



Article Angle-Dependent Raman Scattering Studies on Anisotropic Properties of Crystalline Hexagonal 4H-SiC

Zhe Chuan Feng ^{1,*}, Dishu Zhao ², Lingyu Wan ², Weijie Lu ³, Jeffrey Yiin ¹, Benjamin Klein ¹ and Ian T. Ferguson ¹

- Southern Polytechnic College of Engineering and Engineering Technology, Kennesaw State University, Marietta, GA 30060, USA
- ² Center on Nano-Energy Research, Laboratory of Optoelectronic Materials & Detection Technology, Guangxi Key Laboratory for the Relativistic Astrophysics, School of Physical Science & Technology, Guangxi University, Nanning 530004, China
- ³ Hexagonal Scientific Lab, LLC, Dayton, OH 45459, USA
- * Correspondence: zfeng6@kennesaw.edu or zcfeng@ntu.edu.tw

Abstract: Raman scattering spectroscopy (RSS) has the merits of non-destructiveness, fast analysis, and identification of SiC polytype materials. By way of angle-dependent Raman scattering (ADRS), the isotropic characteristics are confirmed for c-face 4H-SiC, while the anisotropic properties of a-face 4H-SiC are revealed and studied in detail via combined experiments and theoretical calculation. The variation functional relationship of the angle between the incident laser polarization direction and the parallel (perpendicular) polarization direction was well established. The selection rules of wurtzite 4H-SiC are deduced, and the intensity variations of the A₁, E₂, and E₁ Raman phonon modes dependent on the incident angle are calculated, and well-matched with experimental data. Raman tensor elements of various modes are determined.

Keywords: silicon carbide; 4H-SiC; raman scattering; anisotropic property; angular dependence; raman tensor; selection rule

1. Introduction

Silicon carbide (SiC) has been recognized as an important material for a wide variety of high-power and high-temperature electronic applications [1–7]. SiC exhibits a large number (>250) of polytypes with different structural and physical properties, as well as possesses a wide range of applications [8–15]. The SiC polytypes have the same chemical composition but exhibit different crystallographic structures and stacking sequences along the principal crystal axis. Several important polytypes of SiC, such as 4H and 6H have C_{6v} crystallographic symmetry. In the "a" direction 4H– and 6H–SiC are almost identical (<1%) changes; however, the 4H polytype consists of four units in the c direction and the 6H consists of six units. Different polytypes have different band gaps, electron mobility, and other physical properties. 4H–SiC has attracted significant attention due to its high electron mobility and excellent thermal properties [16–35]. Especially in recent years (2020–2022), research activities on 4H-SiC have been extremely active and productive [6,11–15,24–35].

Since the late 1980s, high-quality and large-size wafers of both 6H– and 4H–SiC have come into industrial production. Gradually, the wafer size increased, up to 8 inches recently, and the wafer crystalline quality improved over time and is very widely used for device applications. Wafers of SiC are also promising substrates for nitride semiconductor growth due to their compatible lattice structure and similar thermal expansion coefficients, as well as for other materials.

Raman scattering spectroscopy (RSS) has the merits of non-destructiveness, fast analysis, and being free from special preparation for samples. It has been proven to be a useful and informative tool for the investigation and identification of SiC polytype materials.



Citation: Feng, Z.C.; Zhao, D.; Wan, L.; Lu, W.; Yiin, J.; Klein, B.; Ferguson, I.T. Angle-Dependent Raman Scattering Studies on Anisotropic Properties of Crystalline Hexagonal 4H-SiC. *Materials* **2022**, *15*, 8751. https://doi.org/10.3390/ ma15248751

Academic Editors: Javier Narciso and Mario R. Caccia

Received: 2 November 2022 Accepted: 5 December 2022 Published: 8 December 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Furthermore, the Raman efficiency of SiC is high because of its strong covalence of the bonding, so the Raman signals can be easily detected. The Raman parameters, such as intensity, width, and peak frequency, provide plenty of information on the crystal quality. Up to now, Raman spectroscopy has been widely applied in the SiC bulk and epitaxial materials, especially for 4H-SiC [16–35].

Owing to the different vibrating types, the phonon intensity induced by the electric vector will vary from the polarization of the incident laser beam and will cause the multifold scattered light. The polarizability tensor of the wurtzite crystal [36–41] has been used to verify the Raman selection rule; however, the nonvanishing components of the susceptibility tensor should include the effects from different vibrating components—it is needed to further identify and quantify the anisotropic distribution of Raman signals.

Raman scattering spectroscopy (RSS) is an effective nondestructive method to characterize materials, to analyze the crystal structure, electronic band structure, phonon energy dispersion, and electron–phonon coupling [36,37]. By analyzing Raman spectra of wide bandgap semiconductor (WGS) materials, such as SiC [16–35], GaN [36], and AlN [37,38], one can gain knowledge of their crystal structure, carrier concentration, internal strain/stress and distribution, and other characteristic properties. It is interesting to see, during 2020-22, Raman scattering on 4H-SiC has contributed to many important subjects, such as basal plane stacking faults and associated partial dislocations [24], effects of ion-implantation [25–27,29], ionizing irradiation-induced atomic movement toward recrystallization [26], phase changes from excimer laser doping [32], mechanical stress and nitrogen doping on the defect distribution [31], and so on.

