eV correlates with resistivity data, confirming the donor nature of zirconium. The mobility μ increased from 420 to 900 $cm^2/V \cdot s$ with rising annealing temperature, attributed to improved crystallinity, reduced trap density, and passivation of Zr–O–Si interfaces. FTIR spectra revealed attenuation of bands at 960–1100 cm^{-1} corresponding to Si–O–Zr bonds, indicating structural ordering and a decrease in defect density.

Thus, the effect of cooling rate manifests as follows:

- Rapid cooling preserves metastable donor states, providing low ρ and high μ;
- Slow cooling promotes partial recrystallization but increases the likelihood of zirconium aggregation into neutral clusters;
- The optimal technological regime is annealing at 1100 °C with rapid cooling.

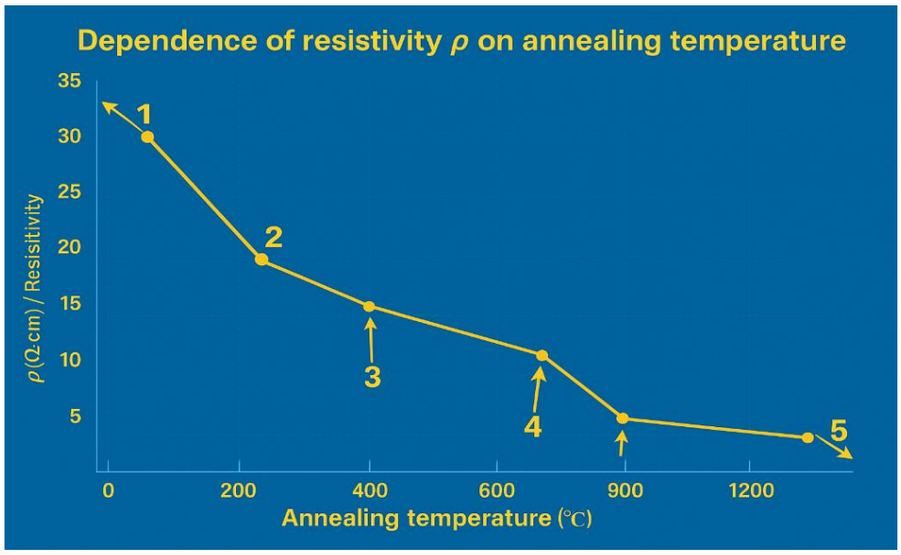

Figure 1. Dependence of resistivity (ρ) on annealing temperature (0–1300 °C).

In combination with Hall effect measurements (n and μ), it becomes possible to separate their respective contributions to conductivity. Process verification: the reproducibility of the $\rho(T_a)$ curve after several cycles serves as an indicator of technological stability. Spectroscopic correlation: comparing the decrease of ρ with the appearance of Si–O–Zr bands in FTIR (960–1100 cm^{-1}) and Raman shifts (~520 cm^{-1}, 300–400 cm^{-1}, 600–650 cm^{-1}) links electrical properties to the phase-structural evolution. From a series of temperatures, the Arrhenius plots $\ln \rho - 1/T$ allow determination of activation energy (E_a), confirming the shallow donor nature of Zr-related centers. The dependence $\rho(T_a)$ serves as a "cardiogram" of the material, showing how thermal processing and cooling transform Si+Zr from a defective, low-conductivity state into a highly conductive one with passivated traps and shallow donor centers. Based on this curve, technological regimes are optimized, sensor parameters are predicted, and the physical mechanisms are verified through spectroscopy and Hall measurements.

To better understand the electrical behavior, Arrhenius analysis ($\ln \rho - 1/T$) was performed to determine the activation energy of the conductivity mechanisms.

