Simplified Band-Structure Models and Carrier Dynamics

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Semiconductor Fundamentals

In this set of lecture notes, we provide a brief review of semiconductor physics relevant to the needs of Computational Electronics. We begin with a brief review of the electronic states in a periodic potential as seen by electrons in crystalline semiconductor materials, i.e. the semiconductor bandstructure. We then introduce the important concepts of effective mass and density of states.

Semiconductor Bandstructure

The basis for discussing transport in semiconductors is the underlying electronic *band structure* of the material arising from the solution of the many body Schrödinger equation in the presence of the periodic potential of the lattice, which is discussed in a host of solid state physics textbooks. The solution of the one-particle Schrödinger equation in the presence of the periodic potential of the lattice (and all the other electronics by an effective one-particle potential) are in the form of Bloch functions

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \qquad (1)$$

where **k** is the wavevector, and n labels the band index corresponding to different solutions for a given wavevector. The cell-periodic function, $u_{n,\mathbf{k}}(\mathbf{r})$, has the periodicity of the lattice and modulates the traveling wave solution associated with the free particle motion of electrons. The energy eigenvalues, $E_n(\mathbf{k})$, associated with the Bloch eigenfunctions, $\psi_{n,\mathbf{k}}$ above, form what is commonly referred to as the energy bandstructure. The energy, $E_n(\mathbf{k})$, is periodic as a function of **k**, with a periodicity corresponding to the reciprocal lattice associated with the real-space lattice. The energy is therefore uniquely specified within the unit cell of this reciprocal lattice, referred to as the first Brillouin zone.

In the usual quantum mechanical picture associated with the wave-particle duality of matter, the electron motion through the crystal is visualized as a localized wave-packet space composed of a superposition of Bloch states of different wavevectors around an average wavevector, **k**. The expectation value of the particle velocity then corresponds to the group velocity of this wave-packet, or

$$\mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E_n(\mathbf{k}) \tag{2}$$

A brief look at the symmetry properties of the Bloch functions gives some insight into the nature of the bandstructure in semiconductors. First consider the atomic orbitals of the individual atoms that constitute the semiconductor crystal. Typical semiconductors have an average of 4 valence electrons per atom composed of partially filled *s*- and *p*-type orbitals that contribute to bonding, primarily tetrahedral bonds that formed through sp^3 hybridization. The symmetry (or geometric) properties of these atomic orbitals are apparent from consideration of their angular components

$$\begin{aligned} s &= 1 \\ p_x &= \frac{x}{r} = \sqrt{3} \sin\theta \cos\varphi \\ p_y &= \frac{y}{r} = \sqrt{3} \sin\theta \sin\varphi \\ p_z &= \frac{z}{r} = \sqrt{3} \cos\theta \end{aligned} \tag{3}$$

Let us denote these states by |S>, |X>, |Y> and |Z>. When individual atoms are brought together, these orbitals combine or hybridize into sp^3 molecular orbitals to form covalent bonds composed of lower energy, filled ‘bonding’ molecular orbitals, and unfilled ‘anti-bonding’ orbitals. The separation in energy between the bonding and anti-bonding orbital states can be viewed as the fundamental origin of the energy ‘gap’ characteristic of all semiconductors. Once all the atoms coalesce to form a crystal, these molecular orbitals overlap and broaden, leading to the energy bandstructure with gaps and allowed energy bands. The mostly filled valence bands are formed primarily from the bonding orbital states, while the unfilled conduction band is primarily associated with the anti-bonding states.

For semiconductors, one is typically worried about the bandstructure of the conduction and the valence bands only. It turns out that the states near the band-edges behave very much like the |S> and the three *p*-type states that they had when they were individual atoms.

