Ab-initio calculations of the photoelastic constants of the cubic SiC polytype

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Abstract: Residual defects after growth of semiconductors crystals is a hot issue to be solved for manufacturing new efficient electronic or optic devices. These defects can be conveniently observed using birefringence optical microscopy for extended defects that will create a local strain field which in turn can cause a nominally isotropic optical material to become anisotropic and induce birefringence. In order to perform a quantitative analysis, the knowledge of the photoelastic constants (P_{ij}) of the material that measure the strength of the change of the refractive index under application of strains or stresses is necessary. As an experimental determination of the whole set of constants is not always possible, a theoretical evaluation can be of valuable interest. In this work, we propose *ab-initio* calculations by the WIEN2k program of the optical properties of the zinc blende silicon carbide polytype with a self-consistent scheme by solving the Kohn-Sham equations using a full potential linearized augmented plane waves (FPLAPW) method in the framework of the density functional theory (DFT) along with the generalized gradient approximation (GGA) pseudo-potentials. A combination of specific compressive and tensile strains is applied to the two atoms unit cell and the tensor containing each specific combination of the P_{ij} constants is extracted.

1. Introduction

People pay more attention to SiC because of its great technological importance for high temperature, high power, high critical breakdown field and high frequency applications in microelectronic and photoelectronic devices [1]. Elaboration is principally done via the seeded physical vapor transport (PVT) technique [2, 3] on silicon substrate or 3C-SiC platelets. Many extended defects can appear during the growth of the crystals such as dislocations [4-8] that constitute a major issue that hampers the development of electronic-grade semiconductors also for diamond [9], which should bring an undisputable advantage over their GaN or SiC counterparts. In case of LaBr$_3$ that is a viable scintillator for gamma ray, the knowledge of the dislocations [10] that can appear in this material during the elaboration process is essential in order to minimize the fracture during the growth and increase further its size. These defects can be conveniently observed using birefringence optical microscopy [4-8] for extended defects such as dislocations that will create a local strain field which in turn can cause a nominally isotropic optical material to become anisotropic and induce birefringence

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in light passing between cross-polarizers. In order to perform a quantitative analysis, the knowledge of the photoelastic constants (P_{ij}) of the material that measure the strength of the change of the refractive index under application of strains is necessary. Experimental determination of the (P_{ij}) constants is possible for large enough transparent anisotropic crystals, as for example, silicon [11], diamond [12], ZnTe [13] and ZnO [14], by the Brillouin light scattering technique [15], and other acousto-optical method as demonstrated for silicon, diamond, germanium and gallium-arsenide crystals [16-18].

It is also very important to know the optical properties of SiC due to their contributions to the photoelectronic device design and as fundamental inputs for radiative transfer models of astrophysical dust environments [19]. It is also useful for electron energy loss spectroscopy (EELS) analysis that can be used to image the dislocations as it was done for diamond [20]. However, the theoretical studies on the optical properties of zinc blende SiC are scarce up to now [21-24] in comparison to experimental works [25-28], and photoelastic data are still not available in the literature.

In this paper, we report a first-principle predictive calculation of the optical and photoelastic properties of β–SiC by using the FPLAPW method based on density functional theory. Firstly, calculations are performed for silicon (Si) and diamond (C), those are compared to the available experimental and theoretical results.

2. Calculation method

The calculation of the optical properties of silicon, carbon and silicon carbide in zinc blende structure, were carried out with a self-consistent scheme by solving the Kohn-Sham equation using a full potential linearized augmented plane waves (FPLAPW) method in the framework of the DFT along with the GGA method [29] as implemented in WIEN2k package [30, 31]. In the calculations, $R_{MT}K_{max}=7$ is used, which determines the matrix size, where K_{max} is the plane wave cut-off and R_{MT} is the smallest of all atomic sphere radii. Since calculations of the optical properties require denser k-space matrix, we used 28000 k-points in whole Brillouin zone. We chose the muffin–tin radii of 1.4, 2.1 Bohr for C and Si, respectively. We used the experimental values of the lattice parameters $a_0 = 0.356685$ nm [32], 0.5429 nm [33], 0.43596 nm [34] for C, Si and β-SiC, respectively.