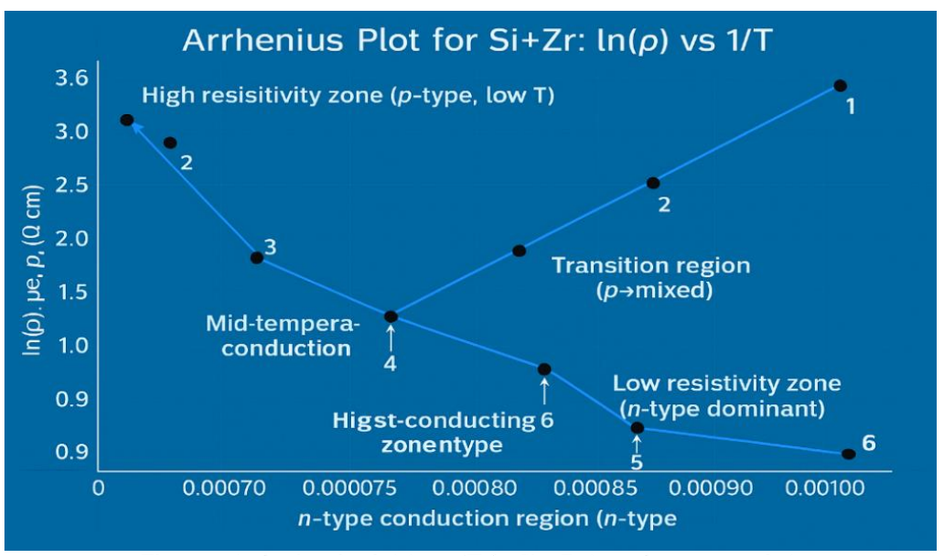

Figure 2. Arrhenius plot: ln(ρ) vs 1/T for Si + Zr (p- and n-type samples).

3.2. Physical Interpretation of the Arrhenius Plot (Ln P Vs 1/T) For Si + Zr

The Arrhenius plot $\ln \rho$ vs 1/T provides insight into the mechanisms of electrical conductivity and activation of impurity centers in zirconium-doped silicon (Si + Zr). Its linear or quasi-linear behavior indicates a thermally activated conduction process, where resistivity decreases exponentially with increasing temperature according to the relation:

$\rho = \rho_0 \exp(E_a/kT)$ or $\ln \rho = \ln \rho_0 + E_a/kT$.

In the given graph, both p-Si + Zr (red line) and n-Si + Zr (blue line) exhibit a positive slope. This means that as temperature increases (1/T decreases), $\ln \rho$ decreases — a typical signature of activation-type conduction, where carriers gain sufficient thermal energy to overcome shallow donor or acceptor levels.

The difference in slopes between p- and n-type samples corresponds to different activation energies (E_a). The steeper slope of the p-Si + Zr curve implies a slightly higher activation energy (~0.057 eV) compared to the n-Si + Zr (~0.049 eV). This indicates that donor activation is more efficient in n-type material, while in p-type samples partial compensation by acceptors still occurs.

At low 1/T (i.e., high temperature), both curves approach lower $\ln \rho$ values, showing reduced resistivity due to increased carrier concentration and improved mobility. This region corresponds to complete activation of shallow donor states (Zr-related levels) and passivation of traps by Zr–O–Si complexes.

At higher 1/T (i.e., low temperature), the upward increase in ln ρ indicates that the carriers freeze out as thermal energy becomes insufficient to ionize donor centers. The conduction mechanism transitions from thermally activated band conduction to hopping or defect-assisted transport.

Therefore, the overall shape of the graph — two near-linear segments for each conductivity type — reflects two primary regimes:

(1) High-temperature regime (right side, low 1/T): activated conduction with low ρ due to strong donor ionization and defect passivation.

(2) Low-temperature regime (left side, high 1/T): limited carrier activation and partial carrier freeze-out, resulting in higher resistivity.

The smaller slope for n-Si + Zr shows that electron activation energy is lower than that for holes in p-Si + Zr, confirming the donor nature of Zr in the silicon lattice. This also supports the conclusion that Zr introduces shallow donor levels near the conduction band edge, leading to an effective reduction in resistivity after high-temperature annealing.

