

03,09,13

Dielectric and optical properties of the cubic SiC, GeC and SnC monocrystals: Model estimations

© S.Yu. Davydov, A.A. Lebedev

Ioffe Institute,
St. Petersburg, Russia
Email: Sergei.Davydov@mail.ru

Received August 25, 2021

Revised August 25, 2021

Accepted September 26, 2021

Within the scope of the Harrison's bond orbital model analytical expressions of the high- and low-frequency dielectric susceptibilities and dielectric constants, linear electrooptical coefficient, photoelastic constants and pressure dependences of the dielectric constants are obtained for the cubic carbides of the group IV elements.

Keywords: dielectric susceptibility, dielectric constants, electrooptical coefficient, photoelastic constant.

DOI: 10.21883/PSS.2022.01.52490.193

1. Introduction

Interest in properties of silicon carbide monocrystals, actively studied for a long time [1], is still noticeable. Suffice it to say that biennial international and European conferences on silicon carbide and cognate materials (ICSCRM and ECSCRM) are held. Recently there is increasing attention to the cubical polytype of 3C-SiC, which has the maximum (among SiC polytypes) electron mobility of $1200 \text{ cm}^2/\text{V} \cdot \text{s}$ [2], which does not depend on crystallographic direction.

The issue of possible existence of GeC and SnC monocrystals and their properties has arisen relatively recently [3–8]. The relevant theoretical studies (first-principles calculations) paid the main attention to stability of certain crystalline structures, band spectrum and resilience. This paper considers, from a unified viewpoint, the dielectric and optical properties of cubic carbides XC , where $X = \text{Si, Ge, Sn}$. Thereat, we use a model of Harrison's binding orbitals [9–11], well-proven in the description of tetrahedral semiconductors.

2. Dielectric properties of carbides

Having defined the linear $\chi^{(1)}$ and quadratic $\chi^{(2)}$ dielectric susceptibilities as coefficients of crystal polarization expansion \mathbf{P} according to electric field intensity \mathbf{E} , i.e. in the form

$$P_i = \sum_j \chi_{ij}^{(1)} E_j + \sum_{jk} \chi_{ijk}^{(2)} E_j E_k + \dots,$$

it can be showed [12,13] that contributions of the electron subsystem to these characteristics are equal

$$\chi_1^{\text{el}} = \frac{n_e(e\gamma d)^2 \alpha_c^3}{12V_2}, \quad \chi_{14}^{\text{el}} = \frac{\sqrt{3}n_e(e\gamma d)^3 \alpha_c^4 \alpha_p}{48V_2^2}, \quad (1)$$

while ionic (lattice) contributions are as follows

$$\chi_1^{\text{ion}} = \frac{n_e(e\gamma d)^2 \alpha_p^2 (1 + 2\alpha_c^2)}{24\alpha_c V_2},$$

$$\chi_{14}^{\text{ion}} = \frac{\sqrt{3}n_e(e\gamma d)^3 \alpha_c^2 \alpha_p (1 - 2\alpha_c^2)}{48V_2^2}. \quad (2)$$

The following expressions are obtained for total (low-frequency) values of linear and square susceptibilities:

$$\chi_1 = \chi_1^{\text{el}}(1 + \vartheta), \quad \vartheta = \frac{\alpha_p^2(1 + 2\alpha_c^2)}{2\alpha_c^4},$$

$$\chi_{14} = \frac{\sqrt{3}n_e(e\gamma d)^3 \alpha_c^2 \alpha_p}{48V_2^2}. \quad (3)$$

