CALCULATIONS OF THE EFFECTIVE MASSES AND EMITTED WAVELENGTHS OF PbSe/PbSrSe QUANTUM WELL NORMAL AND OBLIQUE DEGENERATE VALLEYS

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Abstract

One of the IV-VI material systems that showed promising growth results is PbSe/Pb_{0.93}Sr_{0.066}Se quantum well structure with PbSe as the well material, and Pb_{0.93}Sr_{0.066}Se as the barrier material. However, this material system is a part of the lead salts semiconductor group with constant energy surfaces that are prolate ellipsoids of revolution and its energy bands are highly non-parabolic. The effects of the prolate ellipsoids of revolution are studied using the isotropy of the effective mass. Using these effective masses, we study the effects of non-parabolicity on the energy level and emitted wavelength calculations for the normal and oblique degenerate valleys of the system. The theoretical results are compared with the experimental ones for the first two energy levels and a close match is found.

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1. Introduction

Mid-IR lasers fabricated from lead salts IV-VI semiconductors are proven devices for molecular spectroscopy applications. For example, significant progress in developing mid-IR laser absorption spectrometers for breath analysis has occurred, since the first description of laser-based eNO/eCO₂ measurements in 2002 [1]. The results presented in [2] show that mid-IR lasers based on this material system provide the necessary performance characteristics to enable development of practical applications. Depending on the composition of the IV-VI alloys and temperature, their bandgaps range from 0 to over 500meV. They are direct gap materials with conduction and valence band minima at the L-point in k-space. The bands are almost mirror images of each other, so quantum effects are expected to be the same for both bands. Recent work has focused on MBE growth and characterization of PbSrSe/PbSe MQW structures on (111)-oriented substrates. Detailed procedures for growth and characterization of PbSrSe/PbSe MQWs on (111)-oriented BaF₂ and silicon have been described elsewhere [3-8]. Important results from this work include differential transmission spectroscopy (DTS) measurement of quantized energy levels in quantum wells, which show removal of L-valley degeneracy. Moreover, this material system is with constant energy surfaces that are prolate ellipsoids of revolution and its energy bands are highly non-parabolic. The effects of the prolate ellipsoids are characterized by the longitudinal and transverse effective masses with respect to the growth direction.

In this work, theoretical formulations have been used to calculate the effective mass values due to anisotropy of the PbSe/Pb₀.₉₃₄Sr₀.₀₆₆Se SQW. Based on these values, we calculate the transition energy levels and emitted wavelengths from the degenerate states of the normal and oblique valleys of the system, and compare our results with the experimental data at 200K.
2. Isotropy and Effective Masses Calculations

Lead salts are direct energy gap semiconductors with constant energy surfaces that are prolate ellipsoids of revolution characterized by the longitudinal and transverse effective masses $m_l^*$ and $m_t^*$, respectively. The major axes of the ellipsoids are in the [111] directions. Therefore, to determine $m_w^*$ that will be used to calculate the energy levels of the single quantum well system below, it is necessary to find and use a relationship that relates it with the longitudinal and transverse effective masses. Because the conduction and valence bands at the L points are near mirror images of each other, the electron and hole effective masses are expected to be nearly equal. Furthermore, the bands are strongly non-parabolic. These semiconductors have the face centered cubic crystal structure with (100) cleavage planes, and tend to grow best in the [100] orientation, although they can also be grown in the [111] orientation.

