Electron and hole mobility of rutile GeO$_2$ from first principles: an ultrawide-band-gap semiconductor for power electronics

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Rutile germanium dioxide (r-GeO$_2$) is an ultrawide-band-gap semiconductor with potential applications in high-power electronic devices, for which the carrier mobility is an important material parameter that controls the device efficiency. We apply first-principles calculations based on density functional and density functional perturbation theories to investigate carrier-phonon coupling in r-GeO$_2$ and predict its phonon-limited electron and hole mobilities as a function of temperature and crystallographic orientation. The carrier mobilities at 300 K are $\mu_{\text{elec},\perp} = 154$ cm$^2$ V$^{-1}$ s$^{-1}$, $\mu_{\text{elec},\parallel} = 74$ cm$^2$ V$^{-1}$ s$^{-1}$, $\mu_{\text{hole},\perp} = 5$ cm$^2$ V$^{-1}$ s$^{-1}$, and $\mu_{\text{hole},\parallel} = 2$ cm$^2$ V$^{-1}$ s$^{-1}$. At room temperature, electron mobility is dominated by acoustic-phonon scattering. The predicted Baliga’s figure of merit of $n$-type r-GeO$_2$ surpasses several incumbent semiconductors such as Si, SiC, GaN, and $\beta$-Ga$_2$O$_3$, demonstrating its superior performance in high-power electronic devices.

Power electronics are important for the control and conversion of electricity, but inefficiencies cause energy loss during each step in the conversion process, resulting in a combined efficiency of $\sim$80% or less.$^1$ In the United States, the existing electricity grid is outdated for modern electricity usage and must be replaced with power-conversion electronics that are able to control the power flow more efficiently. Addressing inefficiencies to improve energy sustainability motivates the ongoing search for new materials for power-electronics devices. Ultrawide-band-gap semiconductors with gaps wider than GaN (3.4 eV) have been the focus of power-electronics materials research.$^2$ Important material parameters to consider for power-electronics applications include the possibility of doping (usually $n$-type, but ambipolar dopability is also desirable for heteropolar devices), high carrier mobility $\mu$ for fast switching
and efficient carrier transport, high thermal conductivity for efficient heat extraction, and a high critical dielectric breakdown field $E_C$ and dielectric constant $\varepsilon_0$ to enable high-voltage operation. The Baliga figure of merit BFOM $= \frac{1}{4} \varepsilon_0 \mu E_C^3$ quantifies the performance of a material in power-electronic devices.\textsuperscript{3,4} The BFOM depends most strongly on the breakdown field, which increases superlinearly with increasing band gap and motivates the search for ultrawide-gap dopable semiconductors.

The $\beta$ polymorph of gallium oxide ($\beta$-Ga$_2$O$_3$) has been the recent focus of attention thanks to the availability of native substrates and the $n$-type dopability with Si or Ge.\textsuperscript{2} While its electron mobility is lower than Si, SiC, or GaN, its ultrawide-band-gap of $\approx$4.5 eV produces a high breakdown field and a BFOM superior to these incumbent technologies.\textsuperscript{5–9} However, its low thermal conductivity that prevents heat extraction and the impossibility of $p$-type doping (due to the formation of self-trapped hole polarons\textsuperscript{10}) limit its applicability.\textsuperscript{10–12} To overcome these challenges and advance the frontier of power electronics, new ultrawide-band-gap semiconducting materials must be identified and characterized.

Recently, Chae \textit{et al.} found that rutile germanium dioxide (r-GeO$_2$) is a promising ambipolarly dopable semiconductor\textsuperscript{12} with an ultrawide band gap (4.68 eV). Donors such as Sb$_{\text{Ge}}$ and F$_{\text{O}}$ are shallow (activation energy $\approx$25 meV), while Al$_{\text{Ge}}$ and Ga$_{\text{Ge}}$ acceptors are deeper with ionization energies of $\approx$0.4–0.5 eV. However, high acceptor concentrations, through the co-incorporation with hydrogen and subsequent annealing, can exceed the Mott-transition limit and enable $p$-type conduction. Rutile GeO$_2$ displays similar chemical and structural properties as rutile SnO$_2$, an established $n$-type transparent conductor.\textsuperscript{14,15} However, the wider band gap of r-GeO$_2$ is promising for deep-ultraviolet (UV) luminescence and efficient power-electronics
applications. Yet, the carrier mobilities of r-GeO$_2$, and thus its viability and efficiency for power-electronics applications, remain unexplored.

