

Feasibility of Neutron Transmutation Doping at HANARO for Vanadium-Pinned Semi-Insulating 4H-SiC Substrates

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1. Introduction

Semi-insulating (SI) 4H-SiC substrates with resistivity above $10^5 \Omega\cdot\text{cm}$ are the standard platform for GaN-on-SiC HEMTs used in 5G/6G base stations, satellite communication payloads and radar. Two production routes dominate. In vanadium-doped SI SiC, vanadium is introduced above roughly 10^{17} cm^{-3} so that the $\text{V}^{4+}/\text{V}^{5+}$ deep donor at $E_C - 1.6 \text{ eV}$ pins the Fermi level. Yield is limited because the concentration must stay below the vanadium carbide precipitation threshold yet remain high enough to dominate residual doping [1]. In high-purity semi-insulating (HPSI) SiC, compensation is supplied by intrinsic point defects, mainly the carbon-vacancy-related $\text{Z}_{1/2}$ and EH6/7 centers. These anneal out during epitaxy and device processing above $1,500^\circ\text{C}$, so the resistivity is not thermally stable.

Neutron transmutation doping (NTD) offers a compensation source that neither route uses. In SiC the reaction $^{30}\text{Si}(n,\gamma)^{31}\text{Si} \rightarrow ^{31}\text{P} + \beta^-$ ($T_{1/2} = 2.62 \text{ h}$) converts lattice ^{30}Si into substitutional phosphorus donors with a spatial distribution fixed by the neutron field rather than by vapor transport, and HANARO has operated a commercial Si-NTD service for 5-, 6- and 8-inch ingots since 2002 [2].

The HANARO SiC-NTD irradiation basket developed for the NTD2 vertical hole has already been demonstrated on 4-inch 4H-SiC, with $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$ reaction-rate non-uniformity of 1.0% axially and 4.8% radially [2]. In that test, however, commercial HPSI wafers of $1 \times 10^7 \Omega\cdot\text{cm}$ were irradiated for 16 h and became n-type conductive at about $14.9 \Omega\cdot\text{cm}$, corresponding to a ^{31}P concentration of $4.2 \times 10^{14} \text{ cm}^{-3}$ [2]. Applied to an already semi-insulating crystal, NTD therefore destroys the semi-insulating property.

This work inverts the starting point. If the ingot is grown deliberately p-type, the NTD-generated phosphorus acts as a compensating rather than a doping species, and the same HANARO capability that degraded HPSI material becomes the means of producing SI material. This paper defines the irradiation requirements the scheme imposes on HANARO and evaluates them against the demonstrated NTD2 performance.

2. Process Concept

2.1. Compensation and Fermi-level pinning

A 4H-SiC ingot is grown by physical vapor transport with a boron concentration N_B exceeding the maximum background nitrogen concentration N_N , so that the as-grown crystal is p-type throughout. Vanadium is co-doped in an intermediate window of 1×10^{15} - $5 \times 10^{16} \text{ cm}^{-3}$, one to two orders of magnitude below the concentrations used in conventional V-doped SI SiC and well below the vanadium carbide precipitation threshold of about $3 \times 10^{17} \text{ cm}^{-3}$ [1].

Neutron irradiation then generates phosphorus donors at a concentration $N_P \approx \Delta N$, where $\Delta N = N_B - N_N$ is the excess acceptor concentration, typically 5×10^{14} - $1 \times 10^{16} \text{ cm}^{-3}$. As the net shallow carrier concentration is driven towards zero, the Fermi level moves to the vanadium deep level and is pinned there. The required condition is that, after post-irradiation annealing, the residual $\text{Z}_{1/2}$ concentration remains below the vanadium concentration, $N(\text{Z}_{1/2}) < N_V$, so that pinning is governed by vanadium rather than by irradiation-induced intrinsic defects. Because vanadium deep levels are thermally stable well above $1,500^\circ\text{C}$, the resulting resistivity is expected to survive downstream epitaxy and device processing, unlike the HPSI route.

2.2. Fluence requirement

The phosphorus concentration produced by irradiation is

$$N_P = N(^{30}\text{Si}) \sigma_{\text{th}} \Phi$$

where $N(^{30}\text{Si}) \approx 1.55 \times 10^{21} \text{ cm}^{-3}$ at the natural 3.09% abundance and $\sigma_{\text{th}} \approx 0.107 \text{ b}$. The nuclear design therefore reduces to one quantity, the fluence Φ needed to cancel ΔN , measured on the as-grown ingot before irradiation.

3. HANARO Irradiation Requirements

3.1. Irradiation time

The measured HANARO result [2] serves directly as a calibration. A phosphorus concentration of $4.2 \times 10^{14} \text{ cm}^{-3}$ in 16 h in the NTD2 basket corresponds to $\Phi \approx 2.5 \times 10^{18} \text{ n}\cdot\text{cm}^{-2}$, an effective thermal flux of about $4.4 \times 10^{13} \text{ n}\cdot\text{cm}^{-2}\text{s}^{-1}$, and a production rate near 2.6×10^{13}

cm⁻³ per hour. Table I applies this rate to the excess-acceptor range of interest.

Table I. Irradiation time in the HANARO NTD2 hole

ΔN (cm ⁻³)	Φ (n·cm ⁻²)	Time (h)
5×10^{14}	3.0×10^{18}	19
1×10^{15}	6.0×10^{18}	38
5×10^{15}	3.0×10^{19}	190
1×10^{16}	6.0×10^{19}	381

Irradiation time scales linearly with ΔN and is therefore set entirely by crystal growth, not by the reactor. Holding background nitrogen at or below 1×10^{16} cm⁻³ so that ΔN can be kept near 1×10^{15} cm⁻³ brings the irradiation into a roughly 40 h window, compatible with a normal HANARO operating cycle, whereas a nitrogen-rich ingot requiring ΔN of 1×10^{16} cm⁻³ would occupy the hole for more than two weeks. Low-nitrogen growth is thus a reactor-throughput specification as much as a materials one, and the single most effective lever on the economics of the service.

