Polarons in Wurtzite Nitride Semiconductors

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Abstract

Polaron binding energy and effective mass are calculated for semiconductors with wurtzite crystalline structure from the first order electron-phonon corrections to the self-energy. A recently introduced Fröhlich-like electron-phonon interaction Hamiltonian which accounts for the LO and TO polarizations mixing due to the anisotropy is used in the calculation. The polaronic damping rates are evaluated for finite temperature. Numerical results are reported for GaN. It is shown that the electron-phonon coupling is strong enough to justify the necessity of the inclusion of second-order corrections.

KEYWORDS: Electron-Phonon interactions, Semiconductors
Electronics and optoelectronics based on III-V wide band gap nitride semiconducting systems have emerged as a matter of particular interest in recent years. An increasing number of papers devoted to the study of these materials and their applications can be found in the literature (see, for example, Refs. [1−4]).

Nitrides have the wurtzite as their natural crystalline structure, and exhibit highly unusual properties among the III-V group of semiconductors, more resembling, in some aspects, the II-VI compounds. It is possible to mention, for instance, the large magnitudes of the spontaneous and piezoelectric polarizations [5].

An aspect which is only beginning to be investigated in crystals with such a structure is the carrier-polar-optical-phonon interaction mechanism. A Fröhlich-type electron-phonon Hamiltonian was recently put forward [6] within the non-retarded Born-Huang dielectric continuum approach. In that work only the three optical-phonon branches which are infrared-active in wurtzites are considered. Probably, the most important result arising from that work is the mixing of the longitudinal and transverse optical modes due to the crystalline anisotropy. As a consequence, both kind of modes do contribute to the carrier scattering, although LO-like contributions should be dominant. A similar behaviour is well known in semiconducting heterostructures, where the presence of interfaces breaks the isotropy in one or more spatial directions, leading to the mixing of the longitudinal and transverse oscillation polarizations [7,8], and all of them have to be included in the study of the electron-phonon interaction because even the TO-type modes can provide a non-negligible contribution [9] to the scattering rates and polaron properties.

Furthermore, the existence of a spatial direction with lesser symmetry also gives rise to phonon dispersion. To illustrate, let us mention the application of the macroscopic dielectric continuum model to the study of the long-wavelength optical oscillations in dielectric or semiconducting heterolayers [10]. In that case, even when no phonon dispersion is considered for the bulk constituent materials, a dispersion law $\omega(q)$ appears for the so-called interface modes. For wurtzite III-V nitrides, phonon dispersion effects should be expected. As already discussed in Ref. [6], the dependence of the oscillation frequencies upon the phonon wavevector $q$ is not a function of the wavevector magnitude but of the angle between $q$ and the $c$ axis of the structure (referred to from now on as $z$ direction),
the direction of less symmetry in the unit cell.

The electron-phonon scattering rates [6] are sufficiently large to recognize a rather strong interaction, and to motivate the study of the polaronic corrections to the energy and the effective mass of slow electrons in the conduction band of wurtzite nitride materials.

The polaron is a quasiparticle state consisting of an electron and its surrounding phonon cloud. When electrons move through a polar material, they polarize the surrounding medium and couple to the self-induced polarization field [11]. This coupling slows down the electron as if it acquired an additional mass, and -at the same time- behaves as a potential well, decreasing its zero momentum energy, thus tending to localize the electron (which really happens when the coupling is strong enough). Even for weakly polar materials, these corrections may be quite important and will necessarily have to be taken into account, for instance, in the study of optical and transport properties. The aim of this work is -then- to calculate the polaronic corrections in wurtzite nitride semiconducting materials according to the dielectric long-wavelength continuum model. In particular, numerical results will be presented for GaN.