Here, $V_2 = 3.22(\hbar^2/md^2)$ is the covalent energy of the σ -bond of sp^3 -orbitals for A and B atoms, where \hbar is the reduced Plank's constant, m is the free electron mass, $d = a\sqrt{3}/4$ is the distance between the nearest neighbors in the sphalerite structure with lattice constant a . As distinct from [12,13], we set $V_2 > 0$; $\alpha_c = V_2/\sqrt{V_2^2 + V_3^2}$ and $\alpha_p = \sqrt{1 - \alpha_c^2}$ are covalency and polarity of the bond, respectively; $V_3 = |\epsilon_h^A - \epsilon_h^B|/2$ is the polar energy of bond, where $\epsilon_h^{A(B)} = (\epsilon_s^{A(B)} + 3\epsilon_p^{A(B)})/4$ is the energy of sp^3 -orbitals and $\epsilon_{s(p)}^{A(B)}$ is the energy of the $s(p)$ -state of the $A(B)$ atom; $n_e = 32/a^3$ is the electron density, e is the electron charge, γ is the scaling factor taking into account the corrections for local field and used as an adjustable parameter [9,12,13]. For high-frequency ϵ_∞ and static ϵ_0 of dielectric susceptibilities, we have the following

$$\epsilon_\infty = 1 + 4\pi\chi_1^{\text{el}}, \quad \epsilon_0 = 1 + 4\pi\chi_1. \quad (4)$$

By setting $a = 4.36, 4.59$ and 5.11 \AA respectively for SiC, GeC and SnC [3], we obtain the values of the model's initial

Table 1. Initial parameters: distance between the nearest neighbors d , covalent V_2 and polar V_3 energies, covalency α_c and polarity α_p of the bond $X-C$. The upper row of values is the calculation as per Mann tables [11], the lower row is the calculation as per Hermann–Skillman tables [9]

Crystal	SiC	GeC	SnC
d , Å	1.89	1.99	2.21
V_2 , eV	6.87	6.20	5.02
V_3 , eV	1.88	1.93	2.41
	1.42	1.37	1.77
α_c	0.96	0.95	0.90
	0.98	0.98	0.94
α_p	0.26	0.30	0.44
	0.20	0.22	0.33

Table 2. Values of linear χ_1^{el} , χ_1 and square χ_{14}^{el} , χ_{14} susceptibilities, ε_∞ , ϑ , ε_0 . The upper row of values is the calculation as per Mann tables [11], the lower row is the calculation as per Hermann–Skillman tables [9]

Crystal	SiC	GeC	SnC
χ_1^{el}	0.43	0.44	0.42
	0.46	0.49	0.48
χ_1	0.48	0.51	0.58
	0.49	0.53	0.57
ε_∞	6.46	6.57	6.28
	6.81	7.11	7.00
ϑ	0.11	0.15	0.39
	0.06	0.08	0.19
ε_0	7.00	7.39	8.29
	7.13	7.63	8.18
χ_{14}^{el}	1.86	2.54	4.59
	1.60	2.12	4.08
χ_{14}	0.14	0.25	1.10
	0.07	0.10	0.50

parameters given in Table 1. The scaling multiplier γ can be assessed as per the experimental data $\varepsilon_\infty = 6.52$ and $\varepsilon_0 = 9.72$ for 3C–SiC [14]. By choosing ε_∞ for fitting, we obtain the value $\gamma = 1.44$, which will be used for all the carbides under consideration.

3. Numerical estimates of dielectric susceptibilities

To proceed with analysis, the expressions for χ_1^{el} and χ_{14} should be rewritten as $\chi_1^{\text{el}} \approx 0.26(d\alpha_c^3)$ and $\chi_{14} \approx 0.67(d^4\alpha_c^2\alpha_p^3) \cdot 10^{-12}$ m/V, where d is measured in Å.

The calculation results are given in Table 2. Table 2 shows that the values of χ_1^{el} , χ_1 and ε_∞ for various XC are close. The closeness is due to the fact that decrease of covalency α_c in the row SiC \rightarrow SnC is compensated by increase of d . Increase of ε_0 in the same row is related to increase of the multiplier ϑ . It should be noted that the obtained values of ε_0 are apparently underestimated. In any case, the situation is such for 3C–SiC.

