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Photoelectron holographic study for atomic sites occupancy for Si dopant in Si-doped κ -Ga₂O₃(001)

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Abstract

We investigated atomic sites occupancy for the Si dopant in Si-doped κ -
Ga₂O₃(001) using photoelectron spectroscopy (PES) and photoelectron holography
(PEH). From PES and PEH, we found that the Si dopant had one chemical state and three

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6 types of inequivalent Si substitutional sites (Si_{Ga}) were formed. The ratios for the
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9 inequivalent tetrahedral, pentahedral, and octahedral Si_{Ga} sites were estimated to be
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12 55.0%, 28.1%, and 16.9%, respectively. Higher (lower) ratios for the three inequivalent
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15 Si_{Ga} sites may come from lower (higher) formation energy. The Tetra (Octa) Si_{Ga} site has
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18 the highest (lowest) ratio of the three Si_{Ga} sites since it has the lowest (highest) formation
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21 energy. We suggest that the tetrahedral Si_{Ga} site is due to the active dopant site, whereas
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24 the pentahedral and octahedral Si_{Ga} sites can be attributed to the inactive dopant sites for
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27 the Si-doped $\kappa\text{-Ga}_2\text{O}_3(001)$.
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Introduction

In recent years, gallium oxide (Ga_2O_3) has attracted considerable interest as an ultra-wide bandgap semiconductor because of a bandgap of around 5 eV, high thermal stability, and the availability of large-scale $\beta\text{-Ga}_2\text{O}_3$ single crystal wafers. Such superior Ga_2O_3 properties can apply to the field of power electronics.¹⁻⁷ For Ga_2O_3 , there are five crystal polymorphs: α -, β -, δ -, γ -, and $\kappa\text{-Ga}_2\text{O}_3$.^{3,4} Among them, the most thermodynamically stable is $\beta\text{-Ga}_2\text{O}_3$, which has been widely investigated.⁶⁻⁹

Recently, the orthorhombic $\kappa\text{-Ga}_2\text{O}_3$ polymorph is gaining attention due to its higher symmetry with respect to monoclinic structure, its large spontaneous polarization along the (001) direction, and its ferroelectricity.¹⁰⁻¹³ According to previous studies, this structure can be synthesized by several chemical- and physical-vapor phase epitaxial techniques (e.g., metal-organic vapor phase epitaxy MOVPE, halide vapor phase epitaxy, molecular beam epitaxy, and pulsed laser deposition) on various substrates.¹⁴ Among them, c-plane sapphire has been so far the most frequently used substrate for $\kappa\text{-Ga}_2\text{O}_3$ epitaxy.^{7,15-18} The $\kappa\text{-Ga}_2\text{O}_3$ structure is shown in Figure 1(a). There are three inequivalent Ga atomic sites in $\kappa\text{-Ga}_2\text{O}_3$: octahedral (Octa), pentahedral (Penta), and tetrahedral (Tetra).^{11,19}

For $\kappa\text{-Ga}_2\text{O}_3$, both Si and Sn have been experimentally found to be extrinsic