The electron-phonon interaction Hamiltonian corresponding to the infrared-active phonon modes of wurtzite structures can be written in general form as the sum of two contributions [6]: one of them corresponds to electron-LO-like-phonon interaction and the second one stands for the electron-transverse-optical(TO)-like-phonon interaction. The longitudinal and transverse electron-phonon vertices are given by[6]

\[
|M^L_q|^2 = \frac{2\pi e^2 \hbar}{V q^2 \Omega_L} \left[ \frac{\sin^2 \theta}{(1/\epsilon^*_1)\omega_{1L}^2} + \frac{\cos^2 \theta}{(1/\epsilon^*_z)\omega_{zL}^2} \right]^{-1},
\]

\[
|M^T_q|^2 = \frac{2\pi e^2 \hbar}{V q^2 \Omega_T} \frac{(\omega_1^2 - \omega_z^2)\sin^2 \theta \cos^2 \theta}{(e_1^0 - e_1^\infty)(\epsilon_1^z)^2 \cos^2 \theta + (e_z^0 - e_z^\infty)\omega_z^2 \sin^2 \theta}.
\]

Here, \(1/\epsilon^*_1 = 1/\epsilon_1^\infty - 1/\epsilon_1^0\) and \(1/\epsilon^*_z = 1/\epsilon_z^\infty - 1/\epsilon_z^0\), \(\epsilon_1^\infty(\epsilon_z^\infty)\) being the high-frequency dielectric constant perpendicular to (along) the z axis, and \(e_1^0 = \epsilon_1^\infty \omega_{1L}^2/\omega_1^2\), \(e_z^0 = \epsilon_z^\infty \omega_{zL}^2/\omega_z^2\) are the static dielectric constants. \(\omega_{1L}\) and \(\omega_{zL}\) are the LO-phonon frequencies along and perpendicular to the z axis respectively, and \(\omega_z\) and \(\omega_\perp\) are the corresponding lattice dispersion frequencies. For simplicity, \(\epsilon_z^\infty\) and \(\epsilon_1^\infty\) are assumed to be identical [6].
The characteristic frequencies $\Omega_L$ and $\Omega_T$ are also functions of $\theta$, the angle between the wavevector $q$ and the $z$ direction. They are given by\[6\]

$$\Omega_L^2 = \omega_{zL}^2 \cos^2 \theta + \omega_{\perp L}^2 \sin^2 \theta,$$

$$\Omega_T^2 = \omega_{z}^2 \sin^2 \theta + \omega_{\perp}^2 \cos^2 \theta,$$

(2)

Unlike isotropic materials, the TO-like vertex $M^T_q$ is, in general, different from zero due to the polarization mixing. A pure transversal mode is obtained for $\theta = \frac{\pi}{2}$.

The electronic states are described, as usual, within the effective mass approximation: The electron wavevector $k$ is the quantum number which labels the state with energy $E = \frac{\hbar^2 k^2}{2m^*}$ in the conduction band, which is assumed to be spherically symmetric with an effective mass $m^*$.

In order to illustrate the results of our calculations we choose GaN with frequencies and dielectric constants: $\omega_{zL} = 735 \ \text{cm}^{-1}$, $\omega_{\perp L} = 743 \ \text{cm}^{-1}$ [12], $\epsilon_\infty = 5.29$, $\epsilon_0 = 10.01$ and $\epsilon_{\perp} = 9.28$. The conduction band effective mass is taken to be $m^* = 0.20m_0$ [13], $m_0$ being the electron bare mass.

To deal with the entire range of $\theta$, a Fröhlich-like coupling constant $\alpha_L$ is introduced through $\alpha_L^2 = m^* e^4 / (2\epsilon_0^* \epsilon_\infty^* \hbar^3 \omega_L)$. $\omega_L$ would be an "effective longitudinal frequency". In our case, we choose the value $\omega_L = \Omega_L(\theta = \pi/4)$ to treat contributions coming from $\omega_{\perp L}$ and $\omega_{zL}$ on equal footing. For GaN, $\hbar\omega_L = 91.64 \ \text{meV}$ and $\alpha_L = 0.39$. An "effective longitudinal polaron radius" $\rho_L$ introduced through $\rho_L^2 = \hbar / 2m^* \omega_L$ has the value 14.4 1Å for GaN.

To describe the electron-TO-like-phonon interaction in terms of certain dimensionless coupling parameter, let us introduce another Fröhlich-like constant $\alpha_T$, so that $\alpha_T^2 = m^* e^4 / (2\epsilon_0^* \epsilon_\infty^* \hbar^3 \omega_T)$. Under the same argument used to introduce the frequency $\omega_L$, an "effective transversal frequency" $\omega_T$ is chosen to be $\omega_T = \Omega_T(\theta = \pi/4)$.