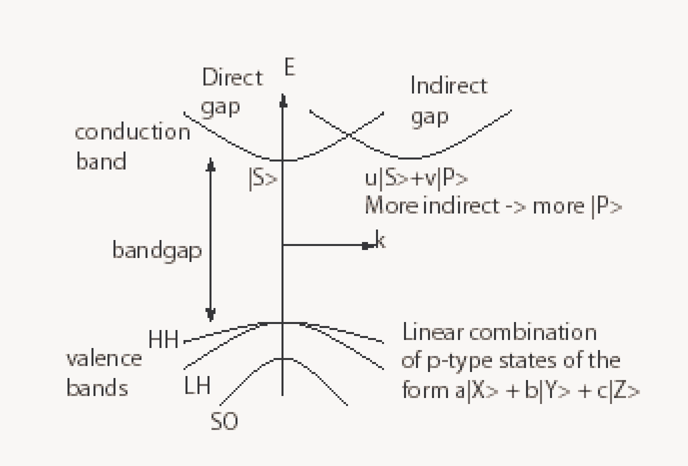

Figure 1: The typical bandstructure of semiconductors. For direct-gap semiconductors, the conduction band state at k = 0 is *s*-like. The valence band states are linear combinations of *p*-like orbitals. For indirect-gap semiconductors on the other hand, even the conduction band minima states have some amount of *p*-like nature mixed into the *s*-like state.

Electronic band structure calculation methods can be grouped into two general categories [1]. The first category consists of *ab initio* methods, such as Hartree-Fock or Density Functional Theory (DFT), which calculate the electronic structure from first principles, i.e. without the need for empirical fitting parameters. In general, these methods utilize a variational approach to calculate the ground state energy of a many-body system, where the system is defined at the atomic level. The original calculations were performed on systems containing a few atoms. Today, calculations are performed using approximately 1000 atoms but are computationally expensive, sometimes requiring massively parallel computers.

In contrast to *ab initio* approaches, the second category consists of *empirical* methods, such as the Orthogonalized Plane Wave (OPW) [2], tight-binding [3] (also known as the Linear Combination of Atomic Orbitals (LCAO) method), the $\mathbf{k}\cdot\mathbf{p}$ method [4], and the local [5], or the non-local [6] empirical pseudopotential method (EPM). These methods involve empirical parameters to fit experimental data such as the band-to-band transitions at specific high-symmetry points derived from optical absorption experiments. The appeal of these methods is that the electronic structure can be calculated by solving a one-electron Schrödinger wave equation (SWE). Thus, empirical methods are computationally less expensive than *ab initio* calculations and provide a relatively easy means of generating the electronic band structure.

Figure 2 shows an example of the calculated bandstructure for Si and Ge using the empirical pseudopotential method. In comparing this figure to the schematic bandstructure shown in **Figure 1**, we see that while the basic features are evident such as the indirect bandgap, the actual *E*-**k** relationship is quite complicated, with multiple conduction and valence bands and band crossings which make the identification of individual bands somewhat ambiguous.

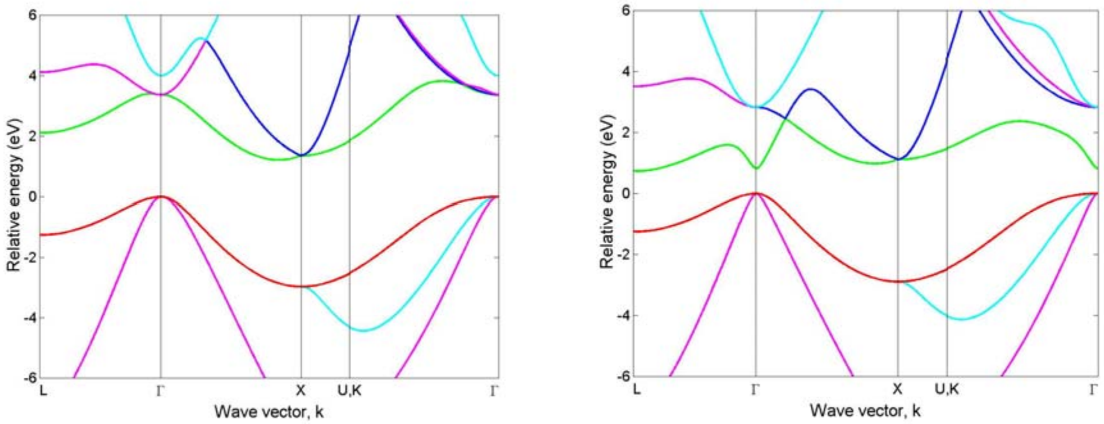

Figure 2. Empirical pseudopotential calculation of the electronic bandstructure in Si (left panel) and Ge (right panel).