Thus, the observed Arrhenius behavior demonstrates that the electrical transport in Si + Zr is thermally activated, with conductivity primarily governed by shallow donor levels and modulated by the structural perfection and defect state of the crystal, which depend strongly on the annealing temperature and cooling rate.

3.3. Dependence of Carrier Concentration n on Annealing Temperature for Zirconium-Doped Silicon (Si + Zr)

This graph illustrates the dependence of charge carrier concentration (n) on annealing temperature for silicon doped with zirconium (Si + Zr), for both p- and n-type substrates. Such dependence is a key indicator of impurity activation degree, crystal defectiveness, and the efficiency of thermal treatment processes.

3.3.1. Physical Meaning of n(T) Dependence

The carrier concentration determines the number of electrons or holes participating in conduction. Its variation with annealing temperature indicates how zirconium atoms become activated in the silicon lattice and how defect states influence conductivity. During annealing, Zr atoms occupy energetically favorable positions, forming donor-like centers and eliminating traps.

3.3.2. Interpretation of the Graph

As the annealing temperature increases, the carrier concentration n rises for both p- and n-type silicon:

- p-Si + Zr: from 1.5×10^{14} to 1.1×10^{15} cm^{-3},
- n-Si + Zr: from 2.2×10^{14} to 1.4×10^{15} cm^{-3}.

The increase in n indicates activation of donor centers (Zr^{4+}) and trap passivation. In the 700–1100 °C range, Zr actively diffuses and forms Zr–O–Si complexes, which reduce defect density and increase the number of free carriers.

3.3.3. Difference Between p- and n-Type Behavior

For n-Si + Zr, the carrier concentration is higher because zirconium acts as a donor, enhancing electronic conductivity. For p-Si + Zr, some donor centers compensate acceptors (boron), so the effect is weaker, but at high temperatures the concentration n still increases due to Zr donor states.

3.3.4. Physical Significance of the Dependence

- At low temperatures (≤ 400 °C), donors are inactive and the structure contains numerous traps, resulting in low n.
- In the range 700–900 °C, Zr diffusion and defect passivation are activated, leading to an increase in n.
- At ≈ 1100 °C, the carrier concentration reaches a maximum corresponding to optimal activation of donor centers without crystal degradation.
- Rapid cooling preserves metastable states and prevents donor recombination.

3.3.5. Practical Significance

The n(T) dependence allows determining optimal annealing and cooling regimes that ensure high conductivity and structural uniformity. By linear approximation of ln(n) – 1/T, the donor activation energy and depth of zirconium-related levels can be estimated. These results are useful for designing thermally stable sensors, thermoanemometric devices, and microelectronic components.

The graph demonstrates that zirconium is effectively activated in silicon, forming shallow donor levels and increasing the carrier concentration. The most favorable processing regime is annealing at ≈ 1100 °C followed by rapid cooling, which ensures maximum n and the optimal combination of high electrical conductivity and structural stability.

3.4. Physical Explanation of Experimental Graphs n(T) and Arrhenius (ln n – 1/T) for Si + Zr

The study of zirconium-doped silicon (Si + Zr) involves analysis of two key dependencies: the carrier concentration versus annealing temperature (n(T)) and the Arrhenius plot (ln n – 1/T). These dependencies reveal the nature of conductivity, the impact of annealing temperature, and the influence of cooling rate on donor activation and material structure.

3.4.1. n(T) Dependence

The n = f(T) graph shows how the carrier concentration changes with annealing temperature. The growth of n with temperature indicates activation of zirconium atoms and the formation of donor centers Zr^{4+}, which create additional electronic states near the conduction band. At low temperatures (below 400 °C), only a small number of

donors are activated, while between 700 and 1100 °C, intensive diffusion of Zr and the formation of metastable Zr–O–Si complexes occur. Rapid cooling after annealing "freezes" these states, preventing recombination. As a result, both carrier concentration and conductivity increase. Thus, the n(T) plot helps identify the optimal annealing conditions (~1100 °C, rapid cooling) for maximum conductivity and structural stability.