The dielectric function of a solid is usually described in terms of complex $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, the imaginary part of the dielectric function $\varepsilon_2(\omega)$ being obtained directly from the band structure calculation. The real part of the dielectric function $\varepsilon_1(\omega)$ can be derived from the imaginary part $\varepsilon_2(\omega)$ by using *Kramers–Kronig* dispersion relationship. When a strain is applied to a crystal there is a corresponding change in the refractive index, arising from a change in the dielectric function. The photoelastic tensor (P_{ij}) relates the change of the inverse dielectric function with the applied strain. The presence of a dislocation or of an extended defect in a crystal causes a local strain field which in turn can lead a nominally isotropic material to become anisotropic and induce birefringence in light passing through cross-polarizers [4]. The accidental birefringence due to dislocations in silicon has been observed [35] and modelled theoretically [36]. However, these calculations require the photoelastic tensor which is not well known in diamond [12, 37-39], compared to silicon [18] or even unknown in the case of the β-SiC polytype.

The change in the inverse dielectric function due to strain is given by equation (1):

$$\delta(\varepsilon^{-1})_{ij} = P_{ijkl}\mu_{kl} \approx -\frac{1}{\varepsilon_b^2}\delta\varepsilon_{ij} \qquad (1)$$

where P_{ijkl} is the fourth rank Pockels photoelastic tensor, μ_{kl} is the strain tensor and ε_b is the value of the dielectric function in the unstrained material. Adopting a contracted notation where $11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3$ and $23, 32 \rightarrow 4$, P_{ijkl} reduces to a symmetric matrix with three non-zero elements for cubic structures:

$$P = \begin{pmatrix} P_{11} & P_{12} & P_{12} & 0 & 0 & 0 \\ P_{12} & P_{11} & P_{12} & 0 & 0 & 0 \\ P_{12} & P_{12} & P_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & P_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & P_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & P_{44} \end{pmatrix} \tag{2}$$

To determine the P_{11}, P_{12} and P_{44}, we calculate the change in the dielectric function for three different strains $[\mu]$:

1) Hydrostatic strain $[\mu] = \left(\frac{\delta a}{a_0}, \frac{\delta a}{a_0}, \frac{\delta a}{a_0}, 0,0,0 \right)^T$

$$\frac{-\delta\varepsilon_{ij}}{(\varepsilon_b^2)} = \left(\frac{\delta a}{a_0} \right) \begin{pmatrix} P_{11} + 2P_{12} & 0 & 0 \\ 0 & P_{11} + 2P_{12} & 0 \\ 0 & 0 & P_{11} + 2P_{12} \end{pmatrix} \tag{3}$$

where a_0 is the lattice constant and $\delta a / a_0$ is the relative strain. The $P_{11} + 2P_{12}$ can be obtained from the difference between strained and unstrained dielectric constant.

2) Strain along the [001] direction $[\mu] = \left(0,0, \frac{\delta a}{a_0}, 0,0,0 \right)^T$

$$\frac{-\delta\varepsilon_{ij}}{(\varepsilon_b^2)} = \left(\frac{\delta a}{a_0} \right) \begin{pmatrix} P_{12} & 0 & 0 \\ 0 & P_{12} & 0 \\ 0 & 0 & P_{11} \end{pmatrix} \tag{4}$$

3) The P_{44} can be determined by changing the length $\frac{\delta l}{l}$ in the [111] direction by applying the strain

$[\mu] = \frac{1}{3}\frac{\delta l}{l}(1,1,1,2,2,2)^T$

$$\frac{-\delta\varepsilon_{ij}}{(\varepsilon_b^2)} = \frac{1}{3}\left(\frac{\delta l}{l} \right) \begin{pmatrix} P_{11} + 2P_{12} & 2P_{44} & 2P_{44} \\ 2P_{44} & P_{11} + 2P_{12} & 2P_{44} \\ 2P_{44} & 2P_{44} & P_{11} + 2P_{12} \end{pmatrix} \tag{5}$$

The unit cells with two atoms are taken and the lattice vectors changed to apply strain in the [001] and [111] directions, and hydrostatically. The values of strain applied do not exceed ±0.4 % and the considered energy is below the first gap, typically below 3 eV. The values of P_{11}, P_{12} and P_{44} are found for an average of these compressive and tensile strains. In the case of strain in the [111] direction, we consider both results from relaxed and un-relaxed unit cell. The relaxed positions of the two atoms along this direction are obtained by minimization of the forces that act on them, for no symmetry arguments can fix them.

