Second-harmonic generation and linear electro-optical coefficients of SiC polytypes and nanotubes

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The second-order nonlinear optical susceptibility [$\chi_{abc}^{(2)}$] and linear electro-optical coefficient (r_{abc}) of a large number of single-walled zigzag, armchair, and chiral silicon carbide (SiC) nanotubes (SiC NTs), as well as bulk SiC polytypes (2H-, 4H-, 6H-, and 3C-SiC) and single graphitic SiC sheet have been calculated from the first principles. The calculations are based on the density-functional theory in the local-density approximation where the highly accurate full-potential projector augmented-wave method was used. Both the zigzag and chiral SiC NTs are found to exhibit large second-order nonlinear optical behaviors with the $\chi_{abc}^{(2)}$ and r_{abc} coefficients being up to ten times larger than that of bulk SiC polytypes and also being up to thirteen times larger than the counterparts of the corresponding BN NTs, indicating that SiC NTs are promising materials for nonlinear optical and optoelectronic applications. The features in the spectra of $\chi_{abc}^{(2)}(-2\omega, \omega, \omega)$ of the SiC NTs are discussed in terms of the single- and two-photon resonances and also related to the features in the linear dielectric function $\varepsilon(\omega)$.

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I. INTRODUCTION

Carbon nanotubes (CNTs) have attracted considerable interest worldwide ever since their discovery in 1991,¹ mainly because of their unusual properties and great potentials for technological applications. CNTs can be regarded as a layer of graphene sheet rolled up in a tubular form² and the structure of a CNT is specified by a chiral vector defined by a pair of integers (n, m). CNTs can be chiral or nonchiral depending on the way they are rolled up. Their physical properties, in particular, optical dielectric functions depend sensitively on their chirality, i.e., the (n, m) indices (see, e.g., Refs. 3 and 4 and references therein). Apart from the CNTs, inorganic tubular materials, such as BN (Refs. 5 and 6), AlN (Ref. 7), and GaN (Ref. 8), have also been predicted and synthesized. These tubular materials also display some very interesting properties distinctly different from their bulks.

Bulk silicon carbide (SiC) crystallizes in either a cubic or in a hexagonal form and exhibits polytypism.^{9,10} The polytypes are made of identical hexagonal layers with different stacking sequences. These polytypes are semiconductors with a range of band gaps from 2.39 eV in the zinc blende (3C) to 3.33 eV in the wurtzite polytype (2H) (Refs. 9 and 11). Furthermore, 3C- and 6H-SiC are used for high-temperature, high-power, and high-frequency devices^{12–15} due to their unique properties,¹⁶ while 6H-SiC with a band gap of 2.86 eV is a useful material for blue light-emitting diode applications.¹¹ Recently, SiC NTs were also synthesized by the reaction of CNTs and SiO at different temperatures.¹⁷ This has stimulated a number of theoretical and experimental investigations on the tubular form of the SiC (Refs. 18–22). Based on the density-functional calculations, Miyamoto and Yu²³ predicted the existence of graphitic and tubular forms of SiC and also proposed their synthesis using an extreme hole injection technique. They also reported that the strain energies of SiC NTs are lower than that of CNTs and that the band gaps of SiC NTs can be direct or indirect, depending on the chirality. Using both tight-

binding molecular-dynamics and *ab initio* methods, Menon *et al.*²⁰ showed that single-walled SiC NTs are highly stable with a large band gap. Zhao *et al.*²⁴ also investigated theoretically the strain energy, atomic, and electronic structures of SiC NTs with or without hydrogenation. Gali²⁵ performed an *ab initio* study of the effect of nitrogen and boron impurities on the band structure of the SiC NTs.

Unlike CNTs, SiC NTs are polar materials and therefore may exhibit some unusual physical properties that CNTs may not have. For example, like BN NTs (Refs. 26 and 27), zigzag SiC NTs may become piezoelectric and may also show second-order nonlinear optical response. Despite many theoretical studies mentioned above, no *ab initio* calculation of the dielectric response and optical properties of SiC NTs has been reported, perhaps because of the heavy demand on computer resources. Knowledge of the optical properties in SiC NTs is important for their optical and electro-optical applications. Therefore, we have recently performed systematic *ab initio* calculations in order to investigate the linear optical responses of all three types of the SiC NTs as well as their possible dependence on diameter and chirality.²⁸ In this work, we study the second-order optical susceptibility and also the linear electro-optical coefficient of the SiC NTs, as well as bulk SiC polytypes. The chief objective of this work is to characterize the features and magnitude of the second-harmonic generation (SHG) and linear electro-optical coefficients of the SiC NTs in order to see whether they have any potential applications in nonlinear optical and electro-optical devices such as SHG, sum-frequency generation, and electrical optical switch. Another objective is to examine possible differences in nonlinear optical properties between SiC NTs and CNTs (Ref. 3) and also between SiC NTs and BN NTs (Ref. 27).

The rest of this paper is organized as follows: in Sec. II the theoretical approach and computational method are described. In Sec. III the calculated second-order nonlinear optical susceptibility and linear electro-optical coefficients of SiC NTs are reported. For comparison, the second-order non-

linear optical susceptibility and linear electro-optical coefficients of bulk SiC polytypes and single graphitic SiC sheet are also presented. Finally, the summary is given in Sec. IV.

II. THEORY AND COMPUTATIONAL METHOD

Our *ab initio* calculations for the SiC NTs were performed using the highly accurate full-potential projector augmented-wave (PAW) method,²⁹ as implemented in the VASP package.³⁰ They are based on the density-functional theory (DFT) with the local-density approximation (LDA). The supercell geometry was adopted so that the NTs are aligned in a square array with the closest distance between adjacent NTs being at least 10 Å. Test calculations for the (6,0) SiC NT with the closest distance between adjacent NTs increased by 3 and 6 Å reveal no discernable changes to the calculated band structure and optical properties. In particular, the second-order nonlinear optical susceptibilities from the calculations with three different supercell sizes hardly differ (within a couple of percents). A large plane-wave energy cutoff of 450 eV was used throughout. We consider a large number of representative SiC NTs with a range of diameters from all three types listed in Ref. 28.

