Photoluminescence Spectral Analysis of GaInAsSb
Semiconductor Layers

Lori Small and Shanthi Iyer

Department of Electrical Engineering,
North Carolina A&T State University, Greensboro, NC 27411

Abstract

A program was written to simulate the peaks using a combination of the Gaussian and Lorentzian distributions. Each peak was simulated and normalized separately over the entire range and then all the data were added together to produce the final spectra. The fitting parameters used were peak intensity, half width, and wavenumber. In order to identify the origin of the spectral peaks, temperature dependence and incident intensity dependence was analyzed. Subroutines were included in the spectral program evaluating the Bimberg, Shockley-Rheed, and Varshni relationships as well as output intensity as a function of input intensity. Error analysis was done using the least-square method. This was performed within the program itself so that the error was calculated for each run. The best fit was then determined by comparing the analytical data to the experimental data and minimizing the error.

Report

The energy band diagram of a semiconductor material consists of a conduction band and a valence band which are separated by a forbidden energy gap. In intrinsic material, the valence band states are completely filled while the conduction band states are empty at 0 K. In the forbidden energy gap there are no allowed states for the occupation of electrons. The width of the energy gap determines the concentration of carriers in the conduction and valence bands and consequently the conductivity of the crystal. The smaller the gap, the less energy required to excite an electron from the valence band to the conduction band. Conductors have small energy gaps or overlapping conduction and valence bands which result in relatively high concentrations of free electrons. Semiconductors have a larger energy gap and, therefore, higher energies are required to excite the valence electrons. Finally, insulators have large energy gaps (≥3 eV) resulting in negligible electron concentrations in the conduction band.1 If impurities or defects are present, additional energy levels are introduced which may accept or donate electrons and contribute to the number of available carriers. Several types of defects are possible, but substitutional impurities are most important with respect to the effect on the available free carriers. A substitutional defect occurs when a regular crystal atom is replaced by an impurity atom. If the impurity atom has more valence electrons than the crystal atom, it can donate the extra electrons to the conduction band with the requirement of a relatively small amount of energy. Accordingly, this donor energy level is located just below the conduction band within the forbidden energy gap. When an electron is excited from the valence band to the conduction band, a hole is formed which is free to recombine with another electron. However, when a donor electron is excited to the conduction band, no hole is generated in the valence band. In contrast, if the impurity atom has fewer valence electrons than the crystal atom, an acceptor energy state results. In other words, an electron can easily be excited from the valence band, generating a hole, without increasing the conduction band electron concentration. Thus, the acceptor energy level is located slightly above the valence band level within the forbidden energy gap.2 As electrons lose energy and drop to lower energy levels, photons are emitted resulting in a distinctive photoluminescence spectra depending upon the type of transitions involved.

An important impurity interaction with the surrounding crystal lattice is the deformation potential, or irregular stress on the lattice due to the differing size of the impurity atom. If the impurity is larger than the regular crystal atom, lattice dilation results. In contrast, if the impurity atom is smaller, lattice compression occurs. These deformations affect the activation energy, or gap energy. The energy will increase with compression and decrease with dilation. Another impurity-related effect is that of band tailing: the perturbation of the energy bands by forming tails of states extending into the forbidden energy gap. This occurs when an ionized donor atom exerts attractive and repulsive forces on the conduction electrons and the valence holes, respectively. An acceptor
atom will react conversely to induce the tailing. This causes the lower energy values of the spectral peak to broaden considerably. Finally, the presence of impurities may also cause bound excitons to exist. At low temperature, electron-hole pairs may be generated which are loosely associated and are free to move together. This phenomenon is referred to as a free exciton. If the pair encounters an impurity, it will be localized at the site of the impurity resulting in a bound exciton. The binding energy of these excitons depends upon the binding energy of the impurities. Spectral peak origin, or the type of transition which gives rise to the peak, can be identified through analysis of the spectra. This information is useful when analyzing sample purity for device applications. At low temperatures, most photoluminescence spectra exhibit Gaussian or Lorentzian distributions. If the transition is from a discrete energy level to another, the resulting peak will be sharp or Lorentzian in nature. On the other hand, if a spread of energy levels is involved, a broader or Gaussian peak will result. The origin of the peaks can be further characterized by examining the temperature-dependent functions such as the Bimberg, Shockley-Rheed, and Varshni relationships. The incident intensity dependence can also aid in identifying the transitions involved. GaInAsSb samples were prepared by liquid phase electro-epitaxy and experimental data were taken at Wright Patterson Lab in Dayton, Ohio. A program was then written in FORTRAN to simulate the spectra, first, with respect to the Gaussian and Lorentzian behaviors, second, the temperature-dependent functions, and, finally, the incident intensity effects. The analytical and experimental data were then compared to determine the origins of the photoluminescence spectral peaks. The results were graphed using IDL and the error was calculated using the least square method.