In this work, we apply predictive atomistic calculations to determine the phonon-limited electron and hole mobilities of r-GeO$_2$ as a function of temperature and crystallographic orientation. We quantify the intrinsic phonon and carrier-phonon-coupling properties that impact carrier transport. Our results demonstrate that r-GeO$_2$ exhibits a superior BFOM than current semiconductor technologies such as Si, SiC, GaN, and $\beta$-Ga$_2$O$_3$ in power-electronics applications.

To accurately predict the carrier and phonon properties of r-GeO$_2$, we use first-principles calculations based on density functional (DFT) and density functional perturbation theories (DFPT) within Quantum ESPRESSO$^{18}$ and the Boltzmann transport equation (BTE) within EPW$^{19,20}$. In previous work,$^{17}$ we calculated the quasiparticle band structure of r-GeO$_2$ for the experimental lattice parameters$^{21}$ using the $G_0W_0$ method. For phonon calculations, the lattice parameters and atomic positions were relaxed to prevent imaginary phonon frequencies, resulting in lattice parameters of $a = 4.516$ Å and $c = 2.978$ Å that differ from experiment$^{21}$ by $+2.5\%$ and $+4.1\%$, respectively. The phonon dispersion, phonon frequencies at $\Gamma$, and sound velocities are included in Fig. S1 and Tables SI and SII in the Supplementary Information. The quasiparticle energies, phonon frequencies, and carrier-phonon coupling matrix elements were calculated on 4×4×6 Brillouin zone (BZ) sampling grids (using the charge density generated on an 8×8×12 BZ sampling grid for higher accuracy) and interpolated to fine BZ sampling grids with the EPW code. Carrier velocities were evaluated with the velocity operator$^{22,23}$ and the Fröhlich correction was applied to the carrier-phonon coupling matrix elements $g$. The phonon-limited carrier mobilities were calculated over the 100–1000 K temperature range for a carrier
concentration of $10^{17}$ cm$^{-3}$. The mobilities were converged for carrier and phonon BZ sampling grids of 120×120×180. We sampled states within energy windows of 225 meV around the carrier Fermi energies, which accounts for energy differences during scattering of up to $h\omega_{\text{max}} + 5k_BT$ at room temperature, where $h\omega_{\text{max}}$ is the highest polar optical phonon energy and $k_B$ is the Boltzmann constant.

We analyzed the phonon-mode-dependent carrier-phonon coupling to understand carrier scattering by phonons in r-GeO$_2$. We first determined the carrier-phonon coupling matrix elements for the bottom conduction and top valence bands for wave vectors along the $\Gamma$—$X$ and $\Gamma$—$Z$ directions [Fig. 1(a,d)]. Our results show that polar optical modes exhibit the strongest carrier-phonon coupling, as expected in polar materials. However, the higher-frequency modes are not as effective at scattering carriers; they either require high temperatures to enable appreciable phonon occupation numbers and scatter carriers by phonon absorption or high carrier energies to scatter electrons to lower-energy states by phonon emission. Taking the thermal occupation of phonon modes at room temperature ($k_BT = 26$ meV) into account, we find the dominant modes for phonon-absorption [$g^2n_q$, Fig. 1(b,e)] and phonon-emission [$g^2(n_q + 1)$, Fig. 1(c,f)] carrier scattering. Electrons and holes most strongly absorb the polar-optical LO modes with frequencies of 44, 50, 95, and 101 meV. Electrons also strongly absorb the transverse-acoustic (TA) modes. As with phonon absorption, carriers scatter most strongly by phonon emission by the polar-optical LO phonons as well as the Raman-active modes at 85 meV and 100 meV. However, the frequencies of most of these phonon modes are high, and carriers are unlikely to possess sufficient thermal energy near room temperature to emit such phonons and scatter to lower-energy states. We thus predict that holes primarily scatter by absorption of
the \( A_{2u} \) and the three \( E_u \) LO modes and emission of the two lower-frequency \( E_u \) LO modes at 44 and 50 meV, while electrons are additionally scattered strongly by the TA modes.