The energy-wave vector relation of the conduction and valence bands of lead salt semiconductors in the two band approximation of Kane is given by [4]:

$$E = -\frac{1}{2}E_g \pm \sqrt{\frac{1}{4}E_g^2 + p_t^2k_t^2 + p_l^2k_l^2},$$

where the + sign is for the conduction band and – sign is for the valence band. The zero energy level is taken at the bottom of the conduction band. The bandgap is $E_g$, $k_t$ and $k_l$ are the transverse and longitudinal components of the wave vector, and $p_t^2$ and $p_l^2$ represent the transverse and longitudinal momentum matrix elements taken between the valence and conduction band states and are related to the effective masses $m_l^*$ and $m_t^*$ by the following relation:

$$p_{t, l}^2 = \frac{\hbar^2 E_g}{2m_{t, l}^*}.$$
This is a direct proportionality relationship between the $E_g$ and the effective masses for a certain material. Thus, to a first approximation, the variations of the effective masses with composition ($x$) and temperature ($T$) are due to the variation of the bandgap with composition ($x$) and temperature ($T$). The energy gap of Pb$_{1-x}$Sr$_x$Se system depends on temperature according to this relation [9]:

$$E_g(x, T) = 0.150 + 3.608x - 1.31x^2 + (0.430 - 3.093x + 6.495x^2) \times 10^{-3}T \text{ (eV)}$$

(for $0 \leq x \leq 0.276$, $0 < T \leq 350\text{K}$). (3)

The energy dispersion relation in the $z$-direction, $E_z(k)$, using Kane’s model is similar to equation (1) and is given by:

$$E_z = -\frac{1}{2}E_g \pm \sqrt{\frac{1}{4}E_g^2 + p_z^2k_z^2},$$

(4)

where $p_z^2 = \frac{\hbar^2E_g}{2m_w^*}$. The energy dispersion for lead salts in the $z$-direction can thus be found by equating equations (1) and (4). This results in the following relation:

$$\frac{k^2}{m_w^*} = \frac{k_l^2}{m_l^*} + \frac{k_t^2}{m_t^*}.$$  

(5)

The wave vectors $k_l$ and $k_t$ can be written in terms of $k$ as:

$$k_l = k \cos \theta,$$

$$k_t = k \sin \theta,$$

(6)

where the angle $\theta$ is between the ellipsoidal major axis and the well growth direction, also the $z$-direction. Substituting equation (6) in equation (5) yields a relation between the effective mass in the well and the longitudinal and transverse effective masses:
The value of the mobility effective mass $m_w^*$ at the band extrema is calculated from the respective carrier longitudinal mass $m_l^*$, transverse mass $m_t^*$, and the angle $\theta$. To determine this angle for a quantum well in the [100] direction, the dot product is taken between the [100] direction and the [111] ellipsoid direction:

$$[100][111] = 1 = \sqrt{3} \cos \theta.$$

Thus,

$$\cos \theta = \frac{1}{\sqrt{3}} \quad \text{and} \quad \sin \theta = \frac{2}{\sqrt{3}}.$$

Now equation (7) gives the effective mass in the [100] direction as [4, 5]:

$$\frac{1}{m_w^*} = \frac{1}{3} \left[ \frac{2}{m_l^*} + \frac{1}{m_t^*} \right] = \frac{1}{m_{100}^*}.$$

This value for the effective mass is in the direction of the well, not in the direction of the ellipsoid major axis [111]. To determine this angle for a quantum well in the [11-1] direction, the dot product is taken between the [11-1] direction and the [111] ellipsoid direction:

$$[11-1][111] = 1 = 3 \cos \theta.$$

Thus,

$$\cos \theta = \frac{1}{3} \quad \text{and} \quad \sin \theta = \frac{2\sqrt{2}}{3}.$$

Now equation (7) gives the effective mass in the [111] direction as:

$$\frac{1}{m_w^*} = \frac{1}{9} \left[ \frac{8}{m_l^*} + \frac{1}{m_t^*} \right] = \frac{1}{m_{111}^*}.$$
This value for the effective mass is in the direction of the well, not in the direction of the ellipsoid major axis [111].