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6 donors.^{7,11,16,20,21} According to electron paramagnetic resonance (EPR), Si is suggested to
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9 be an effective mass donor when it is positioned as a substitutional of Ga (Si_{Ga}) in the
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11 tetrahedral site of the orthorhombic $\kappa\text{-Ga}_2\text{O}_3$ lattice.¹⁶ Nonetheless, despite the possible
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13 incorporation of Si at cation concentrations that might exceed 1% in the metal-organic
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15 vapor phase deposited (MOVPE) layers, the reported Hall-measured charge carrier
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17 density n never exceeded the mid 10^{18} cm^{-3} range.⁷ This net donor density concentration
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19 range was independently confirmed by capacitance-voltage measurements performed in
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21 Schottky diodes based on Si-doped $\kappa\text{-Ga}_2\text{O}_3$.²²
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30 In this framework, the following could all play an important role in the resulting
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32 Si dopant activation efficiency in $\kappa\text{-Ga}_2\text{O}_3$:⁷ (i) the presence of a large concentration of
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34 extended defects (*i.e.*, rotational domain boundaries and plane defects), (ii) the possible
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36 occupation of different reticular Ga sites, and (iii) the presence of a large amount of
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38 compensating defects (deep level acceptors). In particular for point (i) and (iii), the (001)-
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40 oriented heteroepitaxy of $\kappa\text{-Ga}_2\text{O}_3$ on various substrates [*e.g.*, c-plane sapphire, (0001)-
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42 GaN, (111)-MgO]¹⁴ results in the formation of large density of structural defects that are
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44 mostly perfectly vertically oriented, *i.e.*, $3 \times 120^\circ$ rotated domains and anti-phase
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46 boundaries.^{7,23,24} According to the recent work of Vyvenko *et al.*, these vertically oriented
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48 structural defects could be electrically charged.²⁴ We believe that the discrepancy
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6 between the detected level of incorporated Si in the κ -Ga₂O₃ matrix and the net doping
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9 level is in line with a high level of compensation that can be largely induced by such
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12 vertically oriented structural defects. A similar picture of large charge carrier
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15 compensation related to charged structural defects has been reported and modelled in the
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18 case of defective β -Ga₂O₃ layers by Fiedler *et al.*²⁵ In this work, we describe the first
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21 experimental confirmation that the Si impurities incorporated in κ -Ga₂O₃ lattice sites
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24 substitute Ga (target point (ii)), particularly to experimentally clarify the respective
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27 fraction of different reticular Ga sites that are actually occupied by Si (Si_{Ga}), possibly
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30 causing active and inactive dopant in Si-doped κ -Ga₂O₃ thin films.
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33 We employed photoelectron holography (PEH) to clarify the Si dopant site for
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36 the Si-doped κ -Ga₂O₃. In the PEH, the photoelectrons of the target atoms (*e.g.*, dopants)
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39 are excited as the emitter under photoirradiation and scattered by the surrounding atoms.
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42 Finally, interference patterns are formed in the core-level photoelectron angular
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45 distribution. PEH has a great advantage in which non-periodic atomic structures are
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48 applicable. Additionally, since PEH is based on photoelectron spectroscopy, chemical
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51 state-discriminated PEHs can be achieved.²⁶⁻²⁹ Therefore, we can clarify the atomic
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54 structures and the chemical states of the Si dopants in κ -Ga₂O₃. The PEH schematic is
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57 shown in Figure 1(b).
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6 We also performed PEH simulations for the atomic position of the Si dopants in
7 κ -Ga₂O₃ to clarify the Si dopant sites. Since the structure around the dopant atom should
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9 be relaxed as the dopant is introduced into κ -Ga₂O₃, the bond length around the dopant
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11 atom may be different from the length before the dopant introduction. Thus, we performed
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13 extended x-ray absorption fine structure (EXAFS) to estimate the bond length after the
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15 dopant introduction. PEH simulations were done using the bond length after introducing
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17 the dopant. In the present study, we investigated the atomic position of the Si dopant for
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19 Si-doped κ -Ga₂O₃ using PEH to clarify the atomic structures of the active and inactive Si
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21 dopants for the Si-doped κ -Ga₂O₃.
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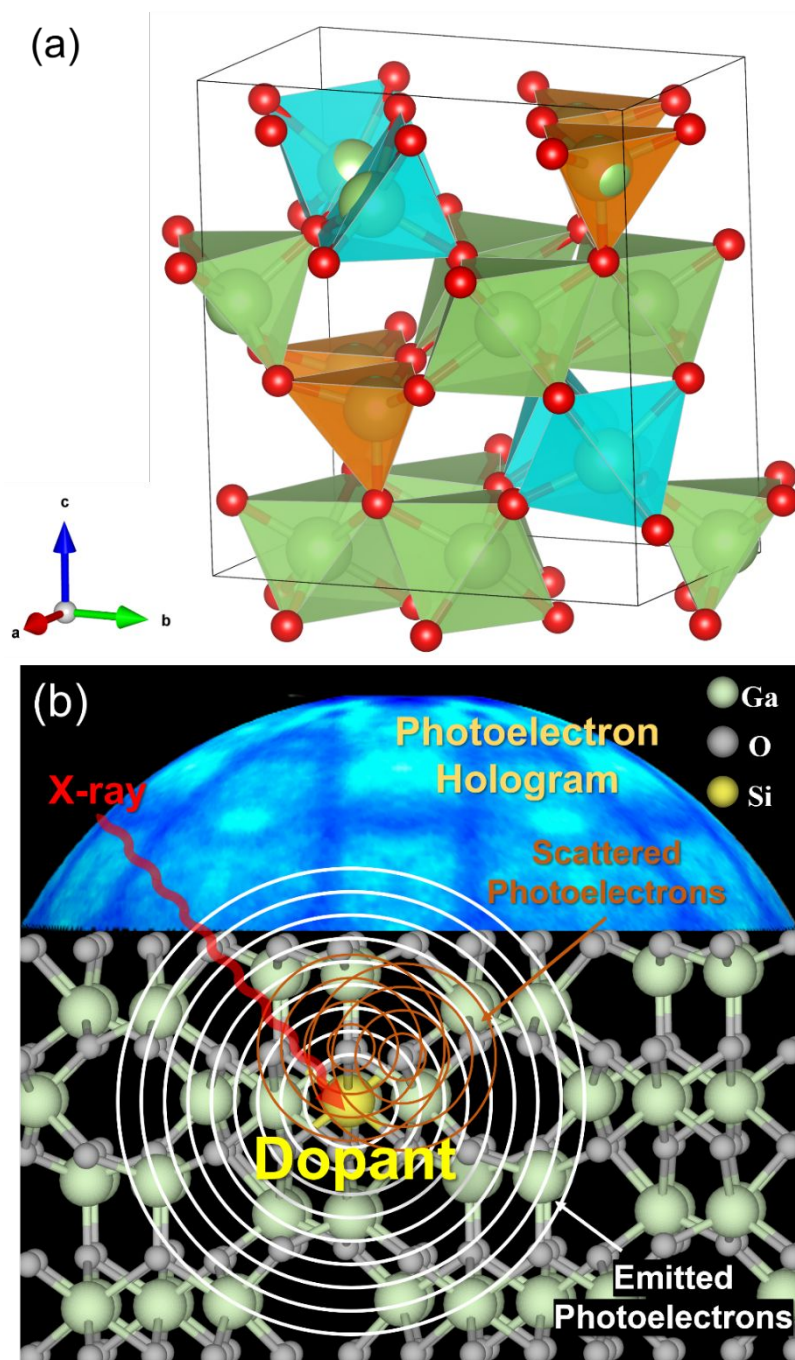