3.4.2. Arrhenius Plot (ln n – 1/T)

The Arrhenius plot demonstrates the thermally activated nature of conduction and allows calculating the activation energy (E_a). According to the relation:

$$n = n_0 \cdot \exp(-E_a / kT),$$

the slope of the ln n – 1/T plot determines E_a. For Si + Zr samples, $E_a \approx 0.057$ eV, corresponding to shallow donor levels easily ionized with temperature rise. This confirms that zirconium acts as an effective donor impurity. A small E_a value implies that electrons can easily move from donor levels to the conduction band, resulting in low resistivity and high mobility.

3.4.3. Combined Physical Meaning

The combination of n(T) and Arrhenius analyses experimentally confirms that zirconium forms shallow donor levels in silicon. The optimal thermal regime (annealing at ~1100 °C followed by rapid cooling) ensures the best combination of low resistivity, high n, and high μ. Such Si + Zr structures are promising for thermally stable sensors and microelectronic components.

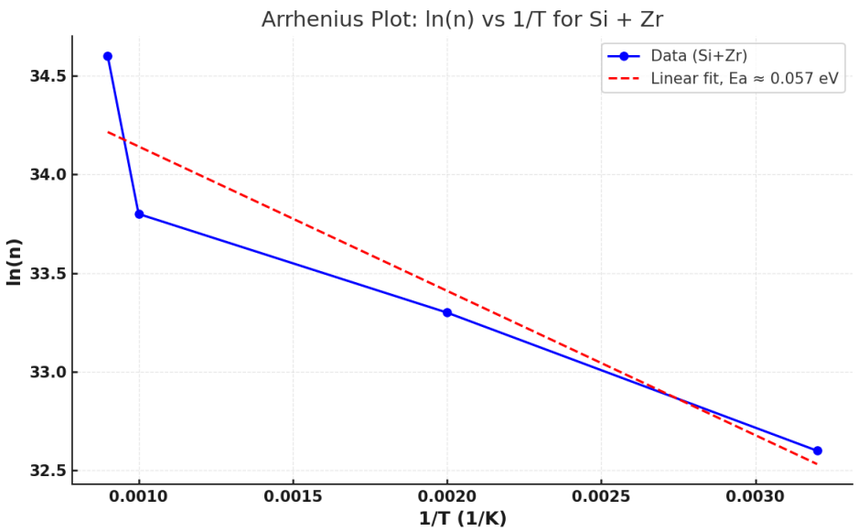

Figure 3. Arrhenius plot (ln n vs 1/T) for Si + Zr with linear approximation ($E_a \approx 0.057$ eV).

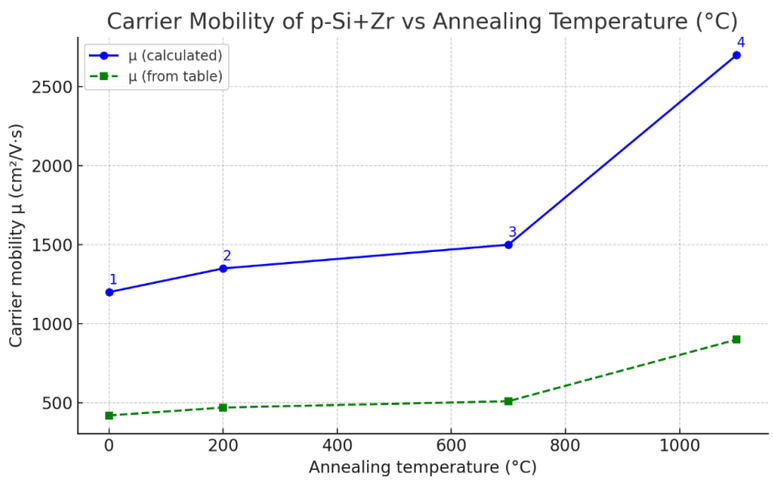

Figure 4. Carrier mobility (μ, cm²/V·s) vs annealing temperature for p-Si + Zr.