3. Results and discussion

3.1. Permittivity function
Figure 1a shows the real and imaginary parts of the calculated dielectric function of silicon (Si). These results compare well to the experimental data from Biegelsen *et al*. [18] and the previous *ab-initio* studies [40, 41] on the dielectric response of silicon, those are partially reported in the table 1. The direct band gap is found to be ~ 2.76 that underestimates the experimental value ~3.45 eV [42]. For theoretical DFT calculations, the use of a rigid shift to compensate for the LDA underestimation of the band gap affects all levels above the valence band top, to the same extent. It was used with some success by Levine *et al*. [40] and Hounsome *et al*. [41], and is often referred to as a 'scissors shift'. The scissors shift becomes important for defective crystals where states are introduced into the band gap and lead to additional optical transitions. In the work of Hounsome *et al*. [41] a shift of 0.52 eV

was used to correct the silicon band gap calculated with the AIMPRO program. Nevertheless, it has been shown that the scissors shift technique of correcting the LDA underestimation of the band gap for one material does not in the same time, uniformly improve the calculated photoelastic constants that will be discussed in the next section. Hence, we will not try to use this technique in this work despite improvement of the DFT+LDA that is called generalized density functional theory (GDFT) [22] and provides appropriate corrections to the energy of conduction bands, to investigate the band structure of semiconductors or insulators, and thus obtains band gaps that are in agreement with experimental results.
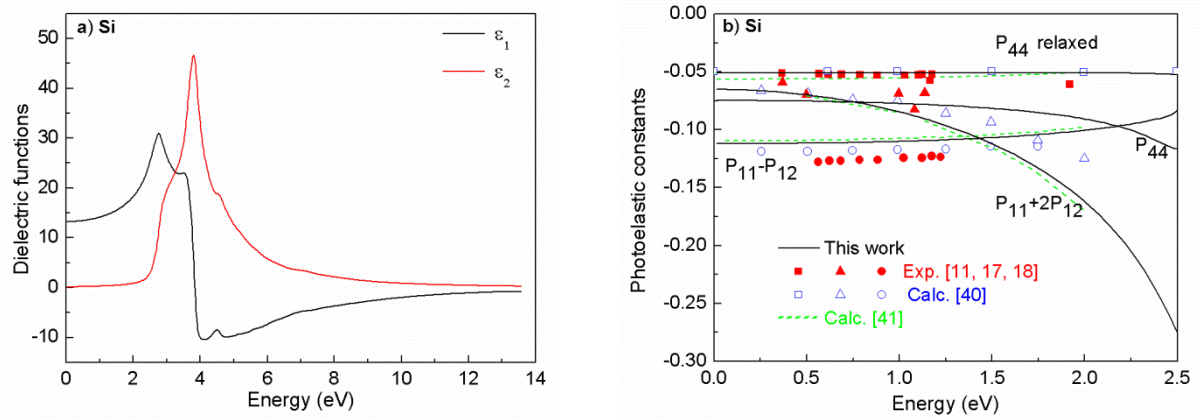

Figure 1. (a) Calculated dielectric function for silicon: real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$. (b) Calculated photoelastic constants for silicon compared to experimental data from [11, 17, 18] and calculated data from [40, 41].

Figure 2a shows the real and imaginary parts of the dielectric function of diamond (C) that compare well to the experimental [43, 44] and theoretical [41, 45] data. Some results are partially reported in the table 1 and compared to available data. In ref. [43], the experimental spectrum for ε_2 shows a threshold around the direct band gap at ~7 eV and a broad peak at ~12 eV due to band-band transitions. It then falls slowly with increasing energy. The theoretical curve displays a threshold at ~5.5 eV, and a peak around ~11.5 eV, which are downshifted from the experimental values due to the underestimation of the gap. In contrast with other semiconductors, diamond does not exhibit additional sharp peaks in this region, due to its band structure. Note that in the long wavelength limit, the calculated value of the real part of the dielectric function $\varepsilon_1 = 5.77$ agree well with the experimental value of the static dielectric function 5.82 [43] and other theoretical ones 5.89 [41] and 5.86 [45]. The experimental peak at 7 eV [43] appears much sharper than the calculated one due to the neglect of excitonic effects in our calculations. However the energy where $\varepsilon_1 = 0$ is in good agreement and corresponds to maximum absorption of light.
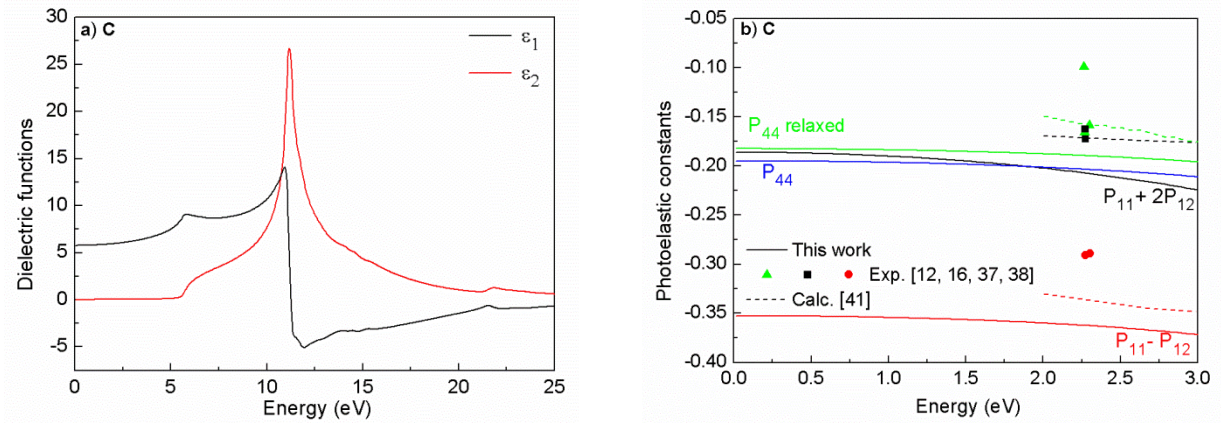
Figure 2. (a) Calculated dielectric function for diamond: real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$. (b) Calculated photoelastic constants for diamond compared to experimental data from [12, 16, 37, 38] and calculated data from [41].