First, the ideal NTs were constructed by rolling up a hexagonal SiC sheet. The atomic positions and lattice constants were then fully relaxed by the conjugate gradient technique. The theoretical equilibrium atomic positions and lattice constant were obtained when the forces acting on all the atoms and the uniaxial stress were less than 0.04 eV/Å and 1.0 kBar, respectively. The calculated equilibrium lattice constants T and curvature energies E_c (total energy relative to that of single SiC sheet), as well as the other computational details, have been reported before.²⁸ The final self-consistent electronic band-structure calculations were then carried out for the theoretically determined SiC-NT structures.

In this work, the nonlinear optical properties were calculated based on the independent-particle approximation. The imaginary part of the second-order optical susceptibility $\chi''_{abc} \times^{(2)}(-2\omega, \omega, \omega)$ due to direct interband transitions is obtained from the final self-consistent electronic band structures by using the expressions already given elsewhere.^{3,27} The real part of the second-order optical susceptibility is then obtained from $\chi''_{abc} \times^{(2)}$ by a Kramer-Kronig transformation,

$$\chi'^{(2)}(-2\omega, \omega, \omega) = \frac{2}{\pi} \mathbf{P} \int_0^\infty d\omega' \frac{\omega' \chi''^{(2)}(2\omega', \omega', \omega')}{\omega'^2 - \omega^2}. \quad (1)$$

The linear electro-optical coefficient $r_{abc}(\omega)$ is connected to the second-order optical susceptibility $\chi_{abc}^{(2)}(-\omega, \omega, 0)$ through the relation,³¹

$$\chi_{abc}^{(2)}(-\omega, \omega, 0) = -\frac{1}{2} n_a^2(\omega) n_b^2(\omega) r_{abc}(\omega), \quad (2)$$

where $n_a(\omega)$ is the refraction index in the a direction. In the zero-frequency limit,

$$r_{abc}(0) = -\frac{2}{n_a^2(0)n_b^2(0)} \lim_{\omega \rightarrow 0} \chi_{abc}^{(2)}(-2\omega, \omega, \omega). \quad (3)$$

For the photon energy $\hbar\omega$ well below the band gap, the linear electro-optical coefficient $r_{abc}(\omega) \approx r_{abc}(0)$ because $\chi_{abc}^{(2)}(-2\omega, \omega, \omega)$ and $n(\omega)$ are nearly constant in this low-frequency region shown in Sec. III and in Ref. 28.

In the present calculations, the δ function in the expressions for $\chi''^{(2)}(2\omega, \omega, \omega)$ (Refs. 3 and 27) is approximated by a Gaussian function with $\Gamma=0.2$ eV. The finite-energy width Γ of ~ 0.1 eV is used to simulate the spectral broadening due to the finite lift time of the photoexcited electron-hole pairs. A uniform k -point grid ($1 \times 1 \times n$) along the NT axis (z axis) with the number n being from 40 to 100 is used. Test calculations for the (6,0) SiC NT with larger n numbers show that the calculated optical properties converge to within a couple of percents. Note that in our present and recent optical property calculations,^{3,4,27,28} a symmetrization of the products of the two and three dipole transition matrix elements over all the transformations of the crystal group is performed, which was done in Ref. 31. This considerably reduces the number of the k points needed by limiting the $\mathbf{k}$ summation to the irreducible Brillouin-zone wedge. Furthermore, to ensure that $\chi'_{abc} \times^{(2)}$ calculated via Kramer-Kronig transformation [Eq. (1)] is reliable, at least ten energy bands per atom are included in the present optical calculations.

The present calculations of the nonlinear optical properties are based on the independent-particle approximation; i.e., quasiparticle self-energy correction, excitonic effect, and the local-field correction are neglected. The band gap of the four bulk SiC polytypes from our LDA calculations is ~ 1.1 eV smaller than the corresponding experimental value (see Sec. III A below), suggesting that the quasiparticle self-energy correction may shift the optical peak positions to the higher energy side by ~ 1.1 eV in the SiC systems. Because of its underestimation in the energy gap, the dielectric function and the second-order nonlinear optical susceptibility in the static limit from the LDA calculation would be too large in general. For example, our calculated dielectric function at 0 eV for the electric field parallel and perpendicular to the c axis of 2H-SiC is 8.33 and 7.90, respectively, being larger than the corresponding measured ϵ_∞ ; 6.84 and 6.51 (Ref. 9). Nonetheless, our recent calculations indicate that the optical dielectric functions of graphite³ and also of h -BN (Ref. 27) calculated within the LDA independent-particle picture are in reasonable agreement with the experiment. Note that large excitonic effects with an exciton binding energy of ~ 0.7 eV in h -BN were recently reported.³² One of the excitonic effects is to shift the optical feature positions toward the lower energies. Therefore, the good agreement between the calculated and measured optical dielectric functions found recently in graphite³ and h -BN (Ref. 27) may be fortuitous and is likely due to the accidental cancellation of the self-energy correction by the excitonic effect. Unfortunately, due to the poorer screening of the electron-hole interaction, the self-energy correction and excitonic effect would be even larger in low-dimensional systems such as NTs (Refs. 33 and 34). Therefore, the present LDA-independent-particle calculations might not be able to be compared quantitatively with

TABLE I. Calculated lattice constants of SiC polytypes, together with other theoretical calculations [Bechstedt *et al.* (Ref. 38)] and experimental (Ref. 9) lattice constants.