3. Degeneracy Valleys Emitted Wavelengths

Recent work has focused on MBE growth and characterization of PbSrSe/PbSe quantum well structures on (111)-oriented substrates. Differential transmission spectroscopy (DTS) measurement of the quantized energy levels showed removal of L-valley degeneracy [5, 8]. Consistent with the quantum size effect, degeneracy splitting energy increases as well width decreases. Radiative interband transitions between degeneracy split normal and oblique L-valleys are observed. The lowest energy intersubband transition, labeled (1-1)$^N$, is between heavier effective mass electron and hole states in L-valleys that are normal to the (111) plane in reciprocal space, while the next lowest transition, labeled (1-1)$^O$, is between lighter effective mass electron and hole states in the three oblique valleys that lie along the equivalent (111) directions. These energy states are shown in Figure 1 obtained from [10].

4. Data and Results

In this work, we first calculate the effective masses in the normal and oblique valleys and then use these values to calculate the transition energy levels and emitted wavelengths assuming parabolic and non-parabolic energy states. Finally, we compare our data with the experimental data as shown in Figure 1.

To find the longitudinal effective mass for the electrons which is the same electron effective mass in the normal valley, we use this widely acceptable linear relationship:

$$m_{l,e}(x, T) = \frac{m_{l,e}(x, 77K)}{E_g(x, 77K)} * E_g(x, T).$$

(10)
Similar relationship can be used for the longitudinal effective mass of the holes which is the same as the holes effective mass in the normal valley. Regarding the transverse effective mass of the electrons and holes, these can be found by using equation (10) and replacing the appropriate symbols. From these effective values, we can use equation (9) to find the effective masses in the oblique valleys. Table 1 shows the calculated effective masses for the electrons and holes in both valleys, for the well material PbSe. Similarly, the calculated effective masses for the barrier material Pb_{0.934}Sr_{0.066}Se can be seen in Table 2. The values are shown calculated at five different temperatures 77K, 150K, 200K, 250K and 300K. Notice that the normal valley electron and hole masses exactly match the longitudinal effective masses.

**Figure 1.** Illustration of interband transitions between degeneracy split \( n = 1 \) and \( n = 2 \) subbands with calculated energies for a 30nm wide PbSe QW at 200K.
Table 1. The normal and oblique valleys effective mass calculations for PbSe well material

<table>
<thead>
<tr>
<th>T (PbSe)</th>
<th>Eg(x, T)</th>
<th>ml, e</th>
<th>mt, e</th>
<th>ml, h</th>
<th>mt, h</th>
<th>meN</th>
<th>mhN</th>
<th>meo</th>
<th>mho</th>
</tr>
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<tbody>
<tr>
<td>77</td>
<td>0.18311</td>
<td>0.0788</td>
<td>0.0475</td>
<td>0.0764</td>
<td>0.0386</td>
<td>0.0788</td>
<td>0.0764</td>
<td>0.049693</td>
<td>0.040845</td>
</tr>
<tr>
<td>150</td>
<td>0.2145</td>
<td>0.092308</td>
<td>0.055643</td>
<td>0.089497</td>
<td>0.045217</td>
<td>0.092308</td>
<td>0.089497</td>
<td>0.058212</td>
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<td>0.101561</td>
<td>0.06122</td>
<td>0.098468</td>
<td>0.049749</td>
<td>0.101561</td>
<td>0.098468</td>
<td>0.064047</td>
<td>0.052643</td>
</tr>
<tr>
<td>250</td>
<td>0.2575</td>
<td>0.110813</td>
<td>0.066797</td>
<td>0.107438</td>
<td>0.054282</td>
<td>0.110813</td>
<td>0.107438</td>
<td>0.069881</td>
<td>0.057439</td>
</tr>
<tr>
<td>300</td>
<td>0.279</td>
<td>0.120066</td>
<td>0.072375</td>
<td>0.116409</td>
<td>0.058814</td>
<td>0.120066</td>
<td>0.116409</td>
<td>0.075716</td>
<td>0.062235</td>
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Table 2. The normal and oblique valleys effective mass calculations for PbSrSe barrier material