Figure 3a shows the real and imaginary parts of the dielectric function of zinc blende silicon carbide (SiC) that compare well to the experimental [25-28] and theoretical [21-24] data. Some results are partially reported in the table 1 and compared to available data. In refs. [26, 28], the experimental spectrum for ε_2 shows a threshold around the direct band gap at ~5 eV and one broad peak at ~7.2 eV due to band-band transitions. It then falls slowly with increasing energy. The theoretical ε_2 curve displays a threshold at ~5 eV, one peak at ~7 eV which are not downshifted from the experimental values as surprisingly noticed by Logothetidis *et al*. [26] and a shoulder at 8 eV,. Note that in the long wavelength limit, the calculated value of the real part of the dielectric function $\varepsilon_1 = 7.05$ agree well with the experimental value of the static dielectric function of 7.29 [25, 26] and other theoretical ones 7.1 [22], 5.03 [24] and 6.95 [45]. The energy ~7.5 eV where $\varepsilon_1 = 0$ is also in good agreement.
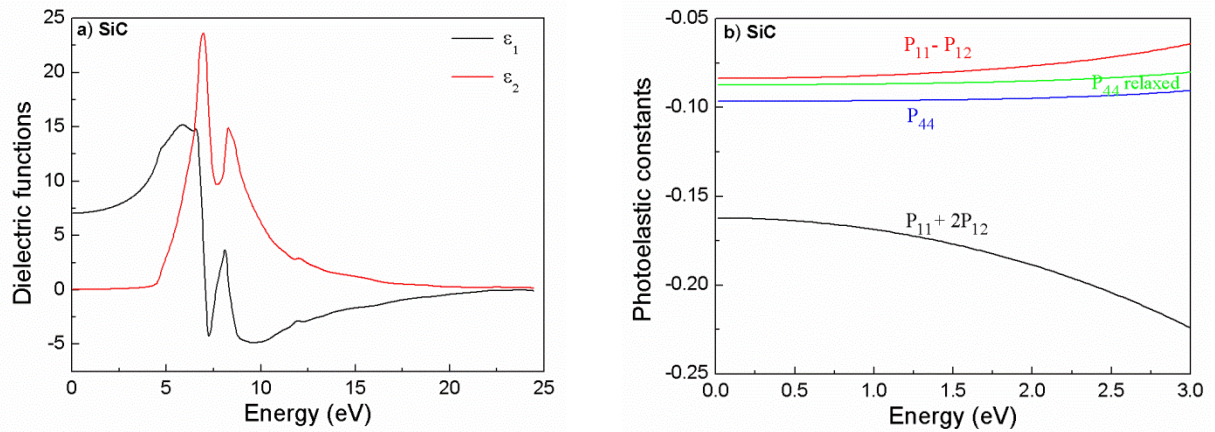

Figure 3. (a) Calculated dielectric function for zinc blende silicon carbide: real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$. (b) Calculated photoelastic constants for zinc blende silicon carbide.

Table 1. Permittivity (ε_b) and photoelastic constant (P_{ij}) for silicon, diamond and zinc blende silicon carbide. Experimental and previous *ab-initio* work is shown for comparison. All values for silicon refer to a wavelength of 3542 nm (0.35 eV), for diamond (2.27 eV) and for β-SiC (0.35, 2.27 and 3 eV).