	2H	4H	6H	3C
	a (Å), c (Å)	a (Å), c (Å)	a (Å), c (Å)	a (Å)
This work	3.057,5.018	3.060,10.018	3.061,15.018	4.331
Cal.	3.057,5.016	3.061,10.012	3.062,15.012	4.332
Exp.	3.076,5.048	3.073,10.053	3.081,15.117	4.360

the future optical experiments on SiC NTs. However, they provide useful information on the trends and characteristics of the optical properties in the SiC NTs. Full-scale *ab initio* many-electron calculations of the optical properties in small-diameter-SiC NTs within the GW approximation and Bethe-Salpeter equation scheme^{32–34} are beyond the scope of this paper. These full-scale *ab initio* many-electron calculations of the second-harmonic polarizability have so far been performed for only a few simple zinc-blende semiconductors AlP, AlAs, GaP, and GaAs (Refs. 35 and 36). These calculations indicate that the combined effect of the self-energy correction and electron-hole interaction would lead mainly to a blueshift of the features in the second-harmonic polarizability spectra by ~ 0.5 eV (Ref. 36) and also reduce the magnitude of the second-harmonic polarizability by about 10 $\sim$ 20% (Refs. 35 and 36).

III. RESULTS AND DISCUSSION

A. Bulk SiC polytypes

We first investigated the second-order nonlinear optical susceptibility of bulk SiC polytypes. SiC exists in either a cubic or in a hexagonal polymorphic structure. The polytypes are made of identical hexagonal layers with different stacking sequences. SiC occurs in nearly 200 polytypes.³⁷ Here we consider only the four common 2H, 4H, 6H, and 3C types of SiC. The atomic positions and lattice constants of the four polytypes were theoretically optimized. In the atomic structure optimizations, a uniform k -point grid of $30 \times 30 \times n$ with n being 15 to 30 was used. The calculated equilibrium lattice constants of the SiC polytypes are listed in Table I, together with the previous theoretical and experimental values. Table I shows that our theoretical lattice constants are in very good agreement with the previous calculations,³⁸ although they are slightly smaller (within 0.7%) than the corresponding experimental values.⁹ Our calculated indirect band gaps for the 3C, 2H, 4H, and 6H types of SiC are, respectively, 1.29, 2.12, 2.17, and 1.96 eV. These band-gap values are smaller by about 1.1 eV than the corresponding experimental values⁹ of 2.39 (3C), 3.33 (2H), 3.26 (4H), and 2.86 eV (6H). Nonetheless, our theoretical band-gap values are in very good agreement with the previous LDA calculations (see, e.g., Ref. 39 and references therein). The difference in the theoretical DFT-LDA and experimental band-gap values can be mostly attributed to the quasiparticle self-energy corrections.³⁹

FIG. 1. (Color online) Real and imaginary parts of $\chi^{(2)}(-2\omega, \omega, \omega)$ of the hexagonal SiC polytypes.

We display the imaginary and real parts of three nonvanishing components of the second-order nonlinear optical susceptibility (tensor) $\chi^{(2)}(-2\omega, \omega, \omega)$ of the three hexagonal SiC polytypes in Fig. 1. The imaginary and real parts of the nonvanishing component $\chi_{xyz}^{(2)}(-2\omega, \omega, \omega)$ of the cubic SiC are plotted in Fig. 2. In the nonlinear optical calculations, we used a denser k -point grid of $50 \times 50 \times n$ with n being 10 to 30 for the three hexagonal SiC polytypes and $n=50$ for the cubic SiC. We find numerically that only the $\chi_{zzz}^{(2)}$, $\chi_{zxx}^{(2)}$, $\chi_{zyy}^{(2)}$, $\chi_{xzx}^{(2)}$, $\chi_{yzy}^{(2)}$, $\chi_{xxz}^{(2)}$, and $\chi_{yyz}^{(2)}$ components are nonzero for the three hexagonal polytypes. Moreover, $\chi_{zyy}^{(2)} = \chi_{zxx}^{(2)}$ and $\chi_{yyz}^{(2)} = \chi_{xxz}^{(2)} = \chi_{xzx}^{(2)} = \chi_{yzy}^{(2)}$. This is consistent with the symmetry consideration.⁴⁰ For 3C-SiC, only $\chi_{xyz}^{(2)}$, $\chi_{zxy}^{(2)}$, and $\chi_{yxz}^{(2)}$ components are nonzero, where all the three components are numerically found to be identical as they should. Figure 1 shows that the line shape, amplitude, and feature positions of the $\chi_{zxx}^{(2)}$ and $\chi_{zxx}^{(2)}$ components for the three hexagonal SiC polytypes are very similar. On the other hand, the $\chi_{zzz}^{(2)}$ component varies significantly as one moves from 2H- to 6H-SiC. This is mainly because, in this case, all the electric fields are polarized parallel to the z axis and hence the $\chi_{zzz}^{(2)}$ component should be rather sensitive to the layer stacking sequence along the z axis. We also note that the shape of the $\chi_{xyz}^{(2)}$ of 3C-SiC is similar to that of the $\chi_{zzz}^{(2)}$ of 6H-SiC (Figs.

FIG. 2. (Color online) Real and imaginary parts of $\chi_{xyz}^{(2)}(-2\omega, \omega, \omega)$ of SiC in the zinc-blende (3C) structure. Previous calculations by Adolph and Bechstedt (Ref. 41) are also displayed for comparison.

FIG. 3. (Color online) Imaginary parts of $\chi^{(2)}(-2\omega, \omega, \omega)$ of SiC in the wurtzite (2H) structure. Previous calculations by Adolph and Bechstedt (Ref. 41) are also displayed for comparison.

1 and 2). Nonetheless, the features in the $\chi_{xyz}^{(2)}$ of the cubic structure appears to have the largest magnitude among the four SiC polytypes studied here.

We find that our calculated nonzero components of $\chi^{(2)}(-2\omega, \omega, \omega)$ in all the four polytypes agree quite well with the recent DFT-LDA calculations by Adolph and Bechstedt.⁴¹ For detailed comparison, we plot the imaginary part of the nonzero components of SiC in the cubic and wurtzite structures from the previous calculations by Adolph and Bechstedt⁴¹ in Fig. 2 (cubic) and in Fig. 3 (wurtzite), together with our results. One can see from Figs. 2 and 3(c) that $\chi_{xyz}^{(2)}(-2\omega, \omega, \omega)$ of 3C-SiC and $\chi_{xzx}^{(2)}(-2\omega, \omega, \omega)$ of 2H-SiC from the present and previous calculations are almost identical. Nonetheless, there are some discernable discrepancies in the $\chi_{zxx}^{(2)}$ and $\chi_{zzz}^{(2)}$ components of 2H-SiC between the two calculations [Figs. 3(a) and 3(b)].

