Supplemental document accompanying submission to *Optical Materials Express*

**Title:** Nonlinear optical properties of 6H-SiC and 4H-SiC in an extensive spectral range

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**Submitted:** 11/25/2020 9:54:33 AM
1. CHARACTERIZATION

The X-ray diffraction (XRD) graphs of Si 6H-SiC and Si 4H-SiC are shown in Figs. S1(a) and S1(b). We can find two characteristic peaks, (0 0 6) and (0 0 12) at 35.6 degree and 75.3 degree, which indicate that the surfaces of the samples are perpendicular to the [0001] orientation. The other peaks correspond to background coming from the substrate. The scanning electron microscope (SEM) graphs of Si 6H-SiC and Si 4H-SiC are shown in Figs. S2(a) and S2(b). Under 2000 times magnification, there are no obvious defects, which proves that the samples are of good quality.

![XRD graphs](a) (0 0 6) SI 6H-SiC (0 0 12) (b) (0 0 6) SI 4H-SiC (0 0 12)

Fig. S1. XRD graphs of (a) Si 6H-SiC and (b) Si 4H-SiC.
Fig. S2. SEM graphs of (a) 6H-SiC and (b) 4H-SiC.
2. CALCULATION OF BAND STRUCTURE

Employing the density functional theory (DFT), the electronic band structures are calculated using Quantum Espresso package [1]. Generalized Gradient Approximation (GGA) [2] using Optimized Norm-Conserving Vanderbilt (ONCV) [3] pseudopotentials in our calculations treats the exchange and correlation (XC) functional. The lattice structures of Si 6H-SiC and Si 4H-SiC are first relaxed, in which the energy cutoff is set to be 80 Ry and the converging threshold for energy and atomic forces are set to be $10^{-12}$ eV and 0.0001 eV/Å, respectively. The $k$ points in the Brillouin zone are sampled with $10 \times 10 \times 3$ for both Si 6H-SiC and Si 4H-SiC.

The electronic band structures of Si 6H-SiC and 4H-SiC along some high symmetry lines in the Brillouin zone are shown in Figs. S3(a) and S3(b), respectively. The highest occupied state of the valence band is at the $\Gamma$-point, and the conduction band minimum is at the $M$-point. The calculated band gaps agree well with our absorption spectral measurements.
Fig. S3. Band structures of (a) 6H-SiC and (b) 4H-SiC.
3. NONLINEAR REFRACTION

Figs. S4 (SI 6H-SiC) and S5 (SI 4H-SiC) show the differences of fitting for nonlinear refraction by 2, 10 and 20 terms. Fitting by 2 and 10 terms shows obvious difference while fitting by 10 and 20 items are well consistent with each other. Therefore, we choose the fitting by 10 terms for the final results to guarantee convergence.

![Fig. S4. Nonlinear refractive index coefficient for SI 6H-SiC by (a) 2 terms, (b) 10 terms, and (c) 20 terms.](image-url)
Fig. S5. Nonlinear refractive index coefficient for SI 4H-SiC by (a) 2 terms, (b) 10 terms, and (c) 20 terms.
4. CROSS SECTIONS OF 2PA AND 3PA

The expressions of transition rate are given by [4, 5]

\[ R_{2PA} = \frac{\beta I^2}{2h\nu} = \frac{\sigma_{2PA} I}{h\nu} N = \frac{\sigma_2^2 I^2}{h\nu} N \]  
\[ R_{3PA} = \frac{\gamma I^3}{3h\nu} = \frac{\sigma_{3PA} I}{h\nu} N = \frac{\sigma_3^3 I^3}{h\nu} N \]  

(S1)  
(S2)

where \( \sigma_{2PA} \) is cross section of two-photon absorption (2PA), \( \sigma_{3PA} \) is cross section of three-photon absorption (3PA), \( \beta \) is 2PA coefficient, \( \gamma \) is 3PA coefficient, \( I \) indicates the laser intensity, \( N \) is the number density of absorbing species, \( h\nu \) is the photon energy and \( \sigma_2, \sigma_3 \) are cross section coefficients of 2PA and 3PA, respectively. Cross sections can be calculated by Eqs. S1 and S2.

Conventionally, absorption cross section is used to describe absorption capability of an individual absorbing unit, such as one dye molecule or one quantum dot. Such absorbing units are usually dispersed into solution or matrix for absorption coefficient measurement, and the obtained absorption coefficient should be converted into cross section of a single absorbing unit. However, semiconductors like SiC are in solid state condensed phase, which are different from dye molecules or quantum dots, so generally absorption coefficient is used to characterize such materials instead of cross section. We believe that cross section can be defined for semiconductors by replacing the number density of molecules \( N \) with population density of electrons, \( N_0 \) which can be expressed as

\[ N_0 = \frac{20 \cdot N_A}{M/\rho} = 9.49 \times 10^{23} \text{cm}^{-3} \]  

(S3)

where \( N_A \) is the Avogadro constant, \( M \) is the molar mass, \( \rho \) is the density and “20” represents the number of electrons in SiC (Si-14, C-6). This is because electrons in semiconductors are the absorbing units. With our measured nonlinear absorption coefficients, the cross section or the cross section coefficient of SiC can be calculated based on Eqs. S1 and S2 if needed.

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