Angle-dependent or rotation Raman scattering has been applied to investigate WGS epitaxial GaN [36] and bulk AlN crystals [37–41]. From these experiments, the Raman tensors are derived, containing various information for the vibration symmetries, polarities, and anisotropies of crystals [39–41]. The so-called "phase difference" is commonly introduced as a phenomenological parameter and recognized as an intrinsic property of crystals, although its physics still remains for further investigation [39–41]. Recently, a combined experiment–theory study on the angle-resolved intensity of polarized micro-Raman spectroscopy by considering the birefringence effect was presented for the c-face of a 4H-SiC wafer, with planar plots for the relationship of Raman normalized intensity versus rotation angle [30]. As pointed out, so far, most of the Raman analysis is not based on the anisotropy of SiC, except for [30]. In early 1995, H. Horima et al. [16] reported Raman scattering from anisotropic LO phonon–plasmon-coupled (LOPC) mode in n-type 4H– and 6H–SiC.

In this paper, we employed the angle-dependent Raman scattering (ADRS) to study the phonon anisotropy property of the wurtzite 4H-SiC crystal both theoretically and experimentally. The angle-dependent polarized RS measurements were performed on the "a" face 4H-SiC crystal, and comparative c-face 4H-SiC, by adjusting the polarized vector of the incident and scattered laser light. Corresponding Raman selection rules are derived according to measured scattering geometries to illustrate the angle dependence. The angle-dependent intensities of phonon modes are calculated and compared to the experimental scattering intensities, yielding the Raman tensor elements of A₁, E₁, and E₂ phonon modes. These detailed theoretical calculation results on the Raman selection role, Raman tensor elements, and the variations of Raman spectral intensities of wurtzite 4H-SiC are in good coincidence with experimental data. To our knowledge, ADRS has been applied to GaN [36], AlN [37–41], MoS₂, and WS₂ [39–41], and Raman tensors for these wurtzite wide gap materials are obtained also. Our current studies of ADRS and Raman tensors for 4H-SiC are intended to advance the knowledge on 4H-SiC and to promote the research and development for SiC more polytype materials and applications.

2. Experimental

The experimental 4H-SiC samples used in this work were purchased from CREE Company. A piece of un-doped a-face (1120) 4H-SiC with the size of 5×5 mm, was cut

from a 2-inch wafer. Some c-face 4H-SiC experimental samples are pieces at the size of 5×5 mm or 10×10 mm, cut of commerce wafer materials (typically 1 3/8 to 2 inch).

Raman spectra were measured in backscattering geometry at room temperature (RT), by a Raman micro-spectrometer, connected with a Charge Coupled Device (CCD) for signal detection, named 'Finder One' from Zolix Company. It is equipped with four diode lasers possessing excitation wavelengths of 457, 532, 650, and 785 nm. In the current work, the 532 nm excitation laser was used, with incident light through the x50 object (with 0.55 numerical aperture and 4 mm focal length) focusing on the "a" surface or c-face of the 4H-SiC crystal sample, while the scattered light was collected via this same object. To make the scattered light parallel with or perpendicular to the incident light, a rotatable polarizer was inserted within the scattered light path. The sample stage could be rotated with 360°, i.e., the incident light could be rotated with 360° to obtain the angular dependent Raman spectra.

Figure 1 shows (a) the hexagonal wurtzite crystal structure and (b) the experimental arrangement. The XYZ coordinates with the crystalline axis of the 4H-SiC crystal. The Z-axis is along the c-axis of the wurtzite 4H-SiC crystal, i.e., (0001) direction. The Y-axis is along the normal direction of the a-face of 4H-SiC. The rotation angle θ is the angle of inclusion between the ξ axis and the X-axis. The incident light travels along the Y-axis, the SiC sample is rotated around the Y-axis, and rotation angle θ lies between the incident light polarizing vector in the X-Z plane and X-axis.



Figure 1. (a) The hexagonal wurtzite crystal structure and (b) the experimental arrangement. The *Z*-axis is along the c-axis of 4H-SiC crystal, i.e., (0001) direction. The a-plane is shown. The array ξ represents the incident light polarizing vector. The θ is the rotation angle with respect to the *X*-axis.

In this paper, we present the RT backscattering Raman spectra of the semi-polar a-face (1120) and c-face (0001) 4H-SiC crystal for the relationship between the lattice phonon vibration modes and the rotation angles of the wurtzite structure, which shows the crystal anisotropy or isotropy characteristics.