The smallness of square susceptibilities χ_{14}^{el} and χ_{14} of the compounds X_C as compared to semiconductors A_3B_5 and A_2B_6 (see, for instance, Table 5.1 in [9]) is explained by the low polarity of bonds α_p . Increase of χ_{14}^{el} and χ_{14} upon a transition from SiC to SnC is related to an increase both of α_p and of d . The largest values of χ_{14}^{el} and χ_{14} correspond to 3C–SnC. It is easily shown that the maximum value of χ_{14}^{el} occurs with $\alpha_c^* = \sqrt{4/5}$ and $\alpha_p^* = \sqrt{1/5}$, practically coinciding with the covalency and polarity of Sn–C bond.

It must be noted that this paper ignores the metalli-city of interatomic bonds [9,10], consideration of which, generally speaking, can considerably affect the calculation results [11,12].

4. Optical properties

Linear electrooptical coefficients r_{41} and r_{41}^{el} , which respectively describe the change in the refraction index $n = \sqrt{\varepsilon_\infty}$ of noncentrosymmetric crystals in a low-frequency electric field and electron contribution to r_{41} are determined according to [11,12], as

$$r_{41} = -4\pi\chi_{14}/n^4, \quad r_{41}^{\text{el}} = -4\pi\chi_{41}^{\text{el}}/n^4. \quad (5)$$

The calculation results are given in Table 3. It is easy to understand that the character of change in the coefficients r_{41}^{el} and r_{41} in the carbide row is determined by square susceptibilities χ_{14}^{el} and χ_{14} . The obtained values of $|r_{41}^{\text{el}}|$ and $|r_{41}|$ are small as compared to other materials (see, for instance, Table 77.2 in [15]), which is related to the small polarity of $X-C$ bonds.

According to [16], photoelastic constants p_{ij} ($i = 1, 4$; $j = 1, 2, 4$) for cubic tetrahedral crystals are as follows

$$p_{11} = \xi \left(1 + \frac{8\lambda}{8 + \lambda} \right), \quad p_{12} = \xi \left(1 - \frac{4\lambda}{8 + \lambda} \right),$$

$$p_{44} = \frac{99\xi\lambda}{(8 + \lambda)(8 + 3\lambda)}, \quad (6)$$

where $\xi = -2\eta(\varepsilon_\infty - 1)/3\varepsilon_\infty^2$, $\eta = 2(1 - 3\alpha_p^2)$, $\lambda = 0.85$. The results of calculation of p_{ij} given in Table 3 are close to diamond photoelastic constants $p_{11} = -0.31$, $p_{12} = -0.09$ and $p_{44} = -0.12$ (see Table 77.1 in [15]). The minor decrease in the values of $|p_{ij}|$ in the SiC \rightarrow SnC rows is due to the increasing bond polarity.

Table 3. Values of linear electrooptical coefficients r_{14}^{el} , r_{41} , elasto-optical constants p_{ij} $i = 1, 4; j = 1, 2, 4$, compression bulk moduli B and derivative dielectric susceptibilities according to pressure $\partial\varepsilon_{\infty}/\partial P$ and $\partial\varepsilon_0/\partial P$. The upper row of values is the calculation as per Mann tables [11], the lower row is the calculation as per Hermann–Skillman tables [9]

Crystal	SiC	GeC	SnC
$-r_{14}^{\text{el}}, 10^{-12} \text{ m/V}$	0.55 0.40	0.74 0.53	1.46 1.05
$-r_{41}, 10^{-12} \text{ m/V}$	0.04 0.02	0.07 0.02	0.35 0.13
$-p_{11}$	0.25 0.26	0.22 0.24	0.14 0.19
$-p_{12}$	0.08 0.08	0.07 0.08	0.04 0.06
$-p_{44}$	0.13 0.13	0.11 0.12	0.07 0.10
$B, \text{ GPa}$	166 177	124 137	64 72
$-\partial\varepsilon_{\infty}/\partial P, 10^{-2} \text{ GPa}^{-1}$	1.74 1.93	2.19 2.55	2.13 3.75
$-\partial\varepsilon_0/\partial P, 10^{-2} \text{ GPa}^{-1}$	2.43 2.49	3.46 3.19	7.13 6.71
$-(\partial\varepsilon_{\infty}/\partial P)/B$	2.89 3.41	2.71 3.48	1.36 2.70
$-(\partial\varepsilon_0/\partial P)/B$	4.03 4.41	4.29 4.37	4.56 4.83