Figure 1. (a) Unit cell of κ - Ga_2O_3 : Green, blue, and brown polyhedrons represent Octa, Penta, and Tetra Ga sites. (b) PEH schematic for Si-doped κ - Ga_2O_3 . Yellow, green, and gray balls represent Si, Ga, and O atoms.

Experimental

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6 A κ -Ga₂O₃ epitaxial layer was grown on a c-plane sapphire substrate with
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9 MOVPE. Trimethylgallium and ultrapure H₂O were used as a metal precursor and an
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11 oxidizing gas. H₂ was used as the gas carrier. The reaction was carried out at a H₂ pressure
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13 of 60 mbar in the growth chamber with a substrate temperature of 610°C. A H₂-diluted
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15 mixture of 0.05% SiH₄ was employed as the Si dopant source. Using a SiH₄ flow of 15
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17 standard cubic centimeters per minute resulted in a Si concentration of 1.02 cation % in
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19 the κ -Ga₂O₃ layer (determined by atom probe tomography, which is the same sample that
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21 was previously investigated.) evenly distributed in the analyzed film volume.⁷ The
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23 dopant's carrier concentration was experimentally determined by Hall effect
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25 measurements to be $2.6 \times 10^{18} \text{ cm}^{-3}$ where the electronic transport was dominated by a
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27 hopping mechanism (further details on the electrical characterization of the very same
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29 sample are available.).⁷ Before PES and PEH measurements, the substrates were cleaned
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31 by the RCA method so that surface contaminations were removed. Then the surface oxide
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33 layer and the particles were removed by concentrated hydrochloric acid for 1 min.,
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35 followed by washing with deionized water.
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51 X-ray photoelectron spectroscopy (XPS) and hard x-ray photoelectron
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53 spectroscopy (HAXPES) measurements were performed using PHI Quantes (ULVAC-
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55 PHI). Monochromatic Al K α (1486.6 eV) and Cr K α (5414.9 eV) were used as incident
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6 x-rays sources for the XPS and HAXPES. The take-off angle (TOA) was 90° (surface
7 normal). We employed the pass energies of 55 and 112 eV for XPS and HAXPES
8 measurements, respectively. The energy resolutions for XPS and HAXPES
9 measurements were estimated to be 0.51 and 1.11 eV, respectively. The total energy
10 resolutions were estimated by measuring the Fermi level of Au polycrystalline sample.
11 We used KolXPD software to perform the XPS and HAXPES peaks fitting.³⁰ We used
12 Voigt function (convolution of Lorentzian and Gaussian functions) for peaks fitting after
13 removal of the background of the Shirley function.³¹⁻³³
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30 PEH measurements were performed at BL25SU at SPring-8. We used a retarding
31 field analyzer (RFA) for PEH measurements. The RFA energy resolution was
32 approximately 0.5 eV.³⁴⁻³⁶ RFA's acceptance angle was approximately ±49°, and the
33 angular resolution was 0.5°.³⁶ The base pressure of the main chamber was 2.8×10^{-8} Pa.
34 PEH simulations were performed using 3D-AIR-IMAGE software (version 1.1.09). The
35 total analysis multiple scattering pattern simulation code was included in the software.³⁷⁻⁴⁰
36 For the simulations, we employed an electron kinetic energy of 800 eV, a temperature of
37 300 K, and an inelastic mean free path of 10 Å.
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54 The EXAFS measurements were carried out at the BL6N1 in the Aichi
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6 The spot-size of the incident photon at the sample position was 2.0 mm × 1.0 mm
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9 (horizontal × vertical). A SPECS PHOIBOS 150 was used as an electron analyzer.⁴¹ The
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12 pass energy was set to 20 eV. The angle between the incident photon and the sample
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15 surface normal was 55°. The TOA was set to 90° (surface normal).^{42,43} For the EXAFS
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18 measurements, the total electron yield was employed. The energy range for the EXAFS
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21 measurements was from 1800 to 2100 eV with 1.0-eV energy steps.
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27 Results and discussion