3. Results and Discussion

3.1. Angular-Dependent Raman Spectra from c-face 4H-SiC

Figure 2 presents the angle-dependent Raman spectra of the c-face (0001) 4H-SiC, measured at RT with the excitation of 532 nm. The hexagonal wurtzite 4H-SiC is a tetrahedrally coordinated semiconductor compound and belongs to the space group $C_{6v}^4(P6_3mc)$ in the primitive cell. All the atoms occupy sites of symmetry C_{3v} [7,11]. Main Raman active modes include E_2 (LA), 203.5 cm⁻¹; A₁ (LA), 610.5 cm⁻¹; E₂ (TO), 777.0 cm⁻¹; E₁ (TO), 788.1 cm⁻¹; and A₁ (LO) 967.0 cm⁻¹, as shown in Figure 2, in which all above Raman phonon modes are identical at different rotation angles of 0°–330° (0°, i.e., 360°). This indicates the isotropic characteristics of the c-face 4H-SiC crystal [30].



Figure 2. The angle-dependent Raman spectra of the c-face 4H-SiC, at different rotation angles of 0° -330°, were measured at RT with the excitation of 532 nm.

3.2. Angular-Dependent Raman Spectra from a-Face 4H-SiC

Figure 3 shows the rotation Raman spectra at the a-plane (1120) of 4H-SiC, in the wavenumber range of 580–820 cm⁻¹ and with the angle rotated from 0° to 360° (step size of 5°), under (a) parallel and (b) perpendicular polarization, respectively. Within Figure 3, the A₁ (LA), E₂ (TO), and E₁ (TO) modes are observed at 610.03 cm⁻¹, 776.49 cm⁻¹, and 788.08 cm⁻¹, respectively. The intensity and phase variations of these Raman modes and their dependences on the rotation angle are clearly shown. Further, there exists a shoulder peak in the close-right of E₂ (TO) at ~783 cm⁻¹, which is assigned as the A₁ (TO) mode of 4H-SiC [29]. In addition, we provide a single point scan Raman spectrum of the a-face 4H-SiC, for reference, included in the Supplementary, with an inset and showing E₁ (TA) at 266 cm⁻¹, E₁ (TA) at 610 cm⁻¹, E₂ (TO) at 775 cm⁻¹, E₁ (TO) at 788 cm⁻¹, A₁ (LO) at 976 cm⁻¹ and LO-plasma coupling (LOPC) broadband in the right side of A₁(LO) [17–19].

3.3. Raman Selection Rules

The 4H-SiC crystal is a compound semiconductor with a hexagonal wurtzite structure and belongs to the space group C_{6v}^4 (P63mc) with eight atoms in the primitive cell [7,11]. In its Brillion zone, the lattice vibration produces nine optic branches and three acoustic branches, including the A₁, B₁, E₁, and E₂ vibration modes [7,11,17]. According to the group theory, A₁ and E₁ acoustic modes are Raman and infrared (IR) active. The A₁ phonon is polarized along the *Y*-axis direction, while the E₁ phonon is polarized within the XZ plane (see the Coordinate System in Figure 1). The E₂ mode is only Raman active, while B₁ belongs to the non-active mode. Due to the creation of polar bonds, there appear frequency shifts for A₁ and E₁ Raman modes with symmetries. The A₁ and E₁ Raman modes are split into the longitudinal phonon and transverse phonon modes, forming the A₁ (TO, LO) and E₁ (TO, LO) modes.



Figure 3. The rotation Raman spectra at the a-plane of 4H-SiC, with the angle varied from 0° to 360° (step size of 5°), under (**a**) parallel and (**b**) perpendicular polarization, respectively.

The Raman scattered light intensities can be expressed as [36-41]:

$$I \sim |\mathbf{e}_{s} \cdot \mathbf{R} \cdot \mathbf{e}_{i}|^{2} \tag{1}$$

where e_i and e_s present the polarization vector for the incident and scattered light, respectively. R is the 2nd-order Raman tensor with the form of a 3 \times 3 vector matrix [36–41]. This

vector matrix represents the characteristics of Raman scattering phonon modes. The A_1 , E_{1} , and E_2 Raman active modes in wurtzite structural materials are expressed below [36–41]:

$$R[A_1] = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix},$$
 (2)

$$R[E_1] = \begin{bmatrix} 0 & 0 & -c \\ 0 & 0 & c \\ -c & c & 0 \end{bmatrix},$$
(3)

$$R[E_2] = \begin{bmatrix} d & d & 0 \\ d & -d & 0 \\ 0 & 0 & 0 \end{bmatrix},$$
 (4)

where a, b, c, and d represent Raman tensor elements. In Raman backscattering measurements on the a-plane of 4H-SiC single crystalline material, referring to the hexagonal axis structure, the polarized vectors for the incident and scattered light can be expressed as:

$$\mathbf{e}_{i} = \begin{pmatrix} \sin(\theta) \\ 0 \\ \cos(\theta) \end{pmatrix}, \tag{5}$$

and

$$\mathbf{e}_{s} = \begin{pmatrix} \sin(\theta_{s}) \\ 0 \\ \cos(\theta_{s}) \end{pmatrix}, \tag{6}$$

where θ (θ_s) represents the angle between the sample *Y*-axis and the incident (scattered) light vector, respectively.