FIG. 1. (a-c) Square of the intraband electron-phonon coupling matrix element \( g^2 \) and scattering of electrons via phonon absorption \( \left( g^2_{el-ph} n_q \right) \) and phonon emission \( \left( g^2_{el-ph} (n_q + 1) \right) \) for the bottom conduction band from \( \Gamma \) to \( q \) as a function of the phonon wave vector \( q \) along the \( \Gamma-X \) (\( \perp \hat{c} \)) and \( \Gamma-Z \) (\( \parallel \hat{c} \)) directions, showing the phonon modes with the largest coupling strengths. Phonon occupations are calculated using room temperature \( (k_B T = 26 \text{ meV}) \). Panels (d-f) contain the same information for hole-phonon interactions (i.e. the top valence band). All four IR-active modes show strong electron or hole-LO-phonon (polar-optical) coupling near \( \Gamma \), while the strongest-coupled Raman-active modes show a weak dependence with respect to \( q \) (optical deformation potential coupling).
We next discuss the mobility obtained from the iterative solution of the BTE. Figure 2 shows the convergence of the electron (a) and hole (b) mobilities at 300 K along both crystallographic axes as a function of electron and phonon BZ sampling. We apply a linear extrapolation based on the two finest grids and extrapolate the mobilities with infinite BZ sampling. The converged carrier mobilities at 300 K are $\mu_{\text{elec,} \perp} = 154 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_{\text{elec,} \parallel} = 74 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_{\text{hole,} \perp} = 5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and $\mu_{\text{hole,} \parallel} = 2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Qualitatively, we expect a lower mobility for transport directions in which carriers have more than one strong perpendicular scattering direction. Our carrier-phonon coupling results show that carrier scattering in r-GeO$_2$ is stronger for scattering along $\Gamma$—X than $\Gamma$—Z, which indicates that the carrier mobility is higher for in-plane ($\perp \vec{c}$) than out-of-plane ($\parallel \vec{c}$) transport since the carriers propagating along $\vec{c}$ have two strong scattering ($\Gamma$—X) directions, while carriers propagating $\perp \vec{c}$ have one stronger ($\Gamma$—X) and one weaker ($\Gamma$—Z) scattering direction. This analysis is validated by our calculated carrier mobilities, which demonstrate that the electron and hole mobilities are approximately twice as high along $\perp \vec{c}$ than $\parallel \vec{c}$. 
FIG. 2. (a) Electron and (b) hole mobility $\mu$ of r-GeO$_2$ at 300 K in the $\perp \bar{c}$ and $\parallel \bar{c}$ directions as a function of the inverse of the total number of electron and phonon Brillouin-zone sampling points (the two grids are equally dense in each calculation) for carrier densities of $10^{17}$ cm$^{-3}$. The extrapolated room-temperature mobility values for r-GeO$_2$ for infinitely fine sampling grids (dotted lines) are $\mu_{\text{elec},\perp \bar{c}} = 154$ cm$^2$V$^{-1}$s$^{-1}$, $\mu_{\text{elec},\parallel \bar{c}} = 74$ cm$^2$V$^{-1}$s$^{-1}$, $\mu_{\text{hole},\perp \bar{c}} = 5$ cm$^2$V$^{-1}$s$^{-1}$, and $\mu_{\text{hole},\parallel \bar{c}} = 2$ cm$^2$V$^{-1}$s$^{-1}$.