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31 Figure 2 shows the XPS and HAXPES spectra for the Si-doped κ -Ga₂O₃(001).
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33 In the Ga 2*p* XPS spectrum (Figure 2(a)), the peak at 1119.0 eV is attributed to the Ga-O
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35 species.⁴⁴⁻⁴⁶ In the Si 1*s* HAXPES spectrum (Figure 2(b)), the peak at 1843.5 eV is due
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37 to the Si-O species.^{47,48} When the different Si oxidation states (from 1⁺ to 4⁺) exist, the
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39 corresponding peaks appear at lower binding energy position from 1 to 3 eV (depend on
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41 the oxidation states),^{49,50} forming an asymmetric peak structure. However, the Si 1*s*
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43 HAXPES spectrum shows a symmetric peak structure. Therefore, we can exclude the
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45 possibility of the presence of the different Si oxidation states. Thus, the chemical state of
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47 the Ga and Si atoms shows one chemical component. Since Si 1*s* shows one chemical
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49 species, the Si atom in the Si-O species may be due to the Si dopants.
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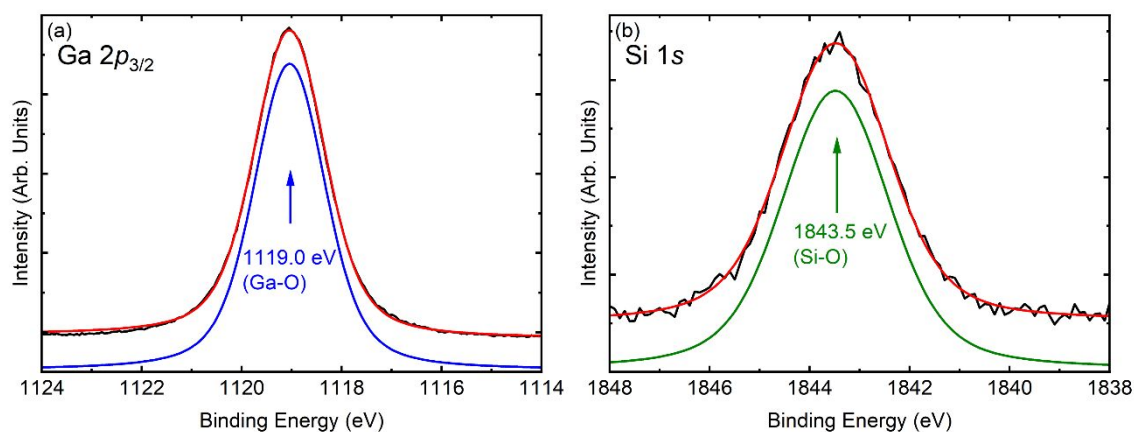


Figure 2. (a) Ga $2p_{3/2}$ XPS (b) Si $1s$ HAXPES spectra measured at photon energies of 1486.6 eV (XPS) and 5414.9 eV (HAXPES), respectively.

Figure 3(a) shows the Ga $3p$ and Si $2p$ PES spectrum for the Si-doped κ -Ga₂O₃(001) measured at an incident photon energy of 911 eV. For them, spin-orbit splitting of 3.46 eV and 0.60 eV was employed for the peaks fitting.⁵¹⁻⁵⁴ The corresponding PEHs for Ga $3p$ and Si $2p$ are shown in Figures. 3(b) and (c). The Si $2p$ PEH shows clear patterns, indicating that the Si dopant may be located at the atomic positions of κ -Ga₂O₃(001).