Simplified Band Structure Models

In terms of charge transport in semiconductors, it is usually too difficult to deal with the complication of the detailed bandstructure shown in Figure 2, and so simplifications are sought. Usually free carriers (electrons or holes) reside at the minimum or maximum of the conduction or valence bands respectively. We see from Figure 2 that the *E* versus **k** relation appears quadratic close to an extremum, either concave up or down, which is similar to simply dispersion relation for free electrons quantum mechanically. Depending on the curvature, however, the *effective mass* of the carrier may be smaller or larger than the free electron mass, m_o, and even negative for the case of holes. Therefore, one often assumes a multi-band or multi-valley model in which carriers are free electron like, with a unique effective mass for each band or valley. There are usually two levels of approximation used in this case, simply parabolic bands, and non-parabolic bands in which a correction is included for higher order effects in the dispersion relationship close to an extremum:

(a) **Parabolic Band**

$$E(\mathbf{k})=\frac{\hbar^2|\mathbf{k}|^2}{2m_0^*} \tag{4}$$

where m_0^* is the effective mass at the conduction band minimum (or valence band maximum). The particle velocity is simply given from Eq. (2) as

$$\mathbf{v}=\frac{1}{\hbar}\nabla_{\mathbf{k}}E(\mathbf{k})=\frac{\hbar\mathbf{k}}{m_0^*} \tag{5}$$

where the mechanical momentum and crystal momentum are now identically equal, $\mathbf{p}=\hbar\mathbf{k}=m_0^*\mathbf{v}$.

(b) **Non-parabolic Band**

$$E(\mathbf{k})\left(1+\alpha E(\mathbf{k})\right)=\frac{\hbar^2|\mathbf{k}|^2}{2m_0^*} \tag{6}$$

where α is the coefficient of non-parabolicity and has the dimensions of an inverse energy. The solution of the second order equation is

$$E(k)=\frac{\sqrt{1+\frac{4\alpha\hbar^2|\mathbf{k}|^2}{2m_0^*}-1}}{2\alpha} \tag{7}$$

The velocity is

$$\mathbf{v}=\frac{1}{\hbar}\nabla_k E(\mathbf{k})=\frac{\hbar\mathbf{k}}{m_0^*}\left(1+4\alpha\frac{\hbar^2|\mathbf{k}|^2}{2m_0^*}\right)^{-1/2}\mathbf{=v}=\frac{\hbar\mathbf{k}}{m_0^*\left[1+2\alpha E(\mathbf{k})\right]} \tag{8}$$

The coefficient of non-parabolicity α is related to the degree of admixture of *s*-like CB states and *p*-like VB states, given by

$$\alpha = \frac{\left(1 - \frac{m_0^*}{m_0}\right)^2}{E_{gap}} \tag{9}$$

where m_0 is the electron mass in vacuum, and E_{gap} is the energy gap between valence and conduction band. Hence, smaller bandgap materials have stronger mixing of CB and VB states, and therefore a stronger non-parabolicity.

Carrier Dynamics

Under the influence of an external field, Bloch electrons in a crystal change their wavevector according to the acceleration theorem

$$\hbar \frac{d\mathbf{k}(t)}{dt} = \mathbf{F}\,, \tag{10}$$

where **F** is the external force (i.e. external to the crystal field itself) acting on a particle, and $\hbar\mathbf{k}$ plays the role of a pseudo or crystal momentum in the analogy to Newton's equation of motion. The effect on the actual velocity or momentum of the particle is, however, not straightforward as the velocity is related to the group velocity of the wave packet associated with the particle, and is given by Eq. (2), where $E_n(\mathrm{k})$ is one of the dispersion relations from Figure 2. As the particle moves through *k*-space under the influence of an electric field, for example, its velocity can be positive or negative, eventually leading to *Bloch oscillations* if scattering did not limit the motion. Only near extremum of the bands, for example, at the Γ point in Figure 2 for the valence band, or close to the L point in the conduction band, does the dispersion relation resemble that of the free electrons, $E(\mathbf{k}) = \hbar^2 k^2 / 2m^*$. There, the electron velocity is simply given by $\mathbf{v} = \hbar\mathbf{k} / m^*$, and the momentum is $\mathbf{p} = \hbar\mathbf{k}$, as discussed in the previous section.

In the case of the valence band, the states are nearly full, and current can only be carried by the absence of electrons in a particular state, leading to the concept of *holes*, whose dynamics are identical to that of electrons except their motion is in the opposite direction of electrons, hence they behave as positively charged particles. In relation to transport and device behavior, these holes are then treated as positively charged particles in the presence of external fields, and one has to simulate the motion of both electrons and holes.