Here, we discuss the case of the parallel and perpendicular configuration, from which, according to the calculation based upon Equation (1), the Raman intensity at the surface of the a-plane from the 4H-SiC crystal can be expressed as:

$$I_{//}(A_1) \sim |a|^2 \sin^4 \theta + |b|^2 \cos^4 \theta + \frac{|a||b|}{2} \sin^2 2\theta \cos(\varphi_{a-b}),$$
(7)

$$I_{\perp}(A_1) \sim \left(\frac{|a|^2 + |b|^2}{4} + \frac{|a||b|}{2}\cos(\varphi_{a-b})\right)\sin^2 2\theta,$$
(8)

$$I(A_1) \sim I_{//}(A_1) + I_{\perp}(A_1),$$
 (9)

$$I_{//}(E_1) \sim |c|^2 \cos(\phi_{a-b}) \sin^2(2\theta),$$
(10)

$$I_{\perp}(E_1) \sim |c|^2 \cos(\varphi_{a-b}) \cos^2(2\theta), \tag{11}$$

$$I(E_1) \sim I_{//}(E_1) + I_{\perp}(E_1),$$
 (12)

$$I_{//}(E_2) \sim |\mathbf{d}|^2 \cos^4 \theta, \tag{13}$$

$$I_{\perp}(E_2) \sim |d|^2 \sin^2 \theta \cos^2 \theta, \tag{14}$$

$$I(E_2) \sim I_{//}(E_2) + I_{\perp}(E_2).$$
 (15)

From the above formalism, we can know that the phase difference φ_{a-b} between the Raman tensor elements a and b possesses an influence on the Raman scattering intensity of A_1 mode. From Equation (7), the values of |a|, |b| and phase difference φ_{a-b} in the scattered light intensity $I_{//}(A_1)$ are certain. They can be determined through the values of $I_{//}(A_1)$ at $\theta = 0^\circ$ and 90° , respectively; however, the values of |a|, |b| and phase difference φ_{a-b} in the scattered light intensity $I_{\perp}(A_1)$ are different from that of $I_{//}(A_1)$. As known

from Equation (8), the values of |a|, |b| and phase difference φ_{a-b} in the scattered light intensity $I_{//}(A_1)$ have also influenced the scattered light intensity $I_{\perp}(A_1)$.

Based on the above formalism, we can perform the theoretical calculation and experimental measurements on the 4H-SiC anisotropy Raman scattering. Based on the dynamic atomic theory, different elements of the vibration modes could display variations related to their space structures. In the following, we discuss the anisotropy characteristics and the effects on the Raman tensor of various vibration modes.

3.4. Rotation Raman Spectral Intensities and Analyses

Figure 4 exhibits the experimental Raman peak values versus the rotation angle in symbols, and the theoretical curves in solid lines, calculated by Equations (7)–(15), which clearly reveal the interaction relationship of Raman intensity and rotation angle. As shown in Figure 4a, under the case of parallel polarization [y(xx)y-y(zz)y], with the rotation angle increased from 0° to 45° , the Raman intensity of A₁ mode decreases continually; while with the rotation angle increased from 45° to 90° , the Raman intensity of A₁ mode increases continually. At the rotation angles of 0° , 90° , 180° , 270° , and 360° , the A₁ mode has the maxima intensity; while at 45° , 135° , 225° , and 315° , the A₁ mode disappears. Under the case of perpendicular polarization [y(xz)y-y(zx)y] in Figure 4b, with the rotation angle increases from 0° to 45° , the Raman intensity of A₁ mode increases continually; while with the rotation angle increases from 45° to 90° , the Raman intensity of A₁ mode decreases continually. At the rotation angles of 0° , 90° , 180° , 270° , and 360° , the A₁ mode disappears; while at 45° , 135° , 225° , and 315° , the A₁ mode has the maxima intensity. These indicate the sinus-like variation of the A_1 Raman mode intensity depending on the rotation angle and the strong anisotropic characteristics of the 4H-SiC crystal. In addition, to determine the Raman tensor for the A_1 mode, it can employ the Raman selection rules to perform the theoretical modeling. Both the A_1 and E_1 phonon modes are both Raman and IR active, as shown in Figure 4c–d, with similar intensity variation trends for both A_1 and E_1 modes; however, the E_2 mode, with only Raman active, is different from A_1 and E_1 modes.

As shown in Figure 4e–f for the strongest E_2 mode, under the case of parallel polarization [y(xx)y-y(zz)y], with the rotation angle increased from 0° to 90°, the Raman intensity of E_2 mode increases continually; while with the rotation angle increased from 90° to 180°, the Raman intensity of E_2 mode decreases continually. At the rotation angles of 0°, 90°, 180°, 270°, and 360°, the A₁ mode has the maxima intensity, under the parallel polarization; while at near 45°, 140°, 225°, and 310°, the A₁ mode is weakest. Under the case of perpendicular polarization [y(xz)y-y(zx)y], the Raman intensity variation of E_2 mode has the same variation trend as the A₁ mode, while the E_1 mode possesses a different variation trend from A₁ and E_2 .