<table>
<thead>
<tr>
<th>T (PbSrSe)</th>
<th>Eg(x, T)</th>
<th>ml, e</th>
<th>mt, e</th>
<th>ml, h</th>
<th>mt, h</th>
<th>meN</th>
<th>mhN</th>
<th>meo</th>
<th>mho</th>
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<td>0.0764</td>
<td>0.049693</td>
<td>0.040845</td>
</tr>
<tr>
<td>150</td>
<td>0.420527</td>
<td>0.082437</td>
<td>0.049692</td>
<td>0.079926</td>
<td>0.040382</td>
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<td>0.079926</td>
<td>0.051987</td>
<td>0.042731</td>
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<tr>
<td>200</td>
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<td>0.051194</td>
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<td>0.041602</td>
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<td>0.042822</td>
<td>0.087419</td>
<td>0.084757</td>
<td>0.055129</td>
<td>0.045313</td>
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<td>300</td>
<td>0.458665</td>
<td>0.08991</td>
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<td>0.087172</td>
<td>0.044042</td>
<td>0.08991</td>
<td>0.087172</td>
<td>0.0567</td>
<td>0.046604</td>
</tr>
</tbody>
</table>

Figure 2. The energy levels as a function of well width at 200K for the normal and oblique valleys.

The first four energy parabolic and non-parabolic energy levels were calculated, however, only the first two energy levels were compared to the experimental data that is available from Figure 1. Also, the emitted wavelengths were calculated for all four energy levels and compared to the experimental data. The normal valley calculations for a single quantum well with well width of 30nm at 200K are shown in Table 3 and those for
the oblique valleys are shown in Table 4. The experimental and theoretical values are closely matched with small variations that could be due to the experimental setup or the original effective mass values used in the calculations. The energy levels as a function of well width at 200K taking into account the bands non-parabolicity effects are shown in Figure 2. It is noticed that the degeneracy splitting is more obvious for higher energy levels and less obvious for the first energy level and it is always higher for the oblique valleys due to the lighter effective masses of the electrons and holes. Also, the effect of non-parabolicity is more obvious for the higher energy levels as explained in previous work [9].

Table 3. The transition energy levels and emitted wavelengths from the normal valley states at 200K and well width of 30nm

<table>
<thead>
<tr>
<th>Energy levels</th>
<th>Transition energy (eV)</th>
<th>λ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parabolic</td>
<td>Non-parabolic</td>
</tr>
<tr>
<td>1st</td>
<td>0.244</td>
<td>0.244</td>
</tr>
<tr>
<td>2nd</td>
<td>0.268</td>
<td>0.264</td>
</tr>
<tr>
<td>3rd</td>
<td>0.306</td>
<td>0.294</td>
</tr>
<tr>
<td>4th</td>
<td>0.358</td>
<td>0.328</td>
</tr>
</tbody>
</table>

Table 4. The transition energy levels and emitted wavelengths from the oblique valley states at 200K and well width of 30nm

<table>
<thead>
<tr>
<th>Energy levels</th>
<th>Transition energy (eV)</th>
<th>λ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parabolic</td>
<td>Non-parabolic</td>
</tr>
<tr>
<td>1st</td>
<td>0.248</td>
<td>0.248</td>
</tr>
<tr>
<td>2nd</td>
<td>0.28</td>
<td>0.274</td>
</tr>
<tr>
<td>3rd</td>
<td>0.338</td>
<td>0.314</td>
</tr>
<tr>
<td>4th</td>
<td>0.418</td>
<td>0.364</td>
</tr>
</tbody>
</table>

5. Summary and Conclusion

In this study, we calculated the effective electron and hole masses in the normal and oblique valleys of PbSe/Pb_{0.934}Sr_{0.066}Se single quantum well laser. These values were used to calculate the first four energy levels of the system taking into consideration the non-parabolicity of the bands. The theoretical values for the emitted wavelengths were verified with the experimental values, and hence we conclude that the theoretical model used and determined effective masses can predict accurate results.
References