In Table II, the calculated zero-frequency linear electro-optical coefficient $r(0)$, as well as the corresponding second-order nonlinear optical susceptibility $\chi^{(2)}(0, 0, 0)$, are listed.

TABLE II. Calculated static refraction index n , second-order optical susceptibility $\chi^{(2)}(0)$ (pm/V), and linear electro-optical coefficient r_{abc} (pm/V) of the hexagonal SiC polytypes (a), zinc-blende SiC (b), and also isolated SiC sheet (c).

(a)	$n_x (n_z)$	$\chi_{zzz}^{(2)}, \chi_{zxx}^{(2)}$	r_{zzz}, r_{zxx}
2H-SiC	2.81(2.88)	11.5, -17.9	-0.33, 0.55
4H-SiC	2.83(2.87)	32.8, -20.4	-0.97, 0.62
6H-SiC	2.82(2.89)	38.6, -20.4	-1.11, 0.61
(b)	n	$\chi_{xyz}^{(2)}$	r_{xyz}
3C-SiC	2.95	34.2	-0.90
(c)	$n_a (n_c)$	$\chi_{bbb}^{(2)}, \chi_{aab}^{(2)}$	r_{bbb}, r_{aab}
SiC sheet	3.19(2.01)	227.8, -227.8	-11.08, 11.08

The $r(0)$ is calculated from the corresponding $\chi^{(2)}(0, 0, 0)$ by using Eq. (3). We find that the calculated $\chi_{xzx}^{(2)}(0)$ and $\chi_{zxx}^{(2)}(0)$ for the three hexagonal SiC polytypes differ slightly from each other, i.e., only approximately satisfying the requirement of the Kleinman⁴² symmetry. In Table II, therefore, $\chi_{zxx}^{(2)}(0)$ is listed as the averaged value of $\chi_{xzx}^{(2)}(0)$ and $\chi_{zxx}^{(2)}(0)$; hence $r_{zxx}(0)$ as the averaged value of $r_{zxx}(0)$ and $r_{xzx}(0)$ for all the hexagonal SiC polytypes. Clearly, Table II shows that $\chi_{zxx}^{(2)}(0)$ and $r_{zxx}(0)$ are nearly the same for all the hexagonal SiC polytypes. In contrast, $\chi_{zzz}^{(2)}(0)$ and $r_{zzz}(0)$ increase substantially as one moves from 2H- to 6H-SiC, indicating that $\chi_{zzz}^{(2)}(0)$ and $r_{zzz}(0)$ are more sensitive to the layer stacking sequence along the z axis.

Our calculated nonvanishing components of $\chi^{(2)}(0)$ for the four polytypes are compared with the previous *ab initio* calculations^{41,43,44} and available experiments^{45,46} in Table III. First, we would consider that the agreement between our results and the experimental values is rather good (Table III), given the large uncertainties in the available experimental data.^{45,46} Second, our results agree rather well with the previous *ab initio* calculations by Chen *et al.*⁴⁴ Nonetheless, both the results of ours and of Chen *et al.*⁴⁴ appear to be nearly two times larger than the *ab initio* calculations by Adolph *et al.*⁴¹ and Rashkeev *et al.*⁴³ This is surprising since the imaginary parts of $\chi^{(2)}$ from both the present and previous⁴¹ calculations are very similar (Figs. 2 and 3). The

TABLE III. Calculated second-order optical susceptibility $\chi^{(2)}(0)$ (pm/V) of the four SiC polytypes together with other theoretical [Adolph *et al.* (Ref. 41), Rashkeev *et al.* (Ref. 43), Chen *et al.* (Ref. 44)] and experimental [Lundquist *et al.* (Ref. 45) and Niedermeier *et al.* (Ref. 46)] results.

	2H $\chi_{zzz}^{(2)}, \chi_{zxx}^{(2)}$	4H $\chi_{zzz}^{(2)}, \chi_{zxx}^{(2)}$	6H $\chi_{zzz}^{(2)}, \chi_{zxx}^{(2)}$	3C $\chi_{xyz}^{(2)}$
This work	11.5, -17.9	32.8, -20.4	38.6, -20.4	34.2
Adolph <i>et al.</i>	4.5, -7.1	15.5, -9.7	18.1, -9.8	17.7
Rashkeev <i>et al.</i>	3.6, -6.1	14.5, -8.9	17.8, -9.7	17.5
Chen <i>et al.</i>	8.6, -13.2	23.3, -14.8	27.6, -15.0	24.4
Lundquist <i>et al.</i>			86, -8.6	17.3
Niedermeier <i>et al.</i>		$18 \pm 8, -4 \pm 2$	$24 \pm 10, -4 \pm 2$	

TABLE IV. Calculated second-order optical susceptibility $\chi^{(2)}(0)$ (pm/V) of BN, AlN, and GaN in the cubic zinc-blende (a) and wurtzite (2H) (b) structures compared with the previous DFT-LDA calculations by Rashkeev *et al.* (Ref. 47) and Chen *et al.* (Ref. 48).

	BN	AlN	GaN
(a)	$\chi_{xyz}^{(2)}$	$\chi_{xyz}^{(2)}$	$\chi_{xyz}^{(2)}$
This work	5.5	-0.43	16.31
Rashkeev <i>et al.</i>	4.5	-0.4	18.3
Chen <i>et al.</i>	5.2	-0.02	16.4
(b)	$\chi_{zzz}^{(2)}$ $\chi_{zxx}^{(2)}$	$\chi_{zzz}^{(2)}$ $\chi_{zxx}^{(2)}$	$\chi_{zzz}^{(2)}$ $\chi_{zxx}^{(2)}$
This work	4.7, -2.5	-9.6, -0.87	11.4, -8.0
Rashkeev <i>et al.</i>		-7.5, 0.4	8.8, -7.1
Chen <i>et al.</i>	5.4, -2.8	-8.4, -0.2	10.4, -6.4

precise origin of these discrepancies is not known at the moment. To understand these discrepancies, we further performed the DFT-LDA calculations for BN, AlN, and GaN in both zinc-blende and wurtzite structures. Our calculated $\chi_{xyz}^{(2)}(0)$ is listed in Table IV, together with the theoretical results by Rashkeev *et al.*⁴⁷ and also by Chen *et al.*⁴⁸ Table IV shows clearly that our results for BN, AlN, and GaN agree very well with that of Rashkeev *et al.*⁴⁷ and also with that of Chen *et al.*⁴⁸