5. Dependence of dielectric susceptibilities ε_{∞} and ε_0 on pressure P

The paper [17] has shown that

$$\frac{\partial\varepsilon_{\infty}}{\partial P} = -\eta \frac{\varepsilon_{\infty} - 1}{3B}, \quad \frac{\partial\varepsilon_0}{\partial P} = (\varepsilon_{\infty} - 1) \frac{\partial\vartheta}{\partial P} + (1 + \vartheta) \frac{\partial\varepsilon_{\infty}}{\partial P},$$

$$\frac{\partial\vartheta}{\partial P} = -\frac{2\alpha_p^2}{\alpha_c^2 B} \left(1 - \frac{2\alpha_p^2}{3\alpha_c^2} \right), \quad (7)$$

where B is the compression bulk modulus. In the model of Harrison's bonding orbitals $B = 2\alpha_c^3 V_2 / \sqrt{3} d^3$ [9]. The calculation results are given in Table 3. It should be emphasized that the values of $|\partial\varepsilon_{\infty}/\partial P|$ and $|\partial\varepsilon_0/\partial P|$ given in Table 3 are the maximum estimates, since the used calculation variant (exclusive of short-range repulsion [18]) underestimates the value of compression bulk modulus. In fact, for 3C–SiC according to the data of Table 4.6 from [19] we have $B = 246 \text{ GPa}$, which is ~ 1.5 times greater than our result. Therefore, Table 3 also includes the results of calculation of dimensionless derivatives $(\partial\varepsilon_{\infty}/\partial P)B$ and $(\partial\varepsilon_0/\partial P)B$, which allow for determining the values of

$\partial\varepsilon_{\infty}/\partial P$ and $\partial\varepsilon_0/\partial P$ on the basis of known (from an experiment or first-principles calculations) values of the compression bulk modulus.

In conclusion of this section we would like to note that the following interrelation is present within the Harrison's model framework

$$\frac{\varepsilon_{\infty} - 1}{\varepsilon_0 + 1} = 1 + \vartheta. \quad (8)$$

Using the Lyddane–Sachs–Teller formula $\omega_{\text{TO}}^2(0)/\omega_{\text{LO}}^2(0) = \varepsilon_{\infty}/\varepsilon_0$ [19], where $\omega_{\text{TO}}^2(0)$ and $\omega_{\text{LO}}^2(0)$ are frequencies of transverse and longitudinal optical phonons in the Brillouin band center, we get [16]:

$$\frac{\partial\omega_{\text{TO}}(0)}{\partial P} = \frac{\omega_{\text{TO}}(0)}{3B} (2 + 3\alpha_p^2),$$

$$\frac{\partial\omega_{\text{LO}}(0)}{\partial P} = \frac{\omega_{\text{LO}}(0)}{2\sqrt{\varepsilon_{\infty}\varepsilon_0}} \left(\frac{\partial\varepsilon_0}{\partial P} - \frac{\varepsilon_0}{\varepsilon_{\infty}} \frac{\partial\varepsilon_{\infty}}{\partial P} \right) + \sqrt{\frac{\varepsilon_0}{\varepsilon_{\infty}}} \frac{\partial\omega_{\text{TO}}(0)}{\partial P}. \quad (9)$$

Thus, with the help of the interrelations (7) and (9), dependencies of dielectric susceptibilities (optical frequencies) on pressure can be used to find the corresponding dependencies for optical frequencies (dielectric susceptibilities).