3.5. Raman Tensor Element Analyses

Raman intensities of A_1 , E_1 , and E_2 phonon modes under the polarization states of parallel [y(xx)y-y(zz)y] and perpendicular [y(xz)y-y(zx)y] are shown in Figure 4. The fitting results for the relationship of Raman intensity and ratio angle under two polarization cases are expressed in Figure 4a–f, with small errors. To determine the Raman tensor elements, the fitting procedure by the least square method and Formulas (7)–(15) with angle variation of function fitting is applied. The best-fitting curves are basically coincident with the experimental data, as shown in Figure 4. The relative values of Raman tensor elements for 4H-SiC crystal are calculated by way of the ratio calculation of fitting parameters are overviewed and shown in Table 1. As applying function fitting with Formulas (7)–(15) on data of Figure 4a–f plus elaboration, proper error bars were obtained and put into Table 1 also. It is found that different Raman modes are completely different. The phase difference and anisotropic ratio of each Raman mode characterize similar information, but there exist phase shifts among different elements. In addition, the values of phase shift and anisotropic ratio are determined from the corresponding Raman mode. Each element of Raman tensor represents its single directional vibration and corelated with another element; therefore,



from experimental and theoretical results, the anisotropies of the 4H-SiC sample can be determined.

Figure 4. (**a**,**b**) The angle-dependent intensity of the A_1 signal from the a-plane surface of the SiC sample for parallel and perpendicular polarization vectors of incoming laser and the scattered light. (**c**,**d**) The intensity of the E_1 signal from the a-plane surface versus the rotation angle for parallel and perpendicular polarization vectors, respectively. (**e**,**f**) The intensity of the E_2 mode signal versus the rotation angle for parallel and perpendicular polarizations.

The 4H-SiC material belonging to a wide bandgap semiconductor compound possesses the wurtzite structure with the hexagonal space group o C_{6v}^4 (P6₃mc). Based upon the atomic dynamics, by way of Raman scattering measurements, different vibration elements can display the sensitivities correlated to their own space group [42]. The A₁, E₁, and E₂ modes in wurtzite 4H-SiC are Raman active. Among these modes, the A₁ polarization direction coincides with the Y-axis. In a doped semiconductor, the A₁ mode, by way of the resonant coupling between polarized phonon and plasma (free carriers), exerts an influence on the electronic transport properties [43]. As expressed in Table 1, the relative values of Raman tensor elements for the 4H-SiC crystal are calculated with the help of the ratio calculation on fitting parameters. From Raman scattering spectra under the parallel and perpendicular polarization, the phase difference φ_{a-b} of Raman tensor elements |a| and |b| (i.e., the parallel and perpendicular vectors) for the 4H-SiC crystal are determined as 117.37° and 92.86°, respectively.

Table 1. The relative values of Raman tensor elements for A_1 , E_1 , and E_2 modes of wurtzite 4H-SiC crystal, which are theoretical fitting results for the incident laser (e_i) and scattered light (e_s) under parallel and perpendicular polarization cases, respectively.

	A-Plane Tensor Element	$\frac{\overrightarrow{e_i} \ \overrightarrow{e_s}}{\mathbf{y(xx)y \leftrightarrow y(zz)y}}$	$\stackrel{\overrightarrow{e_i} \perp \overrightarrow{e_s}}{\underline{y(xz)y}} \stackrel{\overrightarrow{y(zx)y}}{\underline{y(zx)y}}$
A ₁ mode	a/d	1.003 ± 0.024	0.198 ± 0.019
A ₁ mode	b/d	1.004 ± 0.023	0.198 ± 0.020
	φ_{a-b}	111.37°	92.86°
E ₁ mode	lc/dl	0.388 ± 0.029	0.292 ± 0.013
E ₂ mode	d/d	1.000 ± 0.007	1.000 ± 0.006

It can be seen from the article of Strach et al. [44] that the selection of parameters a, b and phase difference φ_{a-b} is not unique for the perpendicular vectors of the incident and scattered light. So, the ratio of perpendicular polarized vectors in Table 1 is not well defined; however, this ratio is comparatively coincident with the result estimated from the incident and scattered polarized vectors in parallel alignment. For wurtzite material, re-collecting measurements on Raman spectra can confirm the relationship between the anisotropy ratio and the phase difference of Raman tensor elements in wurtzite crystal. W. Zheng et al. [39–41] have studied the elucidation of "phase difference" in Raman tensor formalism on wurtzite compounds, namely, AlN, GaN, ZnO, and SiC, and demonstrated the values of phase difference being unanimously confined to around $\pi/2\pi/2$, while the anisotropic ratios display obvious differences in the four compounds. It is reasonable to believe that the phase difference should not be treated as an intrinsic property such as the anisotropic ratio. In addition, it is noted that the anisotropy properties of 4H-SiC materials can also be investigated by way of nanoindentation and scratch experiments [45].