For device modeling and simulation, different approximate band models are employed. As long as carriers (electrons and holes) have relatively low energies, they may be treated using the so called *parabolic band approximation*, where they simply behave as free particles having an effective mass. If more accuracy is desired, corrections due to deviation of the dispersion relation from a quadratic dependence on **k** may be incorporated in the *nonparabolic band model*. If more than one conduction band minimum is important, this model may be extended to a *multi-valley model*, where the term valley refers to different conduction minima. Finally, if the entire energy dispersion is used, one usually referes to the model as *full band*.

Effective Mass in Semiconductors

The effective mass of a semiconductor is obtained by fitting the actual E-k diagram around the conduction band minimum or the valence band maximum by a parabola. While this concept is simple enough, the issue turns out to be substantially more complex due to the multitude and the occasional anisotropy of the minima and maxima. In this section we first describe the different relevant band minima and maxima, present the numeric values for germanium, silicon and gallium arsenide and introduce the effective mass for density of states calculations and the effective mass for conductivity calculations.

Most semiconductors can be described as having one band minimum at $k = 0$ as well as several equivalent anisotropic band minima at $k \neq 0$. In addition there are three band maxima of interest which are close to the valence band edge. As an example we consider the band structure of silicon as shown in the figure below.

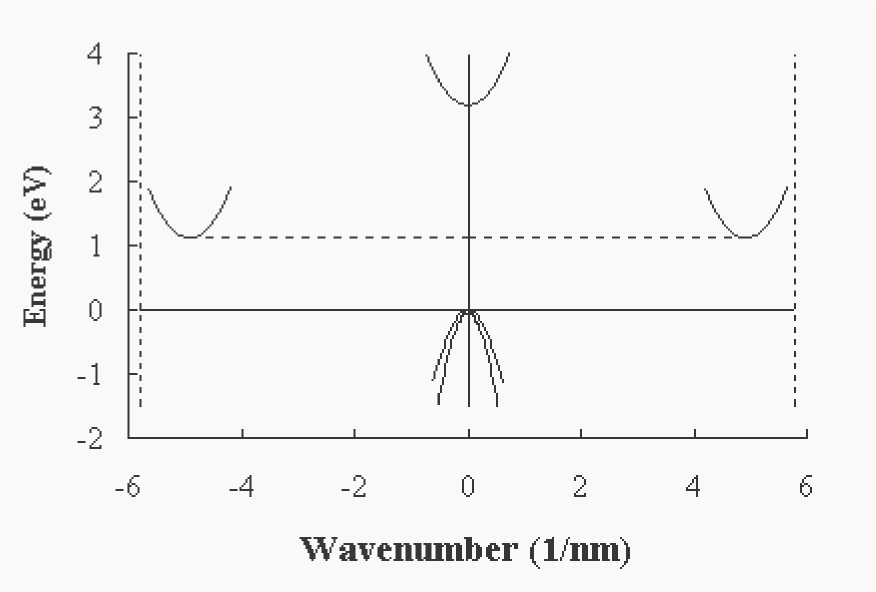

Figure 3. *E*-*k* diagram within the first Brillouin zone and along the (100) direction.

Shown is the *E*-*k* diagram within the first Brillouin zone and along the (100) direction. The energy is chosen to be to zero at the edge of the valence band. The lowest band minimum at $k = 0$ and still above the valence band edge occurs at $E_{\mathrm{c,direct}} = 3.2$ eV. This is not the lowest minimum above the valence band edge since there are also 6 equivalent minima at $k = (x,0,0)$, $(-x,0,0)$, $(0,x,0)$, $(0,-x,0)$, $(0,0,x)$, and $(0,0,-x)$ with $x = 5\ \mathrm{nm}^{-1}$. The minimum energy of all these minima equals 1.12 eV = $E_{\mathrm{c,indirect}}$. The effective mass of these anisotropic minima is characterized by a longitudinal mass along the corresponding equivalent (100) direction and two transverse masses in the plane perpendicular to the longitudinal direction. In silicon the longitudinal electron mass is $m_{e,l}^* = 0.98\ m_0$ and the transverse electron masses are $m_{e,t}^* = 0.19\ m_0$, where $m_0 = 9.11 \times 10^{-31}$ kg is the free electron rest mass. Two of the three band maxima occur at 0 eV. These bands are referred to as the light and heavy hole bands with a light hole mass of $m_{lh}^* = 0.16\ m_0$ and a heavy hole mass of $m_{hh}^* = 0.46\ m_0$. In addition there is a split-off hole band with its maximum at $E_{v,so} = -0.044$ eV and a split-off hole mass of $m_{v,so}^* = 0.29\ m_0$.