Typically, the polar-optical modes limit the room-temperature mobility in oxide materials, but our electron-phonon coupling results combined with the mobility calculations indicate that the acoustic modes play a larger role in r-GeO$_2$. This is consistent with the results of Samanta et al., who found a strong sensitivity of the band gap on strain (i.e., acoustic deformation).\textsuperscript{26} Figure 3 shows the temperature dependence of the mobility, including a power-
law resistivity model fit to each curve. From Matthiessen’s rule, we set the mobility as the sum of two resistivity contributions:

\[
\mu(T) = \frac{1}{(aT^n + bT^m)},
\]

(1)

where \(a\), \(b\) \(n\), and \(m\) are fitting parameters to describe the temperature dependence. Table I lists the fitted values for each carrier type and direction. We find that at all temperatures studied and for both crystal directions, the \(aT^n\) term dominates the electron mobility. This is visualized in Fig. S2(a-b), which shows the calculated mobility data along with the \(aT^n\) and \(bT^m\) terms. The value of \(n\) for electrons is approximately 3/2, which is typically associated with deformation-potential acoustic-phonon scattering. Visually, the slope of the electron \(\mu(T)\) appears constant (Fig. 3), which indicates that acoustic phonons dominate carrier scattering at all investigated temperatures. For the holes, however, there is an obvious change in slope for the hole mobility from the \(aT^n\) term (with an exponent similar to 3/2 for acoustic-phonon scattering) that dominates below 473 K along \(\perp \hat{c}\) (413 K for \(\parallel \hat{c}\)) to the \(bT^m\) term (with an exponent of ~3, characteristic of optical-phonon scattering) dominating at higher temperatures [Fig. S2(c-d)]. Our mobility results are consistent with the carrier-phonon coupling data (Fig. 1), which show that acoustic-phonon scattering is weaker for holes than for electrons and only dominates at low temperatures.
FIG. 3. Electron and hole mobility $\mu$ of r-GeO$_2$ along the $\perp \vec{c}$ and $\parallel \vec{c}$ directions as a function of temperature for a carrier concentration of $n = 10^{17}$ cm$^{-3}$.

TABLE I. Fitted parameters for the power-law resistivity model given by

$$\mu(T) = \frac{1}{aT^n + bT^m}$$

where $\mu$ is in units of cm$^2$ V$^{-1}$ s$^{-1}$ and $T$ in K to describe the mobility versus temperature for electrons and holes along the two main crystallographic directions.

| Parameters | Electron, $\perp \vec{c}$ | Electron, $\parallel \vec{c}$ | Hole, $\perp \vec{c}$ | Hole, $\parallel \vec{c}$ |
|------------|-----------------------------|-----------------------------|----------------------|----------------------|
| $a$        | 4.46×10$^{-7}$              | 1.26×10$^{-6}$              | 6.99×10$^{-5}$      | 1.02×10$^{-3}$      |
| $b$        | 4.27×10$^{-14}$             | 1.61×10$^{-13}$             | 1.32×10$^{-10}$     | 9.61×10$^{-10}$     |
| $n$        | 1.66                        | 1.62                        | 1.34                 | 0.99                |
| $m$        | 3.77                        | 3.64                        | 3.48                 | 3.30                |
Carrier mobility is a crucial semiconductor parameter for the performance of electronic devices. The ultrawide band gap of r-GeO₂ (4.68 eV) makes it especially suited for high-power and high-temperature applications. Table II lists the material parameters of r-GeO₂ relevant for n-type power electronics and compares them to incumbent technologies. The breakdown fields of β-Ga₂O₃ (with a gap of 4.5 eV) and r-GeO₂ are evaluated using the breakdown field versus band gap relation by Higashiwaki et al. The electron mobility of r-GeO₂ is lower than Si, SiC, and GaN by over 80% but higher than β-Ga₂O₃. Although the experimental electron mobilities of Ga₂O₃ have typically been obtained with Hall measurements, it is the drift mobility that should be applied to evaluate the BFOM. A drift mobility of 80 cm² V⁻¹ s⁻¹ was measured in β-Ga₂O₃ at 300 K, while the highest Hall mobility at 300 K is 184 cm² V⁻¹ s⁻¹. However, if the Hall factor at 300 K (rₜ = 1.68) is applied to convert the Hall to drift mobility (μₜ = μₚₜ rₜ), the highest measured room-temperature drift mobility of Ga₂O₃ is 109 cm² V⁻¹ s⁻¹.