4. Conclusions

In summary, from this work for wurtzite 4H-SiC single crystalline material, the rotation, i.e., the angle-dependent Raman scattering (ADSS), has been studied by the combination of experiments and theories. A series of promising and significant results are achieved. The isotropy characteristics were confirmed from the c-face 4H-SiC, while the anisotropy characteristic properties were revealed from the a-face 4H-SiC. The variation functional relationship of the Raman phonon modes versus the angle between the incident laser polarization direction and the parallel (perpendicular) polarization direction was obtained. By way of the parametrization on incident light and scattered light polarization vectors, the selection rules of wurtzite SiC are calculated and well established. Corresponding Raman selection rules are derived according to measured scattering geometries to illustrate the angle dependence. Based upon the selection rules, the intensity variations of the A_1 , E_{2} , and E_{1} modes dependent on the rotation angle are calculated, and the Raman tensor elements of various modes are well-deduced. These detailed theoretical calculation results on the Raman selection role, Raman tensor elements, and the variations of Raman spectral intensities, as well as the phonon anisotropy properties of wurtzite 4H-SiC, are significant and matched well with experimental data.

Our penetrating investigations are helpful to better understand the mechanisms and find ways to further improve the material design and growth of hexagonal SiC, as well as their wide range of applications.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/ma15248751/s1, Figure S1: Raman spectrum of the a-face 4H-SiC, including an inset and showing E_1 (TA) at 266 cm⁻¹, E_1 (TA) at 610 cm⁻¹, E_2 (TO) at 775 cm⁻¹, E_1 (TO) at 788 cm⁻¹, A_1 (LO) at 976 cm⁻¹ and LO-plasma coupling (LOPC) broadband in the right side of A_1 (LO) [17–19].

Author Contributions: Conceptualization, Z.C.F. and L.W.; Data curation, D.Z.; Formal analysis, D.Z. and L.W.; Funding acquisition, L.W.; Investigation, D.Z., L.W., I.T.F. and Z.C.F.; Methodology, D.Z., L.W. and Z.C.F.; Project administration, W.L.; Resources, L.W. and W.L.; Software, D.Z. and J.Y.; Supervision, B.K. and I.T.F.; Validation, B.K. and Z.C.F.; Writing—original draft, D.Z. and L.W.; Writing—review and editing, J.Y. and Z.C.F. All authors have read and agreed to the published version of the manuscript.

Funding: The work was supported by the National Natural Science Foundation of China (NO.61367004) and the Natural Science Foundation of Guangxi Province (No.2013GXNSFFA019001).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author: Z.C.F. (Zhe Chuan Feng), upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Choyke, W.J.; Matsunami, H.; Pensl, G. (Eds.) Silicon Carbide: Recent Major Advances; Springer: Berlin/Heidelberg, Germany, 2004.
- 2. Feng, Z.C. (Ed.) SiC Power Materials—Devices and Applications; Springer: Berlin, Germany, 2004.
- 3. Friedrichs, P.; Kimoto, T.; Ley, L.; Pensl, G. (Eds.) *Silicon Carbide: Volume 1: Growth, Defects, and Novel Applications (2009); Silicon Carbide: Volume 2: Power Devices and Sensors;* WILEY-VCH: Weinheim, Germany, 2011.
- 4. Saddow, S.E. (Ed.) *Silicon Carbide Biotechnology;* Elsevier: Amsterdam, The Netherlands, 2014.
- Kimoto, T.; Co, J.A. (Eds.) Fundamentals of Silicon Carbide Technology: Growth, Characterization, Devices and Applications; Wiley Publishing: Hoboken, NJ, USA, 2014.
- 6. Feng, Z.C. (Ed.) Handbook of Silicon Carbide and Related Materials; Taylar & Francis, CRC Publishing: London, UK; New York, NY, USA, 2022; in press.
- 7. Choyke, W.J.; Pensl, G. Physical properties of SiC. MRS Bull. 1997, 22, 25–29. [CrossRef]
- 8. Wright, N.G.; Horsfall, A.B. SiC sensors: A review. J. Phys. D Appl. Phys. 2007, 40, 6345–6354. [CrossRef]
- 9. Dhar, S.; Haney, S.; Cheng, L.; Ryu, S.R.; Agarwal, A.K.; Yu, L.C.; Cheung, K.P. Inversion layer carrier concentration and mobility in 4H–SiC metal-oxide-semiconductor field-effect transistors. *J. Appl. Phys.* **2010**, *108*, 054509. [CrossRef]
- Saddow, S.E.; Frewin, C.L.; Nezafatil, M.; Oliveros, I.A.; Afroz, S.; Register, J.; Reyes, M.; Thomas, S. 3C-SiC on Si: A Bio- and Hemo-compatible Material for Advanced Nano-Bio Devices. In Proceedings of the IEEE Nanotechnology Materials and Devices Conference (NMDC), Aci Castello, Italy, 12–15 October 2014; pp. 46–53. [CrossRef]
- 11. Zhao, D.; Wang, F.; Wan, L.; Yang, Q.; Feng, Z.C. Raman scattering study on anisotropic property in wurtzite 4H-SiC. *J. Light Scatt.* **2018**, *30*, 37–42. [CrossRef]
- Klahold, W.M.; Choyke, W.J.; Devaty, R.P. Band structure properties, phonons, and exciton fine structure in 4H-SiC measured by wavelength-modulated absorption and low-temperature photoluminescence. *Phys. Rev. B* 2020, 102, 205203. [CrossRef]
- Han, L.; Liang, L.; Kang, Y.; Qiu, Y. Review of SiC IGBT: Models, Fabrications, Characteristics and Applications. *IEEE Trans. Power Electron.* 2021, *36*, 2080–2093. [CrossRef]
- 14. Zhu, S.; Liu, T.; Fan, J.; Maddi, H.J.R.; White, M.H.; Agarwal, A.K. Effects of JFET Region Design and Gate Oxide Thickness on the Static and Dynamic Performance of 650 V SiC Planar Power MOSFETs. *Materials* **2022**, *15*, 5995. [CrossRef]
- Sultan, N.M.; Albarody, T.M.B.; Al-Jothery, H.K.M.; Abdullah, M.A.; Mohammed, H.G.; Obodo, K.O. Thermal Expansion of 3C-SiC Obtained from In-Situ X-ray Diffraction at High Temperature and First-Principal Calculations. *Materials* 2022, 15, 6229. [CrossRef] [PubMed]
- Harima, H.; Nakashima, S.I.; Uemura, T. Raman scattering from anisotropic LOphonon–plasmon–coupled mode in ntype 4H– and 6H–SiC. J. Appl. Phys. 1995, 78, 1996. [CrossRef]
- 17. Nakashima, S.; Harima, H. Raman investigation of SiC polytypes. Phys. Status Solidi A 1997, 162, 37. [CrossRef]