B. Single graphitic SiC sheet

In order to understand the nonlinear optical properties of the SiC NTs, we have also calculated the second-order nonlinear optical susceptibilities for an isolated honeycomb SiC sheet. The isolated SiC sheet is simulated by a slab-supercell approach with an intersheet distance of about 10 Å. The underlying structure was determined theoretically by using k mesh of $100 \times 100 \times 1$ while the theoretical lattice constant is $a = 3.069$ Å. We find numerically that $\chi_{aab}^{(2)}$, $\chi_{baa}^{(2)}$, and $\chi_{bbb}^{(2)}$ for the isolated SiC sheet are nonzero. Here a and b denote the two Cartesian coordinates within the SiC layer. Moreover, $\chi_{baa}^{(2)} = \chi_{aab}^{(2)}$ and $\chi_{bbb}^{(2)} = -\chi_{aab}^{(2)}$. This is consistent with the symmetry consideration, demonstrating again that our numerical method and calculations are qualitatively correct. The isolated SiC sheet does not have the spatial inversion symmetry (D_{6h}^4); its symmetry class is $D_{3h} (P\bar{6}m2)$. Therefore, the isolated SiC sheet has nonzero $\chi_{aab}^{(2)}$, $\chi_{baa}^{(2)}$, and $\chi_{bbb}^{(2)}$ from the symmetry consideration.⁴⁰

We show in Fig. 4 the calculated real and imaginary parts as well as the absolute value of the imaginary part of $\chi_{aab}^{(2)}(-2\omega, \omega, \omega)$ of the single SiC sheet. Figure 4 indicates that the SHG coefficient $\chi_{aab}^{(2)}(-2\omega, \omega, \omega)$ is significant in the entire range of the optical photon energy ($\hbar\omega$). Furthermore, for the photon energy smaller than 1.2 eV, the $\chi_{aab}^{(2)}$ is purely dispersive [Fig. 4(a)], suggesting that the SiC sheet has potential application in nonlinear optical devices. Note that since the SiC sheet has a theoretical band gap (E_g) of ~ 2.6 eV, the absorptive (imaginary) part of the $\chi_{aab}^{(2)}$ becomes zero below the half of the band gap (i.e., ~ 1.2 eV).

FIG. 4. (Color online) (a) Real and imaginary parts as well as (b) the absolute value of the imaginary part of $\chi_{aab}^{(2)}(-2\omega, \omega, \omega)$ of the isolated SiC sheet. In (c) $\epsilon''(\omega)$ and $\epsilon''(\omega/2)$ (imaginary part of the dielectric function) from Ref. 28 are plotted.

The real part of the $\chi_{aab}^{(2)}$ remains nearly constant at low photon energies up to 0.5 eV, then increases steadily in magnitude as the photon energy increases and finally peaks at the absorption edge of ~ 1.2 eV [Fig. 4(a)]. In the energy range from 1.4 to 3.0 eV, the real part of $\chi_{aab}^{(2)}$ becomes positive and forms a broad double peak structure. Beyond 3.0 eV, it becomes negative again and its magnitude gradually diminishes as the photon energy further increases [Fig. 4(a)].

The absorptive part of the $\chi_{aab}^{(2)}$ is nonzero only above ~ 1.2 eV and looks like there is a Lorentzian oscillation between 1.2 and 3.5 eV with one sharp negative peak at ~ 1.4 eV and one broad positive peak around 2.8 eV [Fig. 4(a)]. The $\chi_{aab}^{(2)}$ spectra can have pronounced features due to both single- and double-frequency resonances, demonstrated recently in Ref. 27. Therefore, to characterize the features in the calculated $\chi^{(2)}$ spectra, the calculated ϵ'' from our previous publication²⁸ is shown in Fig. 4(c) as a function of both $\omega/2$ and ω . The first sharp peak at ~ 1.4 eV is clearly due to the two-photon resonances [cf. $\epsilon''(\omega/2)$] while in contrast, the second broad peak around 2.8 eV comes from the single-photon resonances [cf. $\epsilon''(\omega)$]. Nevertheless, both single- and double-photon resonances involve only interband $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ optical transitions for the electric-field vector $\mathbf{E}$ parallel to the SiC layer ($E \parallel \hat{a}$) (Ref. 28).

The calculated zero-frequency linear electro-optical coefficient $r(0)$, as well as the corresponding second-order nonlinear optical susceptibility $\chi^{(2)}(0, 0, 0)$ and the static refraction index $n(0)$, are listed in Table II. The refraction index $n(0) (= \sqrt{\epsilon(0)})$ is derived from the calculated static dielectric constant $\epsilon(0)$, which is reported in our recent publication.²⁸ Note that the linear electro-optical coefficients of the isolated SiC sheet are about ten times larger than the bulk SiC poly-

FIG. 5. (Color online) Real (dotted line) and imaginary (solid line) parts of $\chi^{(2)}(-2\omega, \omega, \omega)$ of the zigzag (6,0), (12,0), (20,0), and (24,0) SiC NTs.

types (Table II). The static second-order optical susceptibility for the SiC sheet is nearly six times larger than the largest component of $\chi^{(2)}(0,0,0)$ of the SiC polytypes. Furthermore, the zero-frequency linear electro-optical coefficient $r(0)$ and the corresponding second-order nonlinear optical susceptibility $\chi^{(2)}(0,0,0)$ in the SiC sheet are more than five times larger than the corresponding values of the BN sheet.²⁷