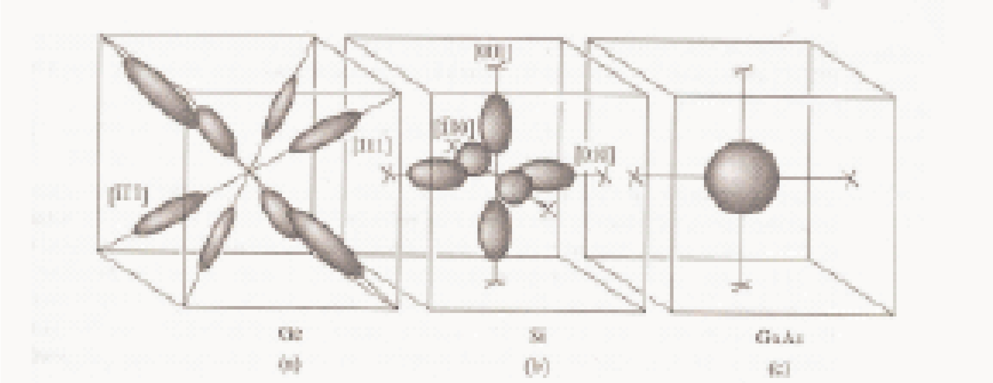

Figure 4. Constant energy surfaces of the conduction band of Ge, Si and GaAs. Note that in the case of Ge we have 4 conduction band minima, in the case of Si we have 6 conduction band equivalent valleys and in the case of Ge we have only one constant energy surface at the center of the Brillouin zone.

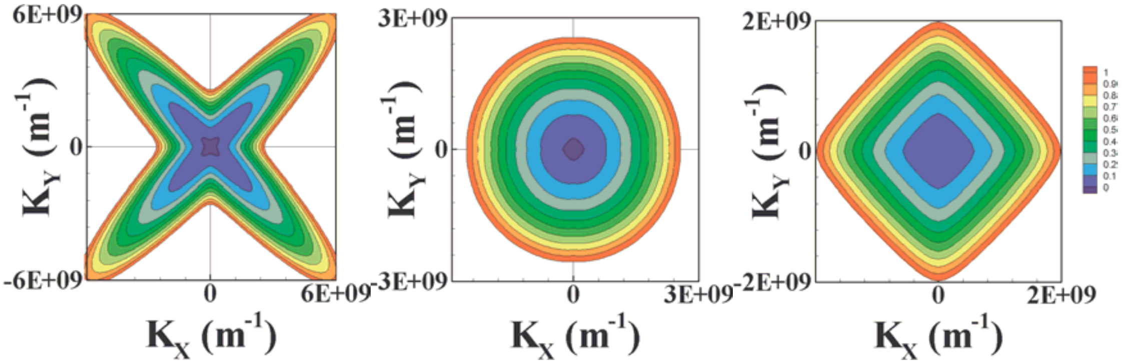

Figure 5. 3D equienergy surfaces of heavy hole, light hole and split off band in Si for $k_z = 0$.

The values of the energy band minima and maxima as well as the effective masses for germanium, silicon and gallium arsenide are listed in

Table 1 below.

Table 1

Name	**Symbol**	**Germanium**	**Silicon**	**Gallium Arsenide**
Band minimum at *k* = 0				
Minimum energy	$E_{\mathrm{g,direct}}$ [eV]	0.8	3.2	1.424
Effective mass	m_e^*/m_0	0.041	0.2	0.067
Band minimum *not* at *k* = 0				
Minimum energy	$E_{\mathrm{g,indirect}}$[eV]	0.66	1.12	1.734
Longitudinal effective mass	$m_{e,l}^*/m_0$	1.64	0.98	1.98
Transverse effective mass	$m_{e,t}^*/m_0$	0.082	0.19	0.37
Wavenumber at minimum	k [1/nm]	xxx	xxx	xxx
Longitudinal direction		(111)	(100)	(111)
Heavy hole valence band maximum at *E* = *k* = 0				
Effective mass	m_{hh}^*/m_0	0.28	0.49	0.45
Light hole valence band maximum at *k* = 0				
Effective mass	m_{lh}^*/m_0	0.044	0.16	0.082
Split-off hole valence band maximum at *k* = 0				
Split-off band valence band energy	$E_{\mathrm{v,so}}$ [eV]	-0.028	-0.044	-0.34
Effective mass	$m_{h,so}^*/m_0$	0.084	0.29	0.154

$m_0 = 9.11 \times 10^{-31}$ kg is the free electron rest mass.