Material	ε_b	P_{44}	$P_{11}+2P_{12}$	$P_{11}-P_{12}$	Ref.
Silicon					
(Si)					
0.35 eV	13.33	-0.051	-0.067	-0.112	Wien2k (this work)
0.35 eV	13.67	-0.051	-0.058	-0.109	AIMPRO [41]
0.35 eV	13.2	-0.046	-0.085	-0.105	DFT+LDA [40]
0.35 eV	11.83	-0.051	-0.054	-0.112	Exp. [18]
Diamond					
(C)					
2.27 eV	6.01	-0.189	-0.207	-0.362	Wien2k (this work)
2.27 eV	6.17	-0.171	-0.160	-0.335	AIMPRO [41]
2.27 eV	5.819	-0.172	-0.164	-0.292	Exp. [12, 39, 43, 44]
2.3 eV	-	-0.172	-0.160	-0.292	Exp. [38]
Silicon carbide					
(β-SiC)					
0.35 eV	7.06	-0.087	-0.163	-0.083	Wien2k (this work)
2.27 eV	7.71	-0.084	-0.196	-0.074	Wien2k (this work)
3 eV	8.34	-0.080	-0.224	-0.063	Wien2k (this work)
3 eV	7.29				Exp. [25, 26]

3.2. Photoelastic constants
Initially, values of P_{11}, P_{12} and P_{44} are calculated for silicon and diamond for these properties are unknown for the zinc blende polytype of SiC (β-SiC). These should demonstrate the reliability of the methodology, as the photoelastic constants for silicon are more studied [11, 17, 18, 40, 41] and in a less extent those of diamond [12, 38, 39, 41, 43, 44]. Previous *ab-initio* studies on the dielectric response of silicon and diamond [40, 41] have reviewed the available experimental data. The photoelastic constants are found using the calculated values of ε_b for various strains and considering an averaged combination of tensile and compressive strain for accuracy.

Figure 1b shows the variation of the calculated photoelastic constants with frequency for silicon. No scissors shift is applied, as described above. Comparisons with experimental values [11, 17, 18] and previous *ab-initio* calculations [40, 41] are shown. Some results are partially reported in the table 1 and compared to available data. The values of $P_{11} - P_{12}$ are slightly larger than experiment by about 3% but the slow dispersion with frequency is in good agreement. Excellent agreement is achieved for P_{44}. The calculated values for $P_{11} + 2P_{12}$ are in good agreement with experiment until ~ 1 eV but disperse quite strongly with increasing frequency. The calculated constants for silicon display on overall agreement with the results of Hounsome *et al.* [41] and relatively little dispersion except for the calculated values of $P_{11} + 2P_{12}$. As stated above, this is due to the lowering of band gap and can be reduced if a shift is used [41] or if excitonic effects are taken into account [22]. One should also notice that calculations of this constant are very sensitive to the value of the lattice parameter used as input [40].

The values of the photoelastic constants for diamond in the literature differ widely and have been reviewed recently [39], where there is very little information on the variation of the constants with frequency. Grimsditch *et al*. [12] evaluate one set of results as being "most reliable", these results are from [38]. In figure 2b, it is evident that P_{11} - P_{12} and P_{11} + $2P_{12}$ are underestimated by ~20-25 % whereas P_{44} is underestimated by ~10 %. Some results are partially reported in the table 1 and compared to available data. The calculated constants for diamond underestimate the results of Hounsome *et al*. [41] by ~10% and show relatively little dispersion. Further experiments are suitable to confirm this behavior.

Figure 3b shows the variation of the calculated predictive photoelastic constants with frequency for β-SiC. P_{11} - P_{12} and P_{44} have closed values (~-0.08) and increase slowly with frequency. P_{11} + $2P_{12}$ is decreasing rapidly as in the case of silicon with values in the same range as for diamond [-0.15, -0.25] for energy below 3 eV.

4. Summary and conclusion

The dielectric function and photoelastic constants for silicon, diamond and β-SiC have been calculated for a large energy range using density functional theory applied to strained unit cells. Experimental [18] and other theoretical [40, 41] data for silicon are accurately reproduced with absolute values and variation with frequency matched for all the constants. Experimental data for diamond is still limited to a very few number of frequencies and recently re-discussed by Lang *et al*. [39]. One particular experimental set [16] has previously been regarded as "most reliable" [12, 38]. However, our calculated values underestimate this particular result from ~10 % for P_{44} and ~25 % for P_{11} - P_{12} and P_{11} + $2P_{12}$.

The agreement for silicon [18, 40, 41] and diamond [12, 16] gives confidence that the β-SiC theoretical photoelastic values should reasonably predict experimental results, unfortunately not yet available. Undoubtedly, synthesis of larger crystal size will motivate this work. Satisfactory agreement is found between our theoretical value of the dielectric function with the experimental ones [26, 28].

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