C. Second-order optical susceptibility

We have calculated the second-order optical susceptibility for the zigzag: (5,0), (6,0), (8,0), (9,0), (12,0), (16,0), (20,0), and (24,0); armchair (3,3), (4,4), (5,5), (8,8), (12,12), and (15,15); and chiral (4,2), (6,2), (8,4), and (10,4) SiC NTs. In the case of CNTs, only the chiral NTs would exhibit second-order nonlinear optical behavior with two nonvanishing components of xyz and xzy of $\chi^{(2)}$ (Ref. 3). Here z refers to the coordinate along the tube axis while x and y denote the two coordinates that are perpendicular to the tube axis. As for CNTs, the armchair SiC NTs are found not to have any nonzero components of $\chi^{(2)}$. In contrast, such as in the case of the BN NTs,²⁷ both the zigzag and chiral SiC NTs are found to show second-order nonlinear optical behavior. Specifically, all the zigzag SiC NTs except (5,0) and (9,0), have six nonvanishing components in the second-order optical susceptibility, namely, xzx , xxz , yyz , zxx , zyy , and zzz . Nevertheless, these components are not completely independent of each other. In particular, $\chi_{xxz}^{(2)} = \chi_{yyz}^{(2)} = \chi_{xzx}^{(2)}$ and $\chi_{zyy}^{(2)} = \chi_{zxx}^{(2)}$. The chiral SiC NTs have eight nonvanishing components in the

second-order optical susceptibility with two additional non-zero components being xyz and yzx . Note that $\chi_{yzx}^{(2)} = -\chi_{xyz}^{(2)}$. These numerical findings are consistent with the consideration in the symmetry of the SiC NTs. The point symmetry groups of the SiC NTs (Ref. 40) are C_{2nv} for zigzag $(n,0)$ NTs, C_{2nh} for armchair (n,n) NTs, and C_N for chiral (n,m) NTs where $N = 2(n^2 + m^2 + nm)/d_R$ with d_R being the greatest common divisor of $2n+m$ and $2m+n$. Therefore, these symmetries would dictate⁴⁰ that all the components vanish for armchair (n,n) NTs and that the nonvanishing components for zigzag $(n,0)$ NTs are $xzx = yzy$, $xxz = yyz$, $zxx = zyy$, and zzz , as well as that the nonvanishing components of chiral (n,m) NTs include all that for zigzag $(n,0)$ NTs plus $xyz = -yzx$.

We display in Fig. 5 the calculated real and imaginary parts of the second-order optical susceptibility $\chi^{(2)}(-2\omega, \omega, \omega)$ for the four selected zigzag NTs [(6,0), (12,0), (20,0), and (24,0)]. As for the single SiC sheet, the SHG coefficients $\chi^{(2)}(-2\omega, \omega, \omega)$ for the zigzag SiC NTs are significant in the entire range of the optical photon energy ($\hbar\omega$). Indeed, they can be up to ten times larger than that of bulk SiC polytypes (see Figs. 1 and 5). Moreover, for the photon energy smaller than 2.0 eV, $\chi^{(2)}$ is purely dispersive (Fig. 5). The magnitude of $\chi_{zzz}^{(2)}$ is the largest (Fig. 5). For $\chi_{zzz}^{(2)}$, the electric field of both the incoming and outgoing photons is parallel to the tube axis and thus the electric depolarization effect would be essentially zero (see Ref. 49 and references therein). This may be particularly important for nonlinear optical applications. The prominent features in each nonzero

FIG. 6. (Color online) Absolute value of the imaginary part of $\chi^{(2)}(-2\omega, \omega, \omega)$ (a)–(d) as well as $\varepsilon''(\omega)$ and $\varepsilon''(\omega/2)$ (imaginary part of the dielectric function) (b)–(e) from Ref. 28 of the zigzag (12,0) SiC NT.

component of $\chi^{(2)}$ for all the zigzag SiC NTs, except the small-diameter (6,0) SiC NT, look rather similar (Fig. 5). In particular, the spectra of the three xzx , zxx , and zzz components of $\chi^{(2)}$ for the (20,0) and (24,0) SiC NTs are nearly identical (Fig. 5). We also note that the shape of the spectra of $\chi_{zzz}^{(2)}$ and $\chi_{zxz}^{(2)}$ for all the zigzag SiC NTs look very similar, except the difference in sign. For the zigzag SiC NTs with a larger diameter such as (12,0), (20,0), and (24,0), the spectrum of $\chi_{zxz}^{(2)}$ is also similar to that of $\chi_{zxx}^{(2)}$ (Fig. 5). The magnitude of the $\chi_{zxz}^{(2)}$ and $\chi_{zxx}^{(2)}$ components decreases slightly as the diameter of the tubes increases [e.g., from (6,0) to (24,0)], while the magnitude of the $\chi_{zzz}^{(2)}$ remains nearly independent of the diameter (Fig. 5). Furthermore, both the magnitude and shape of the $\chi_{zzz}^{(2)}$ spectrum for the zigzag SiC NTs with a larger diameter, e.g., (20,0) and (24,0), approach to that of the single SiC sheet (Fig. 4).

To understand the features in the calculated $\chi^{(2)}$ spectra of the zigzag SiC NTs, the absolute values of the imaginary part $\chi^{(2)}$ of the nonzero components in the (12,0) SiC NT are plotted and compared with the absorptive part of the dielectric function ε'' from our previous publication²⁸ in Fig. 6. The first prominent peak between 1.0 and 2.0 eV in the $\chi_{zzz}^{(2)}$ spectrum is nearly identical to the first peak in the $\varepsilon_z''(\omega/2)$ [see Figs. 6(d) and 6(e)], indicating that it is due to the two-photon resonances. On the other hand, the second peak between 2.5 and 3.0 eV in the $\chi_{zzz}^{(2)}$ spectrum is rather similar to the first peak in the $\varepsilon_z''(\omega)$, suggesting that it is due to the single-photon resonances. Both these single- and double-photon resonances involve only interband $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ optical transitions for the electric-field vector $\mathbf{E}$ parallel to the tube axis ($E \parallel \hat{z}$) (Ref. 28). Figure 6 also shows that

the double peak structure between 1.0 and 2.0 eV in both the $\chi_{zxz}^{(2)}$ and $\chi_{zxx}^{(2)}$ spectra is mainly due to the two-photon resonances with $E \perp \hat{z}$ [cf. $\varepsilon_x''(\omega/2)$] [see Figs. 6(a)–6(c)], while the second feature in the photon energies above 3.0 eV perhaps comes primarily from the single-photon resonances for $E \perp \hat{z}$ [cf. $\varepsilon_x''(\omega)$]. This is further supported by the fact that the magnitude of $\varepsilon_x''(\omega)$ [$\varepsilon_x''(\omega/2)$] is only about half of that of $\varepsilon_z''(\omega)$ [$\varepsilon_z''(\omega/2)$] and concurrently the magnitude of $\chi_{zxz}^{(2)}$ and $\chi_{zxx}^{(2)}$ is only about half of that of $\chi_{zzz}^{(2)}$ too.