Overall, r-GeO₂ displays the largest BFOM out of the materials considered here as it exhibits the largest $E_C$ value (since it has the widest band gap) the highest $\varepsilon_0$, and a higher electron mobility than Ga₂O₃. The combination of a higher BFOM with the prediction of p-type doping and the possibility of hole conduction demonstrate the promise of r-GeO₂ as a superior semiconductor compared to incumbent technologies such as β-Ga₂O₃ for high-power electronic applications.

**TABLE II.** Baliga’s figure of merit (BFOM = $1/4 \varepsilon\mu E_C^2$) for silicon and common ultra-wide-band-gap semiconductors. Electron mobilities and dielectric breakdown fields for all materials are for carrier densities of $10^{16}$ cm⁻³ except those of β-Ga₂O₃ ($10^{16}$ cm⁻³ and $10^{12}$ cm⁻³ for $\mu_{Hall}$ and $10^{17}$ cm⁻³ for $\mu_{drift}$) and r-GeO₂ ($10^{17}$ cm⁻³).
In summary, we calculate the phonon-limited electron and hole mobilities of r-GeO$_2$ as functions of temperature and crystallographic orientation from first principles, and provide atomistic insights on the dominant phonon-scattering mechanisms. The combination of its ultrawide band gap of 4.68 eV (and ensuing breakdown field of 7 MV/cm) with its electron mobility of 154 cm$^2$ V$^{-1}$s$^{-1}$ at 300 K, which is higher than $\beta$-Ga$_2$O$_3$, enable a BFOM that surpasses established power-electronics materials such as Si, SiC, GaN, and $\beta$-Ga$_2$O$_3$. In combination with the theoretical prediction of its ambipolar dopability, our results highlight the advantages of r-GeO$_2$ compared to incumbent material technologies for power-electronics applications.

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Supplementary Material for:

“Electron and hole mobility of rutile GeO₂ from first principles: an ultrawide-band-gap semiconductor for power electronics”

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I. Phonon properties

The phonon dispersion of a material strongly affects the carrier mobilities. Figure S1 shows the wave vector dependence of each mode along the \( \perp \bar{c} \) and \( \parallel \bar{c} \) directions. The lowest-frequency optical mode (\( B_{1g} \), 98 cm\(^{-1}\)) occurs at \( \Gamma \). Along the in-plane direction, all phonon modes with frequencies above 179 cm\(^{-1}\) are optical modes, while the acoustic modes extend to a higher frequency (391 cm\(^{-1}\)) in the out-of-plane direction. Table SI lists the phonon frequencies of all modes, including the transverse optical (TO) and longitudinal optical (LO) splitting for each of the four infrared (IR)-active modes. Also shown is additional data from two computational studies and two experimental studies. Our calculated phonon frequencies are in overall good agreement with previous experimental and theoretical reports. An exception is the TO/LO modes reported by Kahan et al. at 652/680 cm\(^{-1}\), which have not been reproduced in other experimental or theoretical reports.\(^2,3\) A notable discrepancy also occurs for the lowest-frequency (98 cm\(^{-1}\)) of the Raman-active \( B_{1g} \) mode at \( \Gamma \), which Kaindl et al. calculated at 182 cm\(^{-1}\) for a unit-cell volume of 56.5 Å\(^3\).\(^3,3\) However, Samanta et al. show that of both the band gap and the phonon frequencies of r-GeO\(_2\) are very sensitive to the unit cell volume and calculated a \( B_{1g} \) frequency (109 cm\(^{-1}\)) similar to ours.\(^4\) This sensitivity explains the difference between our calculated \( B_{1g} \) mode frequency and experiment.\(^5\) Table SII lists the values of the sound velocity
of r-GeO\textsubscript{2} in the $\perp \hat{c}$ and $\parallel \hat{c}$ directions for each acoustic mode and are compared to experimental measurements of the sound velocities derived from the elastic constants.\textsuperscript{6}