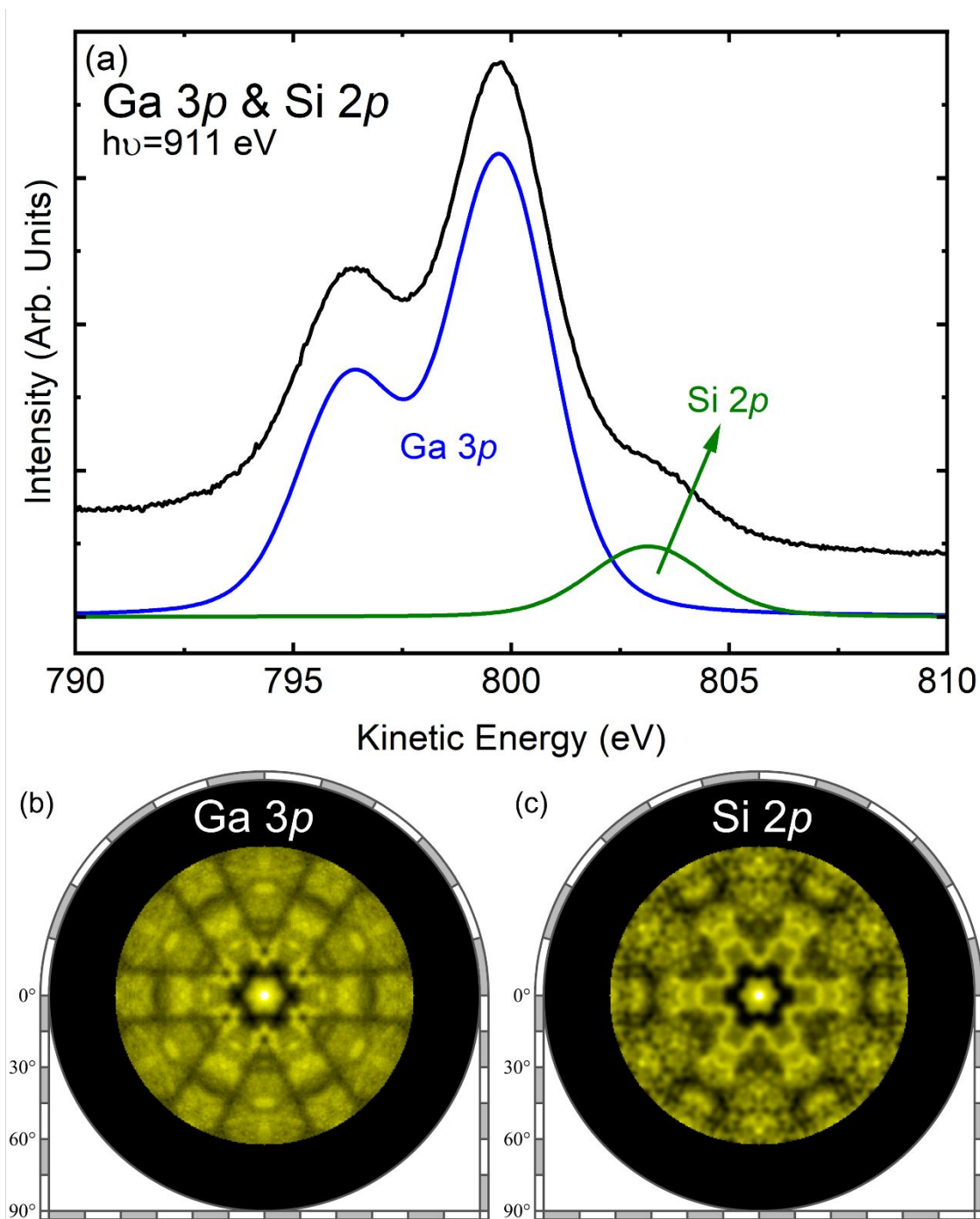


Figure 3. (a) Ga 3p and Si 2p PES spectrum for Si-doped κ -Ga₂O₃(001). PEHs of (b) Ga 3p and (c) Si 2p for Si-doped κ -Ga₂O₃(001).

Figures 4(a) and (b) show the EXAFS and the oscillation for the Si-doped κ -Ga₂O₃(001). Fig. 4(c) shows k^2 -weighted Si *K*-edge EXAFS spectrum plotted with the

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6 fitting result for Si-doped κ -Ga₂O₃(001). The fitting range in k-space was chosen at 2–
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9 7.2 Å⁻¹ with a good signal-to-noise ratio. Fig. 4(d) shows the radial distribution function
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12 of the k²-weighted EXAFS and the fitting result of the Octa Si_{Ga} site as an example. The
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15 fitting was performed using ARTEMIS software, and the reliable factor was set to
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18 0.015.^{55,56} The nearest Si-O distance was estimated to be 2.01 Å, a value shorter than the
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21 Ga-O bond length of 2.02 Å observed for the non-doped κ -Ga₂O₃ Octa site.²³
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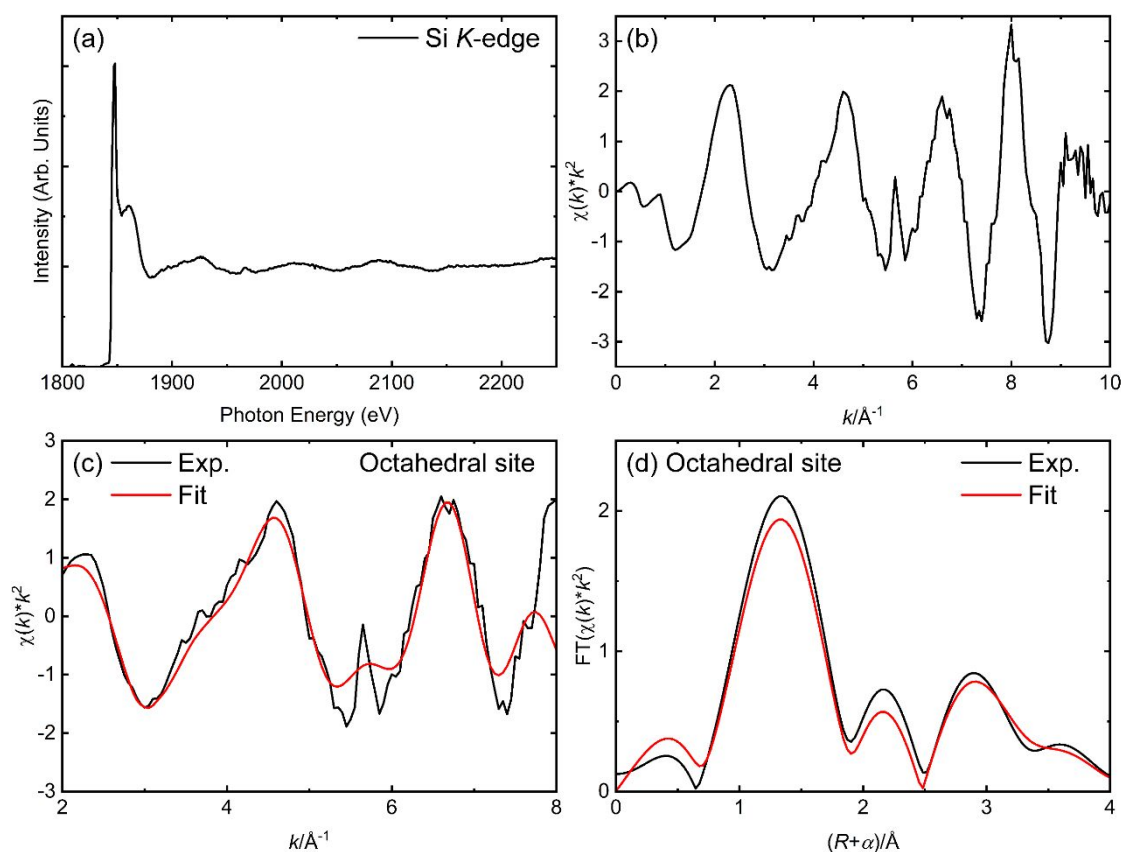