The calculated real and imaginary parts of the second-order optical susceptibility $\chi^{(2)}(-2\omega, \omega, \omega)$ for all the four chiral NTs [(4,2), (6,2), (8,4), and (10,4)] are displayed in Fig. 7. The spectra of each component in the second-order optical susceptibility for the chiral SiC NTs with a moderate diameter [e.g., (8,4) and (10,4)] are similar. For all the chiral SiC NTs, except the ultrasmall diameter (4,2) SiC NT, the zzz component is nearly four times larger than all the other nonvanishing components. Another common feature is that both the real and imaginary parts of $\chi_{xyz}^{(2)}(-2\omega, \omega, \omega)$ show a rather oscillatory behavior (Fig. 7). The amplitude of these oscillatory real and imaginary parts is rather large in the photon energies of 1.0–4.0 eV for the chiral SiC NTs with a small diameter. Note also that the shape and magnitude of the xzx and zxx components appears rather similar [Figs. 7(b) and 7(c)]. Finally, both the magnitude and shape of the $\chi_{zzz}^{(2)}$ spectrum for the chiral SiC NTs with a larger diameter, e.g., (10,4), approach to the single SiC sheet (Fig. 4), as expected.

The absolute values in the imaginary part $\chi^{(2)}$ of the nonzero components of the (8,4) SiC NT are displayed in Fig. 8, together with the absorptive part of the corresponding dielectric function ε'' from our previous publication²⁸ in order to understand the structures in the calculated $\chi^{(2)}$ spectra of the chiral SiC NTs. The first prominent peak between 1.0 and 2.0 eV in the $\chi_{zzz}^{(2)}$ spectrum is very similar to the first peak in the $\varepsilon_z''(\omega/2)$ [see Figs. 8(d) and 8(e)], suggesting that it is due to the two-photon resonances. The second structure between 2.5 and 3.5 eV in the $\chi_{zzz}^{(2)}$ spectrum may be correlated with the first peak in the $\varepsilon_z''(\omega)$, indicating that it is caused by the single-photon resonances. As for the zigzag SiC NTs, both these single- and double-photon resonances involve only interband $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ optical transitions for the electric-field vector $\mathbf{E}$ parallel to the tube axis ($E \parallel \hat{z}$) (Ref. 28). Figure 8 also suggests that the feature between 1.0 and 2.0 eV in the spectra of both the $\chi_{zxz}^{(2)}$ and $\chi_{zxx}^{(2)}$ as well as $\chi_{xyz}^{(2)}$ may be attributed to the two-photon resonances with $E \perp \hat{z}$ [cf. $\varepsilon_x''(\omega/2)$] [see Figs. 8(a)–8(c)], while the second feature in the photon energies above 3.0 eV is mainly due to the single-photon resonances for $E \perp \hat{z}$ [cf. $\varepsilon_x''(\omega)$].

D. Linear electro-optical coefficient

We list in Table V the calculated zero-frequency linear electro-optical coefficient $r(0)$ as well as the corresponding second-order nonlinear optical susceptibility $\chi^{(2)}(0,0,0)$ of the SiC NTs. The $r(0)$ is obtained from the corresponding $\chi^{(2)}(0,0,0)$ by using Eq. (3). The refraction index $n(0) (= \sqrt{\varepsilon(0)})$ is derived from the calculated dielectric constant $\varepsilon(0)$ reported in Ref. 28. Table V shows that apart from the (5,0) and (9,0) SiC NTs, which have no nonvanishing $r_{abc}(0)$

FIG. 7. (Color online) Real (dotted line) and imaginary (solid line) parts of $\chi^{(2)}(-2\omega, \omega, \omega)$ of the chiral (4,2), (6,2), (8,4), and (10,4) SiC NTs.

and also the small-diameter- (6,0) and (8,0) SiC NTs, all the other zigzag SiC NTs have very similar linear electro-optical coefficients, also for the static dielectric constant and polarizability.²⁸ Nevertheless, $r_{zzz}(0)$ decreases slightly as the diameter increases, while $r_{xxz}(0)$ and $r_{zxx}(0)$ increase slightly as the diameter goes up. The $\chi_{zzz}^{(2)}(0,0,0)$ for the ultrasmall diameter (6,0) is very large (Table V), being nearly thirteen times larger than the largest component of $\chi^{(2)}(0,0,0)$ for all the four bulk SiC polytypes (Table II). This suggests that the SiC NTs would be useful for the applications in the nonlinear optical devices. Nonetheless, the $\chi_{zzz}^{(2)}$ decreases rapidly as the diameter of the zigzag SiC NTs increases and for the large diameter (24,0) SiC-NT approaches the value of $\chi_{aab}^{(2)}$ in the single SiC sheet (Table II). The magnitude of the $\chi_{aab}^{(2)}$ is about half of the magnitude of the $\chi_{zzz}^{(2)}$ for the (6,0) SiC NT. We note that $\chi_{xxz}^{(2)}$ and $\chi_{zxx}^{(2)}$ are rather similar and their magnitudes increase as their tube diameters increase. Finally, for the larger diameter zigzag SiC NTs, the $\chi_{zzz}^{(2)}$ is about two times larger than $\chi_{xxz}^{(2)}$ and $\chi_{zxx}^{(2)}$ (Table V).