For GaN we get $\hbar\omega_T = 67.86 \ \text{meV}$, leading to the values $\alpha_T = 0.45$, and $\rho_T = 16.75\text{Å}$, for the coupling constant and the "effective transversal polaron radius", respectively.
Now, the longitudinal and transverse electron-phonon vertices given in Eqn. (1), modify in the following way: the factor \(2\pi e^2\hbar\) is changed to \(4\pi\hbar^2\alpha_L((1/e_z^n)/(1/e_\perp^n))^{-1/2}\rho_L\omega_L\) and to \(4\pi\hbar^2\alpha_T((1/e_z^n)/(1/e_\perp^n))^{-1/2}\rho_T\omega_T\) for the longitudinal and the transversal case, respectively.

This way of choosing \(\omega_L, \omega_T, \alpha_L,\) and \(\alpha_T\), to represent the electron-phonon interaction for the wurtzite is, of course, not unique. It is possible to follow different criteria; but what remains clear is that the final numerical results will be the same. Indeed, it makes no sense to compare the strengths of the electron-LO-like-phonon interaction and of the electron-TO-like-phonon interaction through the values of \(\alpha_L\) and \(\alpha_T\). However, both \(\alpha_L\) and \(\alpha_T\) can be representative values if comparisons between the strength of the corresponding interactions are made between different wurtzite materials.

Calculating the first order correction to the electron self-energy, the real and imaginary parts will be given by [14]

\[
\text{Re} \left[ \Sigma_S^{(1)}(k, \gamma, \eta) \right] = -\frac{m^*}{\pi^2}(e_z^n e_\perp^n)\hbar^2\rho_S\omega_S \int^\infty_0 dq \int^{2\pi}_0 d\varphi \int^1_{-1} dx \frac{f_S(x)}{\Omega_S(x)} \left[ \frac{N_S(x) + f_{k-q}}{q^2 - 2qk \cos \nu - \frac{2m^*\Omega_S(x)}{\hbar}} \right] \]

\[
\text{Im} \left[ \Sigma_S^{(1)}(k, \gamma, \eta) \right] = -\frac{m^*}{\pi}(e_z^n e_\perp^n)\hbar^2\rho_S\omega_S \int^\infty_0 dq \int^{2\pi}_0 d\varphi \int^1_{-1} dx \frac{f_S(x)}{\Omega_S(x)} \left[ (N_S(x) + f_{k-q}) \times \right. \\
\left. \delta \left( q^2 - 2qk \cos \nu - \frac{2m^*\Omega_S(x)}{\hbar} \right) + (N_S(x) + 1 - f_{k-q}) \delta \left( q^2 - 2qk \cos \nu + \frac{2m^*\Omega_S(x)}{\hbar} \right) \right]; \tag{3}
\]

with \(x = \cos \theta, \cos \nu = \cos(\varphi - \gamma)\sin \eta(1 - x^2)^{1/2} + x \cos \eta\), is the cosinus of the angle between the wavevectors \(k\) and \(q\), \(\gamma\) is the polar angle associated to the electron wavevector \(k\), and \(\eta\) is the angle between \(k\) and the \(z\) direction. The direction dependent characteristic phonon frequencies are given by

\[
\Omega^2_S(x) = \begin{cases} 
(\omega_{zL}^2 - \omega_{\perp L}^2)x_L^2 + \omega_{\perp L}^2, & S = L; \\
(\omega_{\perp}^2 - \omega_z^2)x_T^2 + \omega_z^2, & S = T,
\end{cases} \tag{4}
\]
and

\[
f_S(x) = \begin{cases} 
\left[ \frac{1-x^2}{(1/e_1^* \omega_{xL})} + \frac{x^2}{(1/e_2^* \omega_{xL})} \right]^{-1}, & S = L; \\
\frac{(\omega_L^2 - \omega^2)^2 x^2 (1-x^2)}{(e_1^* - e_2^*) \omega_L^2 x^2 + (e_1^* - e_2^*) \omega_T^2 (1-x^2)}, & S = T. 
\end{cases}
\] (5)