Figure 4. (a) Si *K*-edge EXAFS and (b) k^2 -weighted Si *K*-edge EXAFS for Si-doped κ - $\text{Ga}_2\text{O}_3(001)$. (c) k^2 -weighted Si *K*-edge EXAFS spectrum (black solid line) plotted with best fit (red solid line) for Si-doped κ - $\text{Ga}_2\text{O}_3(001)$ sample. The fitting range was 2–7.2 \AA^{-1} . (d) Radial distribution function of the k^2 -weighted EXAFS (black solid line) and the fitting results (red solid line) for Si_{Ga} in Octa site. The fitting range was 1–4 \AA . The amplitude reduction factors, ΔR , and MSRD values were set to 1, -0.011 \AA , and 0.015, respectively.

We also performed fitting for the other Si_{Ga} sites in κ - Ga_2O_3 (Figure S2). The first nearest Si-O distance was estimated to be 2.02 \AA and 1.83 \AA for the Penta and Tetra Si_{Ga} sites. We performed PEH simulations based on the bond length obtained from EXAFS. This is because when the dopants are introduced to the sample, the bond length should be changed around the dopant atom. Thus, we have to use the bond lengths around the Si dopant atom obtained from EXAFS.

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According to previous studies, dopant atomic positions are Ga replaced by Si, that is, Si_{Ga} in $\kappa\text{-Ga}_2\text{O}_3$.^{7,20} Therefore, PEH simulations were performed for the Octa, Penta, and Tetra Si_{Ga} sites. Figure 5 shows the experimental and simulated Si 2*p* PEHs for the Octa, Penta, and Tetra Si_{Ga} sites. Not every simulated PEH for the respective Octa, Penta, and Tetra Si_{Ga} sites explains the experimental Si 2*p* PEH, indicating that the Si dopant sites may be due to the mixture of inequivalent Si_{Ga} sites.

To determine the dopant site ratio for the Si-doped $\kappa\text{-Ga}_2\text{O}_3$, we mixed the simulated Si 2*p* PEHs of the Tetra, Penta, and Octa Si_{Ga} sites. The simulated PEH with the three inequivalent Si_{Ga} site ratios is shown in Figure 5(d). The best fit for the experimental PEH data was obtained using the ratios for Tetra, Penta, and Octa Si_{Ga} sites of 55.0%, 28.1%, and 16.9%, respectively. Note that the occupancy ratios of the Tetra, Penta, and Octa Si_{Ga} sites were estimated using the equations shown in Supporting Information.