- Burton, J.C.; Sun, L.; Pophristic, M.; Long, F.H.; Feng, Z.C.; Ferguson, I. Spatial characterization of doped SiC wafers by Raman spectroscopy. J. Appl. Phys. 1998, 84, 6268–6273. [CrossRef]
- Burton, J.C.; Sun, L.; Long, F.H.; Feng, Z.C.; Ferguson, I. First- and second-order Raman scattering from semi-insulating 4H-SiC. Phys. Rev. B 1999, 59, 7282–7284. [CrossRef]
- Han, R.; Han, B.; Wang, D.H.; Li, C. Temperature dependence of Raman scattering from 4H-SiC with hexagonal defects. *Appl. Phys. Lett.* 2011, 99, 011912. [CrossRef]
- Sun, H.Y.; Lien, S.C.; Qiu, Z.R.; Wang, H.C.; Mei, T.; Liu, C.W.; Feng, Z.C. Temperature dependence of Raman scattering in bulk 4H-SiC with different carrier concentration. *Opt. Express* 2013, 21, 26475–26482. [CrossRef] [PubMed]
- 22. Tseng, Y.C.; Cheng, Y.C.; Lee, Y.C.; Ma, D.L.; Yu, B.Y.; Lin, B.C.; Chen, H.L. Using Visible Laser-Based Raman Spectroscopy to Identify the Surface Polarity of Silicon Carbide. *J. Phys. Chem. C* 2016, *120*, 18228–18234. [CrossRef]
- 23. Wan, L.; Zhao, D.; Wang, F.; Xu, G.; Tin, C.C.; Lin, T.; Feng, Z.; Feng, Z.C. Efficient quality analysis of homo-epitaxial 4H-SiC thin films by the forbidden Raman Scattering Mode. *Opt. Mater. Express* **2018**, *8*, 119–127. [CrossRef]
- 24. Shimada, K.; Asada, K.; Yodo, M.; Ohtani, N. Raman scattering microscopy imaging of basal plane stacking faults and associated partial dislocations in 4H-SiC crystals. *J. Appl. Phys.* **2020**, *127*, 165704. [CrossRef]
- Song, Y.; Xu, Z.; Liu, T.; Rommel, M.; Wang, H.; Wang, Y.; Fang, F. Depth Profiling of Ion-Implanted 4H–SiC Using Confocal Raman Spectroscopy. *Crystals* 2020, 10, 131. [CrossRef]
- Chakravorty, A.; Singh, B.; Jatav, H.; Ojha, S.; Singh, J.; Kanjilal, D.; Kabiraj, D. Intense ionizing irradiation-induced atomic movement toward recrystallization in 4H-SiC. J. Appl. Phys. 2020, 128, 165901. [CrossRef]
- Huang, M.; Yang, Z.; Wang, S.; Liu, J.; Gong, M.; Ma, Y.; Liu, J.; Zhai, P.; Sun, Y.; Li, Y. Recrystallization effects in GeV Bi ion implanted 4H-SiC Schottky barrier diode investigated by cross-sectional Micro-Raman spectroscopy. *Nucl. Inst. Methods Phys. Res. B* 2020, 478, 5–10. [CrossRef]
- 28. Wang, C.; Fang, Z.; Yi, A.; Yang, B.; Wang, Z.; Zhou, L.; Shen, C.; Zhu, Y.; Zhou, Y.; Bao, R.; et al. High-Q microresonators on 4H-silicon-carbide-oninsulator platform for nonlinear photonics. *Light Sci. Appl.* **2021**, *10*, 139. [CrossRef] [PubMed]
- 29. Meli, A.; Muoio, A.; Trotta, A.; Meda, L.; Parisi, M.; La Via, F. Epitaxial Growth and Characterization of 4H-SiC for Neutron Detection Applications. *Materials* **2021**, *14*, 976. [CrossRef] [PubMed]
- 30. Chang, Y.; Xiao, A.; Li, R.; Wang, M.; He, S.; Sun, M.; Wang, L.; Qu, C.; Qiu, W. Angle-Resolved Intensity of Polarized Micro-Raman Spectroscopy for 4H-SiC. *Crystals* **2021**, *11*, 626. [CrossRef]