The effective mass for density of states calculations equals the mass which provides the density of states using the expression for one isotropic maximum or minimum or

$$g_C(E) = \frac{8\pi\sqrt{2}}{h^3} m_e^{*3/2} \sqrt{E - E_C}, \quad \text{for} \quad E \geq E_C \ , \tag{11}$$

for the density of states in the conduction band, and

$$g_V(E) = \frac{8\pi\sqrt{2}}{h^3} m_h^{*3/2} \sqrt{E_V - E}, \quad \text{for} \quad E \leq E_V \ , \tag{12}$$

for the density of states in the valence band. For instance for a single band minimum described by a longitudinal mass and two transverse masses the effective mass for density of states calculations is the geometric mean of the three masses. Including the fact that there are several equivalent minima at the same energy one obtains the effective mass for density of states calculations from:

$$m^*_{e,dos} = M_C^{2/3}\left(m_l m_t m_t\right)^{1/3} \qquad (13)$$

where M_c is the number of equivalent band minima. For silicon one obtains

$$m_{\mathrm{e,dos}}{}^* = (m_l\ m_t\ m_t)^{1/3} = (6)^{2/3}\ (0.89\times0.19\times0.19)^{1/3}\ m_0 = 1.08\ m_0. \qquad (14)$$

The effective mass for conductivity calculation is the mass which is used in conduction related problems accounting for the detailed structure of the semiconductor. These calculations include mobility and diffusion constants calculations. Another example is the calculation of the shallow impurity levels using a hydrogen-like model. As the conductivity of a material is inversionally proportional to the effective masses, one finds that the conductivity due to multiple band maxima or minima is proportional to the sum of the inverse of the individual masses, multiplied by the density of carriers in each band, as each maximum or minimum adds to the overall conductivity. For anisotropic minima containing one longitudinal and two transverse effective masses one has to sum over the effective masses in the different minima along the equivalent directions. The resulting effective mass for bands which have ellipsoidal constant energy surfaces is given by:

$$m^*_{e,cond} = \frac{3}{\dfrac{1}{m_l} + \dfrac{1}{m_t} + \dfrac{1}{m_t}} \qquad (15)$$

provided the material has an isotropic conductivity as is the case for cubic materials. For instance electrons in the X minima of silicon have an effective conductivity mass given by:

$$m_{\mathrm{e,cond}}{}^* = 3\times(1/m_l + 1/m_t + 1/m_t)^{-1} = 3\times(1/0.89 + 1/0.19 + 1/0.19)^{-1}\ m_0 = 0.26\ m_0. \qquad (16)$$

Table 0-2. Effective mass and energy bandgap of Ge, Si and GaAs

Name	**Symbol**	**Germanium**	**Silicon**	**Gallium Arsenide**
Smallest energy bandgap at 300 K	E_g (eV)	0.66	1.12	1.424
Effective mass for density of states calculations				
Electrons	$m_\mathrm{e}^{*}{}_{,\mathrm{dos}}/m_0$	0.56	1.08	0.067
Holes	$m_\mathrm{h}^{*}{}_{,\mathrm{dos}}/m_0$	0.29	0.57/0.81[1]	0.47
Effective mass for conductivity calculations				
Electrons	$m_\mathrm{e}^{*}{}_{,\mathrm{cond}}/m_0$	0.12	0.26	0.067
Holes	$m_\mathrm{h}^{*}{}_{,\mathrm{cond}}/m_0$	0.21	0.36/0.386 [7]	0.34

$m_0 = 9.11 \times 10^{-31}$ kg is the free electron rest mass.

References

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[7] Due to the fact that the heavy hole band does not have a spherical symmetry there is a discrepancy between the actual effective mass for density of states and conductivity calculations (number on the right) and the calculated value (number on the left) which is based on spherical constant-energy surfaces. The actual constant-energy surfaces in the heavy hole band are "warped", resembling a cube with rounded corners and dented-in faces.