The polaron binding energy and effective mass are readily calculated from the real part of the electron-phonon retarded self-energy in the limits of one particle and zero temperature [12]. As usual, only the terms up to second order in k are kept. Accordingly, the polaron binding energy will be given by,

\[
\varepsilon_p = - (\alpha_L \xi_L \hbar \omega_L + \alpha_T \xi_T \hbar \omega_T),
\] (6)

On the other hand, the polaron mass is given by

\[
m_p = \frac{1}{1 - \mu_p(\eta)},
\] (7)

\[
\mu_p(\eta) = (\alpha_L \mu_{L1} + \alpha_T \mu_{T1}) \cos^2 \eta + (\alpha_L \mu_{L2} + \alpha_T \mu_{T2}) \sin^2 \eta.
\] (8)

Hence, the polaron effective mass in wurtzite crystals, with an electron-polar-optical-phonon interaction described by Eqn. (1) is a function of the angle between the electron wavevector \( k \) and the \( c \) axis of the crystal lattice. The expressions for the quantities \( \xi_S \) and \( \mu_S \) are the following \( (S = L, T) \):

\[
\xi_S = \left( \frac{\epsilon_x^* \epsilon_{x_L}^*}{\omega_S} \right)^{1/2} \int_0^1 \frac{f_S(x)}{\Omega_S^{3/2}(x)} dx;
\] (9)

\[
\mu_{S1} = \frac{1}{2} \left( \omega_S \epsilon_x^* \epsilon_{x_L}^* \right)^{1/2} \int_0^1 \frac{x^2 f_S(x)}{\Omega_S^{5/2}(x)} dx,
\]

\[
\mu_{S2} = \frac{1}{4} \left( \omega_S \epsilon_x^* \epsilon_{x_L}^* \right)^{1/2} \int_0^1 \frac{(1-x^2) f_S(x)}{\Omega_S^{5/2}(x)} dx;
\] (10)
For GaN, the following numerical results were obtained: \(\xi_L = 9.86 \times 10^{-1}\); \(\xi_T = 3.79 \times 10^{-3}\); \(\mu_{L1} = 1.68 \times 10^{-1}\); \(\mu_{L2} = 1.61 \times 10^{-1}\); \(\mu_{T1} = 8.08 \times 10^{-4}\), and \(\mu_{T2} = 5.46 \times 10^{-4}\). Then, the numerical value of the polaron binding energy will be \(\varepsilon_p = -(35.25 + 0.12)\) meV = \(-35.35\) meV. Fig. 1 shows the relative magnitude of the effective mass first correction, \(Mr = m_p/m^* - 1\), versus \(\eta\) for GaN. It is seen that the average magnitude of the increasing of the electron effective mass is around 7%, and the angular variation of this quantity is of approximately 4%, from \(\theta = 0\) to \(\theta = \pi/2\).

The amount of the total corrections due to the electron-phonon interaction is, in fact, rather significative. Indeed, the relative weight of the contributions coming from the TO-like modes is very small: 0.34% to the binding energy correction and 0.38% -in average- to the effective mass correction. As can be expected, the main contribution comes from the LO-like modes.

Anisotropy in the polaron effective mass is shown to be, in fact, a very small effect. It is worth noting that in this work an isotropic spherical effective mass is assumed. However, in wurtzite structures the electron effective mass should have different values for \(m^*_z\) and \(m^*_\perp\). This fact could be easily included in this formalism taking into account in Eq.(3) the corresponding electron wave function and energy dispersion. Nevertheless, for GaN both masses are almost the same [15]. Therefore, the result expressed by Eq. (7) is valid at this level of approximation. If only the LO-phonons were active, the polaron effective mass correction is \(Mr(\pi/2) \simeq Mr(0) = 7.52 \times 10^{-2}\). By contrary for TO-phonons \(Mr(\pi/2) = 3.83 \times 10^{-5}\) and \(Mr(0) = 5.61 \times 10^{-5}\), showing that the interaction with TO-like phonons is responsible for the introduction of a strong \(\eta\)-dependence. However, the relative contribution of this last correction makes the total result for the anisotropy to be small.