- 31. Steiner, J.; Wellmann, P.J. Impact of Mechanical Stress and Nitrogen Doping on the Defect Distribution in the Initial Stage of the 4H-SiC PVT Growth Process. *Materials* **2022**, *15*, 1897. [CrossRef] [PubMed]
- 32. Usami, Y.; Imokawa, K.; Nohdomi, R.; Sunahara, A.; Mizoguchi, H. Phase Changes of 4H-SiC in Excimer Laser Doping. J. Electron. Mater. 2022, 51, 3766–3772. [CrossRef]
- Zhang, S.; Yang, Y.; Liu, H.; Chen, H.; Li, X.; Liu, D.; Zhu, F.; Liu, Z.; Cheng, Y. Investigation of the recovery behavior of irradiation defects induced by a neutron in 4H-SiC combining Raman scattering and lattice parameters. *J. Mater. Res.* 2022, 37, 2910–2919. [CrossRef]
- 34. Zhang, Y.; Wang, Y.C.; Wang, L.; Zhu, L.; Wang, Z.L. Highly Sensitive Photoelectric Detection and Imaging Enhanced by the Pyro-Phototronic Effect Based on a Photoinduced Dynamic Schottky Effect in 4H-SiC. *Adv. Mater.* **2022**, *34*, 2204363. [CrossRef]
- 35. Wang, J.; Zhao, S.; Yan, G.; Shen, Z.; Zhao, W.; Wang, L.; Liu, X. Investigation on Step-Bunched Homoepitaxial Layers Grown on On-Axis 4H-SiC Substrates via Molten KOH Etching. *Crystals* **2022**, *12*, 788. [CrossRef]
- Lin, H.C.; Feng, Z.C.; Chen, M.S.; Shen, Z.X.; Ferguson, I.T.; Lu, W. Raman Scattering Study on Anisotropic Property of Wurtzite GaN. J. Appl. Phys. 2009, 105, 036102. [CrossRef]
- Zheng, W.; Zheng, R.S.; Wu, H.L.; Li, F.D. Strongly anisotropic behavior of A1(TO) phonon mode in bulk AlN. J. Alloys Compd. 2014, 584, 374–376. [CrossRef]
- Jin, L.; Wu, H.L.; Zhang, Y.; Qin, Z.Y.; Shi, Y.Z.; Cheng, H.J.; Zheng, R.S.; Chen, W.H. The growth mode and Raman scattering characterization of m-AlN crystals grown by PVT method. J. Alloys Compd. 2020, 824, 153935. [CrossRef]
- Zheng, W.; Zheng, R.S.; Huang, F.; Wu, H.L.; Li, F.D. Raman tensor of AlN bulk single crystal. *Photonics Res.* 2015, 3, 38–43. [CrossRef]
- 40. Zheng, W.; Yan, J.; Li, F.; Huang, F. Elucidation of "phase difference" in Raman tensor formalism. *Photonics Res.* 2018, 6, 709–712. [CrossRef]
- 41. Zheng, W.; Yan, J.; Li, F.; Huang, F. Raman spectroscopy regulation in van der Waals crystals. *Photonics Res.* **2018**, *6*, 991–995. [CrossRef]
- 42. Inui, T.; Tanabe, Y.; Onodera, Y. Group Theory and Its Applications in Physics; Springer: Berlin/Heidelberg, Germany, 1996.
- 43. Olego, D.; Cardona, M. Raman scattering by coupled LO-phonon-plasmon modes and forbidden TO-phonon Raman scattering in heavily doped p-type GaAs. *Phys. Rev. B* **1981**, *24*, 7217–7232. [CrossRef]
- Strach, T.; Brunen, J.; Lederle, B.; Zegenhagen, J.; Cardona, M. Determination of the phase difference between the Raman tensor elements of the A1g-like phonons in SmBa₂Cu₃O_{7-δ}. *Phys. Rev. B* 1998, 57, 1292–1297. [CrossRef]
- 45. Shi, S.; Yu, Y.; Wang, N.; Zhang, Y.; Shi, W.; Liao, X.; Duan, N. Investigation of the Anisotropy of 4H-SiC Materials in Nanoindentation and Scratch Experiments. *Materials* **2022**, *15*, 2496. [CrossRef]