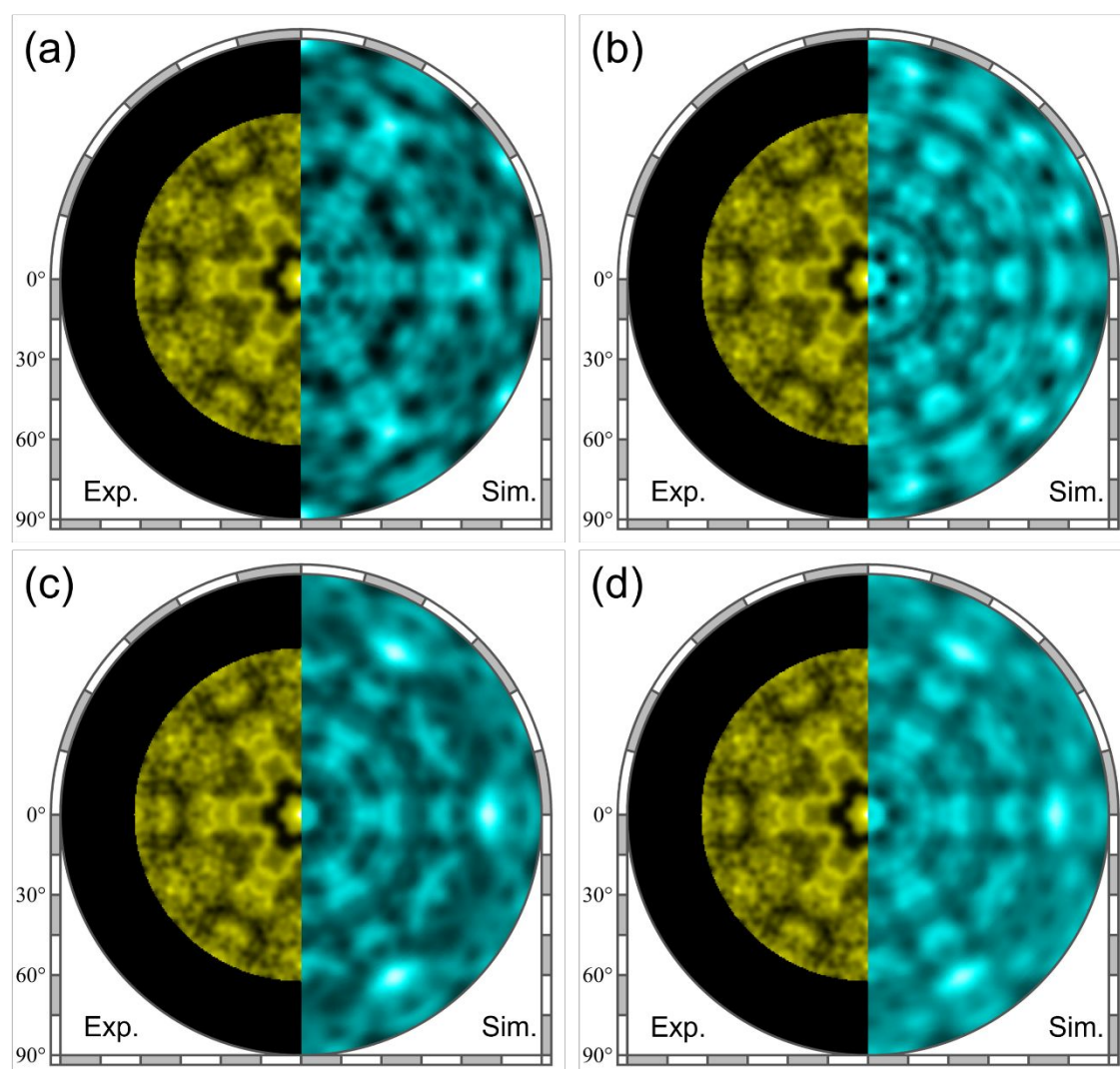


Figure 5. Experimental (yellow) Si 2*p* and the simulated (blue) PEHs. The simulated PEHs of (a) Octa Si_{Ga} site (b) Penta Si_{Ga} site (c) Tetra Si_{Ga} site, and (d) their sum are 16.9%, 28.1%, and 55.0%.

For the undoped κ -Ga₂O₃, the ratios for the Tetra, Penta, and Octa sites were 25%, 25%, and 50%.^{11,19} Therefore, based on our results, in the case of the Si-doped κ -Ga₂O₃, the Tetra Si_{Ga} site is strongly favored with respect to the Penta and Octa sites (55.0% with respect to the presence of just 25% of the Ga tetrahedral sites in the κ -Ga₂O₃ lattice). The Penta Si_{Ga} (28.1%) is almost half of the tetrahedral site occupation despite sharing an identical amount of available sites in the orthorhombic lattice (25% of the