3.2. Uniformity

Conventional NTD-Si maps resistivity directly onto fluence, which makes radial gradient specifications of 4-5% demanding. In the present scheme the coupling is weaker. Once the shallow system is close to compensation, resistivity is set by the vanadium level rather than by the exact ratio of phosphorus to excess acceptors, so local departures from $N_p = \Delta N$ are buffered by the deep level provided the sign of the net doping does not vary across the wafer. The demonstrated NTD2 values of 1.0% axial and 4.8% radial [2], with rotational irradiation to average the radial flux gradient, are therefore more than sufficient. The fast-to-thermal flux ratio should nevertheless be minimized, since displacement damage is the limiting factor here.

4. Post-irradiation Annealing

Annealing in the range 1,600-1,700 °C is specified to recover displacement damage, place phosphorus on substitutional Si sites, and electrically activate vanadium. This is the least-established part of the process. In-core irradiated epitaxial 4H-SiC annealed at 1,700 °C for 2 h recovered about 77% of the carrier concentration at fluences of $1.3\text{-}2.7 \times 10^{17}$ n·cm⁻², and higher temperatures were concluded to be necessary for full recovery [3]. The fluences in Table I are one to two orders of magnitude higher, so incomplete recovery would leave a large residual $Z_{1/2}$ population, precisely the condition $N(Z_{1/2}) > N_V$ that must be avoided.

Establishing the annealing window is accordingly the principal experimental task, and it must be verified by deep-level measurement rather than by resistivity alone. EH6/7 lies at $E_C - 1.55$ eV, nearly degenerate with the V^{4+}/V^{5+} level at $E_C - 1.6$ eV, so an activation energy near 1.6 eV does not by itself demonstrate vanadium pinning.

5. Radioactivation and Clearance

Residual activity governs whether irradiated material can leave the site, and it arises from three sources that behave differently.

The first is intrinsic to the matrix. ¹⁴C is produced by ¹⁴N(n,p)¹⁴C and ¹³C(n,γ)¹⁴C, and with a half-life of 5,730 y its specific activity is effectively independent of cooling time [4]. At the fluences of Table I the estimated ¹⁴C specific activity is of the order of several Bq·g⁻¹, above the IAEA unconditional clearance level of 1 Bq·g⁻¹ for ¹⁴C [5]. This is a floor that no cooling period and no purification of metallic impurities can lower.

The second is the intentional dopant set of the present scheme, which adds nothing long-lived. ⁵¹V(n,γ)⁵²V yields a 3.75 min activity, boron produces no long-lived product, and the ³²P generated by ³¹P(n,γ) decays with a 14.3 d half-life within a normal cooling period. Deliberately co-doping a transition metal therefore does not worsen the release problem.

The third is trace contamination, and it dominates the measured activity. Neutron activation analysis of HPSI 4H-SiC wafers irradiated in the HANARO NTD2 hole identified ⁶⁰Co, ⁹⁵Zr and ¹⁸²Ta, with ¹⁸²Ta reaching 7,330 Bq per wafer from a ¹⁸¹Ta mass of up to 1.37 μg [6]. Because the ¹⁸²Ta half-life is 114.7 d, a full year of cooling reduces its activity by only about one order of magnitude, so decay alone is not a practical remedy on a commercial schedule.

The origin of that contamination decides how it should be treated. In [6] the Ta and Zr were attributed to crucible and susceptor coatings, TaC-coated graphite being standard in PVT growth and in epitaxy, and the ⁶⁰Co to handling during wafer fabrication. Our own neutron activation analysis of SiC feedstock powder synthesized in-house for ingot growth supports that attribution directly. Co, Zr and Ta were all below the detection limits, while Na, Al, Sc, V, Cr, Fe, La, Ce and W were quantified. The dominant activation contributors are therefore introduced during growth and handling rather than carried by the raw material, which makes them an engineering variable rather than a property of SiC. Ta-free crucible and susceptor materials, combined with activation analysis of feedstock as an incoming quality gate, should remove the largest contributor. Of the elements that remain, only ⁴⁶Sc at 83.8 d has a half-life comparable to ¹⁸²Ta and needs quantification.

The practical division is therefore clear. ¹⁴C fixes the clearance category, so NTD-SiC cannot be released under unconditional clearance at any cooling time and requires a conditional or case-by-case framework. ¹⁸²Ta fixes the shielding burden and the margin available inside that framework, and unlike ¹⁴C it can be engineered away at source. Since the ¹⁴N(n,p) channel also scales with nitrogen content, low-nitrogen growth works in favor of both.

6. Conclusions

An NTD route to thermally stable semi-insulating 4H-SiC has been formulated in terms of what it asks of HANARO. Starting from p-type, boron-rich, low-vanadium material, the required fluence is 3×10^{18} – 6×10^{19} n·cm⁻², corresponding to 19–381 h in the NTD2 hole at the demonstrated production rate, with roughly 40 h for the preferred design point. The uniformity already achieved by the SiC-NTD basket exceeds what the scheme requires, because deep-level pinning buffers fluence non-uniformity. The open items are the annealing window at these fluences, verification that vanadium rather than $Z_{1/2}$ controls the Fermi level, and a conditional clearance pathway for ¹⁴C. These will be addressed by irradiating B/V co-doped p-type material in NTD2, followed by high-temperature annealing.

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