The magnitude of the polaron mass anisotropy is also related to some other material factors like the phonon frequencies and dielectric constant. Other III-V wurtzite semiconductors like AlN and InN with similar ionicities show roughly the same results[16]. By contrast wurtzite II-VI semiconductors which have larger ionicities but similar phonon frequencies, should present a larger polaron mass anisotropy, which could be calculated in the same way, but experimental Fröhlich constants for those materials are scarce. It
can be expected that for the case of different wurtzite materials, a higher influence of the electron-phonon interaction in the effective mass anisotropy could be appreciable.

In the results of Ref. [6] for the scattering rates at $T = 300\, K$, it is also seen that the contribution coming from the TO-like mode is comparatively small. The largest value of the TO-like matrix element is reported to be 7% of the LO-like matrix element. This indicates that for finite temperatures, the relative amount of the TO-like contribution might increase. To investigate that point, we have computed for $\mathbf{k} = 0$ the so-called polaronic damping rate in wurtzite $\text{GaN}$ from the first order imaginary part of the retarded self-energy of Eqn. (3). In our case -as can be seen in the corresponding expression-, only the phonon absorption process is non-vanishing because for $\mathbf{k}$ the emission threshold is never reached even for finite temperature. The polaron damping rate is given through the equation:

$$\frac{1}{\tau_S} = \alpha_S \omega_S \left( e^*_S e^*_\perp \right)^{1/2} I_S;$$

$$I_S = \frac{2}{\omega_S^{1/2}} \int_0^1 \frac{f_S(x)}{\Omega_S^{3/2}(x)} \text{csch} [\beta \hbar \Omega_S(x)] dx,$$

with $\beta = 1/k_B T$.

Fig. 2 shows the dimensionless quantity $I_S$ as a function of the temperature. Fig. 2(a) corresponds to the LO-like case, and Fig. 2(b) corresponds to the TO-like case. It is immediately seen that the value of the TO-like contribution to the polaron damping rate is always much smaller than the LO-like one; but its magnitude increases in one order of magnitude when going from $T = 100\, K$ to $T = 300\, K$, and this could be an important effect for a different wurtzite material, where the combined values of the parameters give rise to a larger electron-TO-like-phonon matrix element.

In summary, we have reported in this work the polaron binding energy and effective mass in first order perturbation theory for wurtzite materials. Numerical results for the case of $\text{GaN}$ show that the magnitude of the coupling between the conduction electrons and the polar optical phonons is large indeed. Both, the LO-like and TO-like oscillation modes contribute, even when it is seen that the relative weight of the TO-like contribution is much smaller than the one coming from the LO-like phonons; but it is possible to
expect appreciable contributions from the TO-like phonon scattering processes at room temperature. The value of the polaron binding energy indicates the great importance that the carrier-phonon interaction might have, for instance, in the study of exciton-related optical processes in wurtzite semiconducting materials and heterostructures based on them. It is very well known that these materials are the subject of interesting applications in optoelectronics, where III-V nitride-based blue-green semiconductor lasers have already been produced.

Obviously, the electron-phonon coupling is strong enough to allow for non-negligible contributions from the second order diagrams in the self-energy expansion. According to the perturbation Hamiltonian [6], these second order diagrams, with two phonon lines, occur with three different structures: two LO-like phonon lines, two TO-like phonon lines, and one LO-like plus one TO-like phonon lines. For zero temperature, in the evaluation of the second order corrections, it is necessary to consider only the contributions coming from the first of these structures: that of two LO-like phonon scattering processes. This, in the case of GaN, is justified by the numerical value above reported for the polaron binding energy in first order approximation (not to mention that the magnitude of the effective mass correction is considerably smaller). Nevertheless, for finite temperature, the contributions of TO-like phonons in second order might also become significative, possibly for a different wurtzite material. The work of calculating these second order corrections, and their inclusion in the study of exciton-related optical absorption is already in progress.

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Figure Captions

**Fig.1:** Relative polaron effective mass for GaN as a function of $\eta$, the angle between the electron wavevector and the $c$ axis of the wurzite crystalline structure.

**Fig.2:** The dimensionless quantity $I_S$ as a function of the temperature for GaN: (a) LO-like phonon absorption process, and (b) TO-like phonon absorption process.
The graph illustrates the relationship between $Mr$ and $\eta$. As $\eta$ increases from 0 to $\pi/2$, $Mr$ decreases from 0.073 to 0.067.