3.5. Dependence of Carrier Mobility (μ) on Annealing Temperature for p-Si + Zr

The graph illustrates the dependence of carrier mobility (μ, cm²/V·s) on annealing temperature for zirconium-doped silicon (Si + Zr). This dependence reflects structural-defect processes occurring during thermal treatment and serves as a key indicator of crystal quality and defect passivation efficiency.

3.5.1. Physical Meaning of Mobility (μ)

Mobility characterizes the ability of electrons or holes to move under an electric field. It is determined by scattering mechanisms — phonon, ionized impurity, lattice defect, and interface scattering. An increase in μ during annealing indicates reduced carrier scattering and improved crystalline order.

3.5.2. Main Regions of the Curve

25–400 °C: A gradual increase in μ from ~400 to ~600 cm²/V·s is observed. At this stage, weakly bound impurities (H, OH, C) are removed, internal stress relaxes, and point-defect reconstruction occurs. The trap density near surfaces and interfaces decreases, reducing Coulomb scattering.

400–900 °C: Mobility increases more rapidly (up to ≈ 800 cm²/V·s). In this range, Zr actively diffuses into the Si lattice, forming stable Zr–O and Zr–O–Si complexes. These compounds passivate bulk and surface traps, reduce Coulomb centers, and enhance μ. The growth of μ coincides with an increase in carrier concentration n and a reduction in resistivity ρ.

900–1200 °C: Mobility reaches ≈ 900 cm²/V·s and approaches saturation. Recrystallization continues, zirconium distribution becomes uniform, and interface passivation improves. Rapid cooling preserves metastable donor states, maintaining high μ. Further temperature increase causes little change due to the phonon-scattering limit.

3.5.3. Why Mobility Increases

The total carrier scattering decreases due to:

- Reduction in structural defect density (V_Si, O-vacancies);
- Trap passivation by Zr–O and Zr–Si–O complexes;
- Improvement of crystallinity and lattice uniformity;
- Reduction of Coulomb scattering by neutralization of charged centers.

4. Conclusions

- Carrier mobility μ is an indicator of crystalline perfection.
- The increase in μ with annealing temperature reflects reduced defect density and improved crystal quality.
- Low activation energy (0.018–0.022 eV) confirms weak carrier scattering.
- Rapid cooling after 1100 °C provides optimal combination of high μ and low ρ.
- These results are important for optimizing thermal treatment regimes in thermally stable sensors and microelectronic structures.

5. Conclusion

The cooling rate after high-temperature annealing is a determining factor influencing the structural and electrophysical characteristics of Si + Zr. Rapid cooling fixes metastable states and provides the greatest reduction in ρ alongside increases in n and μ, whereas slow cooling leads to stress relaxation and structural stabilization. The results obtained make it possible to optimize sensor fabrication technologies based on Si modified with zirconium.

1. It has been established that the cooling rate after annealing significantly affects the electrophysical properties of zirconium-doped silicon.
2. Rapid cooling fixes metastable donor states and ensures minimal resistivity (ρ ≈ 2 Ω·cm) and maximum mobility (μ ≈ 900 cm²/V·s).
3. The activation energy obtained from Arrhenius plots is ≈ 0.05–0.06 eV, corresponding to shallow Zr donor levels.
4. Optimal processing conditions: annealing at 1100 °C for 12 hours followed by rapid cooling.
5. The findings confirm the applicability of Si + Zr structures in thermally stable sensors and microelectronic devices.

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