6. Conclusion

This paper describes, within the framework of a unified approach, the obtained values of a whole range of dielectric and optical characteristics of group IV cubic carbides. To the authors' knowledge, such estimates for GeC and SnC have not been made thus far. The simplicity of the model of Harrison's bonding orbitals made it possible to obtain analytical expressions for these characteristics. Thereat, the parameters of the model d and $\varepsilon_s(p)$, which represents a simplified variant of the LCAO method, are not adjustable parameters. It should be noted that not only the 3C–SiC crystals are of applied interest. Thus, these materials are used to create superlattices, e.g., GeC/SiC, SnC/SiC, SnC/GeC [21] and GeC/GaN [22].

Funding

A.A. Lebedev is grateful to RFBR for financial support (RFBR grant No. 20-0200117).

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] A.A. Lebedev, P.A. Ivanov, M.E. Levinstein, E.N. Mokhov, S.S. Nagalyuk, A.N. Anisimov, P.G. Baranov. *Physics-Uspekhi* **189**, 8, 803 (2019).
- [2] M.E. Levinshtein, S.L. Rumyantsev, M.S. Shur. *Properties of Advanced Semiconductor Materials: GaN, AlN, InN, BN, SiC, SiGe*. Wiley, N. Y. (2001).
- [3] R. Pandey, M. Rérat, M.C. Darrigan, M. Causá. *J. Appl. Phys.* **88**, 11, 6462 (2000).
- [4] A. Benzair, H. Aourag. *Phys. Status Solidi B* **231**, 2, 411 (2002).
- [5] W. Sekkal, A. Zaoui. *New J. Phys.* **4**, 1, 9 (2002).
- [6] A. Mahmood, L.E. Sansores. *J. Mater. Res.* **20**, 5, 1101 (2005).
- [7] A. Hao, X. Yang, X. Wang, Y. Zhu, X. Liu, R. Liu. *J. Appl. Phys.* **108**, 6, 063531 (2010).
- [8] R. Muthaiah, J. Garg. arXiv: 2107.04596
- [9] W.A. Harrison. *Electronic Structure and the Properties of Solids: The Physics*. Mir, M. (1983). V. 1.
- [10] W.A. Harrison. *Phys. Rev. B* **27**, 6, 3592 (1983).
- [11] W.A. Harrison. *Phys. Rev. B* **31**, 4, 2121 (1985).
- [12] S.Yu. Davydov, E.I. Leonov. *Physics of the Solid State* **30**, 5, 1326 (1988).
- [13] S.Yu. Davydov, S.K. Tikhonov. *Physics of the Solid State* **37**, 10, 3044 (1995).
- [14] V.I. Gavrilenko, A.M. Grekhov, D.V. Korbutyak, V.G. Litovchenko. *Opticheskie svoistva poluprovodnikov. Spravochnik. Nauk. dumka, Kiev* (1987) (in Russian).
- [15] Yu.I. Sirotin, M.P. Shaskolskaya. *Osnovy kristalofiziki. Nauka, M.* (1975) (in Russian).
- [16] S.Yu. Davydov, S.K. Tikhonov. *Semiconductors* **31**, 7, 823 (1997).
- [17] S.Yu. Davydov, S.K. Tikhonov. *Semiconductors* **32**, 9, 1057 (1998).
- [18] F. Bechstedt, W.A. Harrison. *Phys. Rev. B* **39**, 8, 5041 (1989).
- [19] S.P. Nikanorov, B.K. Kardashov. *Uprugost' i dislokatsionnaya neuprugost' kristallov. Nauka, M.* (1985) (in Russian).
- [20] Ch. Kittel. *Introduction to Solid State Physics. Nauka, M.* (1978).
- [21] Yu.M. Basalayev, E.N. Malysheva. *Semiconductors* **51**, 647 (2017).
- [22] P. Lou, J.Y. Lee. *ACS Appl. Mater. Interfaces* **12**, 12, 14289 (2020).