The chiral SiC NTs have two additional nonvanishing components $\chi_{xyz}^{(2)}$ and $\chi_{yzx}^{(2)}$. Nevertheless, the calculated values of $\chi_{xyz}^{(2)}(0,0,0)$ and $\chi_{yzx}^{(2)}(0,0,0)$ are negligibly small (i.e.,

within the numerical uncertainty), thereby satisfying the requirement by the so-called Kleinman symmetry,⁴² which requires that $\chi_{xyz}^{(2)}(0) = \chi_{yzx}^{(2)}(0)$. As a result, the corresponding linear electro-optical coefficients $r_{xyz}(0)$ and $r_{yzx}(0)$ are zero too. Therefore, $\chi_{yzx}^{(2)}$, $\chi_{xyz}^{(2)}$, $r_{xyz}(0)$, and $r_{yzx}(0)$ for the chiral SiC NTs are not listed in Table V. For the remaining nonvanishing components, $r_{xxz}(0)$ and $r_{zxx}(0)$ for the (6,2), (8,4), and (10,4) SiC NTs are quite similar. $\chi_{zzz}^{(2)}(0)$ and $r_{zzz}(0)$ decrease as the tube diameter increases, while $\chi_{xxz}^{(2)}(0)$ and $r_{zxx}(0)$ increase with the tube diameter. $r_{xxz}(0)$ and $r_{zxx}(0)$ for the (4,2) is somewhat smaller than the other chiral SiC NTs.

The zero-frequency second-order nonlinear optical susceptibility $\chi^{(2)}(0,0,0)$ of the SiC NTs (Table V) is generally a few times larger than the counterparts of the corresponding BN NTs (Ref. 27). In particular, the $\chi_{zzz}^{(2)}(0,0,0)$ of the (6,0) SiC-NT is about thirteen times larger than the (6,0) BN NT (Ref. 27). On the other hand, the $\chi_{zzz}^{(2)}(0,0,0)$ of the (24,0) SiC-NT is only about six times larger than the (24,0) BN NT (Ref. 27). This suggests that compared to BN NTs, SiC NTs would be a better nonlinear optical material. However, the low-frequency linear electro-optical coefficient $r(0)$ of the SiC NTs (Table V) is only slightly larger than the counter-

FIG. 8. (Color online) Absolute value of the imaginary part of $\chi^{(2)}(-2\omega, \omega, \omega)$ (a)–(d) and $\varepsilon''(\omega)$ and $\varepsilon''(\omega/2)$ (imaginary part of the dielectric function) (b)–(e) from Ref. 28 of the zigzag (8,4) SiC NT.

parts of the corresponding BN NTs (Ref. 27). For example, $r_{zzz}(0)$ of the (6,0) and (24,0) SiC NTs are, respectively, 1.7 and 1.3 times larger than that of the (6,0) and (24,0) BN NTs. This is because the refraction index n of the SiC NTs (Table V) is also larger than the BN NTs (Ref. 27) [see Eq. (7)].

IV. SUMMARY

The systematic *ab initio* study of the second-order nonlinear optical properties of SiC NTs within DFT-LDA has been performed. The highly accurate full-potential PAW method was used. The underlying atomic structure of the SiC nanotubes was determined theoretically. Specifically, the properties of the single-walled zigzag [(5,0), (6,0), (8,0), (9,0), (12,0), (16,0), (20,0), and (24,0)], armchair [(4,4), (5,5), (8,8), (12,12), and (15,15)], and chiral [(4,2), (6,2), (8,4), and (10,4)] NTs have been calculated. For comparison, the second-order nonlinear optical properties of bulk SiC polytypes (2H-, 4H-, 6H-, and 3C-SiC) and the single graphitic

TABLE V. Calculated static refraction index n , second-order optical susceptibility $\chi^{(2)}$, and linear electro-optical coefficient r_{abc} of the zigzag and chiral SiC NTs.

n_x (n_z)	$\chi_{xxz}^{(2)}, \chi_{zxx}^{(2)}, \chi_{zzz}^{(2)}$ (pm/V)	$r_{xxz}, r_{zxx}, r_{zzz}$ (pm/V)
(5,0)	2.50(3.39)	0.0,0.0,0.0
(6,0)	2.53(3.31)	78.5,45.5,-479.4
(8,0)	2.56(3.23)	87.6,68.0,-323.1
(9,0)	2.58(3.23)	0.0,0.0,0.0
(12,0)	2.60(3.21)	98.9,88.1,-255.4
(16,0)	2.62(3.21)	104.7,96.9,-241.9
(20,0)	2.68(3.27)	125.0,119.6,-279.2
(24,0)	2.63(3.19)	107.1,102.1,-227.7
(4,2)	2.74(3.37)	23.9,4.46,-410.4
(6,2)	2.56(3.16)	58.2,37.0,-236.6
(8,4)	2.62(3.17)	50.3,43.6,-138.6
(10,4)	2.62(3.17)	65.3,59.3,-164.3

SiC sheet have also been calculated. It is found that $\chi_{aab}^{(2)}$, $\chi_{baa}^{(2)}$, and $\chi_{bbb}^{(2)}$ of the isolated SiC sheet are large and generally several times larger than that of the SiC polytypes. Unlike carbon NTs, both the chiral and zigzag SiC NTs have pronounced second-harmonic generation and linear electro-optical coefficients, which are comparable to or even larger than the single SiC sheet. The prominent structures in the spectra of $\chi^{(2)}(-2\omega, \omega, \omega)$ in the SiC NTs have been related to the features in the corresponding linear optical dielectric function $\varepsilon(\omega)$ in terms of the single- and double-photon resonances. It is also found that the $\chi_{abc}^{(2)}$ and r_{abc} coefficients of the SiC NTs are up to thirteen times larger than the counterparts of the corresponding BN NTs. Therefore, the SiC NTs would be promising nonlinear optical materials for applications in, e.g., SHG, sum-frequency generation, and electro-optical switches. We hope that this work would stimulate experimental investigations into the second-order nonlinear optical properties of the SiC NTs.

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