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6 Penta Ga sites in the undoped κ -Ga₂O₃). Even though the Octa Ga sites are the highest
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9 occupation in the κ -Ga₂O₃ lattice (50%), the Octa Si_{Ga} site occupation in Si-doped κ -
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12 Ga₂O₃ is the lowest (16.9%).
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15 The difference in these Si_{Ga} ratios might be related to the formation energy of
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17 such defects. In this framework, our data suggest that the Tetra sites of the Si_{Ga} defect
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19 should have the lowest formation energy with respect to the Octa and Penta coordinations.
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22 Nevertheless, this does not fully agree with the first principles calculations of Zeman et
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25 al. that predicted the Octa Si_{Ga} site to have the lowest formation energy for the κ
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28 polymorph, followed by the Tetra and Penta sites.⁵⁷
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33 The discrepancy between the experimental and theoretical results might be
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35 explained as follows. As we already described the introduction section, our sample has
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37 large density of structural defects. The defects are mostly perfectly vertically oriented,
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40 *i.e.*, 3 x 120° rotated domains and anti-phase boundaries.^{7,23,24} In addition, these vertically
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43 oriented structural defects could be electrically charged.²⁴ On the other hand, the first
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46 principles calculations of Zeman et al. do not contain the charged structural defects,
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49 vertically oriented and rotated domains, and anti-phase boundaries.⁵⁷ As a result, the first
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52 principles calculations might not fully agree with the experimental results.⁵⁸⁻⁶⁰
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57 Von Bardeleben et al. investigated the electrically active dopant in Si-doped κ -
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6 Ga₂O₃ with EPR and concluded that the detected dopant site was due to the Tetra Si_{Ga}
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9 site.¹⁶ Thus, based on the present investigation, that site may be attributed to the active
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12 dopant site for the Si-doped κ-Ga₂O₃. The Si impurity in other Ga sites might be
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15 electrically inactive dopants for the Si-doped κ-Ga₂O₃ (Penta and Octa Si_{Ga} sites). Further
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18 investigations are required to clarify the origin of the suggested inactivity of the Si_{Ga} Penta
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21 and Octa sites.
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27 Conclusion

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30 We used XPS, HAXPES, PEH, and EXAFS to clarify the chemical states and
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33 the atomic positions of Si dopants for Si-doped κ-Ga₂O₃(001). From XPS and HAXPES,
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36 we found that the Si dopant shows one chemical state for the Si-O species in Si-doped κ-
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39 Ga₂O₃(001). Since the Si 2*p* PEH showed clear hologram patterns for the Si dopant, it
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42 should be located at the cationic positions of κ-Ga₂O₃(001). We experimentally
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45 demonstrated that Si is effectively incorporated in Ga sites. We simulated the PEH
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48 patterns to clarify the precise occupation site of Si dopants in the orthorhombic lattice and
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51 found that the simulated PEH of each inequivalent Si_{Ga} site (i.e., Tetra, Penta, Octa) could
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54 not explain the experimental Si 2*p* PEH. Thus, the Si dopant was found to occupy all the
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57 different cationic sites (i.e., mixture of inequivalent Si_{Ga} sites). With the ratios of the Tetra,
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6 Penta, and Octa Si_{Ga} sites of 55.0%, 28.1% and 16.9%, respectively, we obtained a best
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9 fit of the PEH experimental data. The recorded differences should be considered in light
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12 of the overall amount of different Ga inequivalent sites in the orthorhombic unit cell (i.e.,
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15 Tetra, Penta, and Octa sites of 25%, 25%, and 50%) and may be attributed to different
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18 Si_{Ga} formation energies. In this framework, the Tetra Si_{Ga} site has by far the highest
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21 occupation ratio among the three inequivalent Ga sites in the lattice. We suggest that this
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24 result is related to the Si_{Ga} in the Tetra site that has the lowest formation energy; whereas,
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27 the Octa Si_{Ga} site exhibited the lowest ratio, suggesting that this defect configuration has
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30 the highest formation energy. The current findings in the framework of previous
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33 investigations suggest that the Tetra Si_{Ga} site may be the only active dopant site in Si-
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36 doped $\kappa\text{-Ga}_2\text{O}_3$, and the Penta and Octa Si_{Ga} sites may be inactive.
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42 **Supporting Information**

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46 The supporting information contains additional experimental data. Figure S1 shows Si 2s
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49 XPS spectrum of Si-doped $\kappa\text{-Ga}_2\text{O}_3(001)$. Figure S2 shows k^2 -weighted Si *K*-edge
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52 EXAFS and the radial distribution function of the k^2 -weighted EXAFS and the fitting
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55 results for the Penta and the Tetra Si_{Ga} sites for Si-doped $\kappa\text{-Ga}_2\text{O}_3(001)$ sample. Figure
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58 S3 shows the difference images between experimental PEH and simulated PEHs for Octa,
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6 Penta, Tetra Si_{Ga} sites, and the sum of Octa, Penta, and Tetra Si_{Ga} sites where the
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respective ratio of 16.9%, 28.1%, and 55.0% (the best fit). (Figure 5(d))

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Author Contributions

Y.Y. designed, planned, led the research. Data analysis was performed by Y.T and Y.Y.

P.M., A.P., M.B. and L.S. fabricated the Si-doped $\kappa\text{-Ga}_2\text{O}_3$ samples. Y.T., Z.S., T.M.,

T.T. and T.N. performed the experiments under the supervision of Y.H., T.M. and Y.Y.

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