**FIG. S1.** Phonon dispersion of r-GeO\textsubscript{2} along the $\Gamma$—X ($\perp \hat{c}$) and $\Gamma$—Z ($\parallel \hat{c}$) directions, including LO-TO splitting.
TABLE SI. Calculated phonon frequencies (in cm$^{-1}$) at $\Gamma$ for r-GeO$_2$. The activity of each mode is indicated as R (Raman-active), IR (infrared-active), or — (silent). The TO and LO frequencies for the IR-active modes, including the direction of splitting, are indicated. Our theoretical values are compared to other computed results by (a) Samanta et al.$^4$ and (b) Kaindl et al.$^3$ as well as experimental results by (c) Kaindl et al.$^3$, and (d) Kahan et al.$^1$

| Mode Type | Activity | Present work | (a)$^4$ | (b)$^3$ | (c)$^3$ | (d)$^1$ |
|-----------|----------|--------------|---------|---------|---------|---------|
|           |          | Calculated   | Experimental |
| $B_{1g}$  | R        | 98           | 109     | 182     | 170     |
| $B_{1u}$  | —        | 194          | 211     | 219     |         |
| $E_u$     | I (TO)   | 252          | 293     | 317     | 334     |
| $E_u$     | I (LO, $\Gamma$—X) | 331   | 362     | 484     |         |
| $E_u$     | I (TO)   | 363          | 383     | 364     | 652     |
| $E_u$     | I (LO, $\Gamma$—X) | 398   | 474     | 680     |         |
| $A_{2g}$  | —        | 377          | 447     | 479     | 476     |
| $A_{2u}$  | I (TO)   | 535          | 543     | 521     | 496     | 522     |
| $A_{2u}$  | I (LO, $\Gamma$—Z) | 762   | 801     | 792     | 816     |
| $E_g$     | R        | 537          | 549     | 546     |         |
| $B_{1u}$  | —        | 655          | 553     | 672     | 680, 687 |
| $E_u$     | I (TO)   | 656          | 679     | 665     | 648     | 709     |
| $E_u$     | I (LO, $\Gamma$—X) | 806   | 837     | 849     | 852     |
| $A_{1g}$  | R        | 700          | 693     | 711     | 700     |
| $B_{2g}$  | R        | 819          | 880     | 869     | 874     |

TABLE II. Calculated sound velocities (in km/s) of r-GeO$_2$ along the $\Gamma$—X ($\perp \vec{c}$) and $\Gamma$—Z ($\parallel \vec{c}$) directions for each acoustic phonon branch. We show experimental sound velocities derived from the elastic constant measurements by Wang and Simmons for comparison.$^6$

| Direction | (Bottom) TA | (Top) TA | LA | Source |
|-----------|-------------|----------|----|--------|
| $\Gamma$—X | 4.70 | 6.60 | 6.74 | This work |
| $\Gamma$—X | 6.415 | 7.328 | Ref. $^6$ |
| $\Gamma$—Z | 4.67 | 4.67 | 9.44 | This work |
| $\Gamma$—Z | 5.072 | 9.770 | Ref. $^6$ |
II. Mobility model

![Graph showing electron and hole mobility](image)

**FIG. S2.** Terms of the power-law resistivity model plotted separately to show their contribution to the mobility at each temperature. The model is given by $\mu(T) = 1/(aT^n + bT^m)$ where $\mu$ is in units of cm$^2$ V$^{-1}$ s$^{-1}$ and $T$ in K. Panels (a-b) show the electron mobility, while panels (c-d) contain the hole mobility information. The full power-law fits are shown with solid black curves in each panel. The $aT^n$ term (acoustic-mode scattering) dominates for electrons from 100 K to 1000 K, while it only dominates up to ~400 K for the hole mobility.
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