Initially, each peak of the experimental spectra was simulated using the Gaussian or Lorentzian distributions (Eq. 1 and Eq. 2, respectively) where peak intensity was a function of wavenumber:

\[
I = \frac{I_0}{(2\pi)^{3/2}} \frac{\exp \left\{ -(X-X_0)^2 \right\}}{2\sigma^2} \tag{1}
\]

where \(2.355\sigma = \Delta_{ik}\)

\[
I = \frac{I_0}{2\pi} \frac{1}{(X-X_0)^2+(\sigma/2)^2} \tag{2}
\]

where \(\sigma = \Delta_{ik}\)

Then each peak was normalized over the entire range and all the data were added to produce the final spectra. The fitting parameters were sigma (a function of the peak halfwidth), wavenumber, and maximum peak intensity. These parameters were entered at execution and manipulated until a good fit was attained. For those spectra that had considerable noise, a "noise level" parameter was added over the entire range. In analyzing the β sample at 4.2K, three obvious peaks were identified (Fig. 1). The first peak, at the highest energy level, is most likely a bound exciton (BE) transition. In addition, the second peak, at a lower energy level, has also been identified as a bound exciton (BE) recombination. Finally, impurity-related donor or band to acceptor level transitions (BA) yield a peak at the lowest energy level shifted by approximately 33 meV.

The relationship between incident intensity and output intensity was studied. The slope of the log-log plot is related to the probability of recombination which is a function of the number of holes and electrons generated. Since the number of holes generated for a band-band transition is equal to the number of electrons, a slope of two would be expected. In contrast, if a donor-acceptor or band-acceptor transition is involved, the recombination process depends only upon the number of electrons generated and hence a slope of one is expected. A plot was made for the band-acceptor peak (Fig. 1), and as expected, the band-acceptor peak gave a slope of 1.00 (Fig. 2).

The binding energy of the bound exciton can be determined using Bimberg's equation (Eq. 3), which uses
Fig. 2 PL intensity dependence on laser intensity for a band-acceptor transition (slope = 1.00)

Fig. 3 Bimberg plot ($C_1 = 2.4$, $C_2 = 1706$, $E_1 = 1.1$ meV, $E_2 = 9.9$ meV)

Fig. 4 Activation energy plot for a band-band transition ($E_a = 20.1$ meV)

the three level Boltzmann distribution:

$$I = \frac{I_0}{1+C_1 \exp(-\Delta E_1/KT)+C_2 \exp(-\Delta E_2/KT)}$$

Again, this sample appears to have donor and acceptor impurities, so bound excitons are present. Free excitons are close to the conduction band and can only be resolved if the crystal quality is good. Bimberg's formula relates the simultaneous transitions of the bound and free excitons. The fitting parameters were the constants $C_1$ and $C_2$, which are a function of the density of states for the impurity levels, and the individual activation energies associated with each transition. A good fit was made for the deeper bound exciton in Fig. 1 with $C_1=2.4$, $C_2=1706$, $E_1=1.1$ meV, and $E_2=9.9$ meV (Fig. 3). These values are in good agreement with those reported in the literature for GaSb by Rühle et al. This confirms the assignment of this peak as bound exciton.

The activation energy of the band-band transition is determined using Eq. [4]:

$$I = I_0 \exp(\Delta E/kt)$$

where $k$ is Boltzmann's constant

A plot of the log of the intensity versus the inverse of the temperature yields a slope whose value is directly proportional to the activation energy. The band to band transition at higher temperatures exhibited an activation energy of approximately 20 meV as shown in Fig. 4. This value was lower than the activation energy of the impurity and hence is attributed to nonradiative recombination within the semiconductor, a process which does not result in the emission of a photon. This is not unusual, and a similar result has also been obtained in another quaternary InGaAsP system. Such nonradiative recombination processes will decrease the device efficiency. An empirical relationship derived from the activation energy equation defines intensity as a function of temperature with respect to a device temperature, $T_0$. 

529
Fig. 5 Determination of $T_o$ for a band-band transition ($T_o = 82K$) which represents a characteristic temperature related to the threshold current density, a measure of device efficiency (Eq. 5):

$$I = I_0 \exp \left(-\frac{T}{T_o}\right)$$

The higher the $T_o$ value, the lower the threshold current for the device. A simulation of the band to band transition yielded a value for $T_o$ of approximately 82K (Fig. 5) which is consistent with the value of 80K reported by Caneau et. al on a similar device.

The Shockley-Rheed equation describes the photoluminescence (PL) peak shape which depends upon the density of states, the transition probability, and the occupational probability of the free carriers (Eq. 4):

$$I = (\hbar \omega - E_g)^a \exp\left(-\frac{(\hbar \omega - E_g/kT)}{(\hbar \omega)^2}\right)$$

The fitting parameters were the energy gap ($E_g$), the temperature, and the maximum peak intensity. The analytical peak was simulated and normalized over the entire range. A good fit was made for the gamma sample at 40K with an $E_g$ of 660.1 meV (Fig. 6). The value of $E_g$ was $kT/2$ less than the PL peak energy.

The temperature dependence of the energy gap was examined using Varshni's relation (Eq. 7):

$$E_g = E_{g0} - \frac{\alpha T^2}{\beta + T}$$

This equation relates the transition energy as a function of temperature. It is a measure of lattice dilation effects and electron-phonon interactions which both increase at higher temperatures resulting in a narrowing of the energy gap. This information is an indication of the drift of the emitted radiation with temperature which is useful when considering device applications. The third peak of Fig. 1 was simulated with a best fit using the $E_g$ of 703.84 meV and $\alpha$ and $\beta$ values of 0.471 meV/K and 309.5 K respectively (Fig. 6). These values are close to that of GaSb.

Error analysis was performed for all the functions using a least-square-fit method. First, an approximate fit was made quickly by overlaying the graphs. Then each parameter was further refined. This was done by comparing the experimental and analytical data until the sum square of the dependent variable error was minimized yielding the statistical best fit. This was done by squaring the difference of the analytical and experimental $y$ values for a given $x$ value and then summing them over the range examined. The tolerance levels were determined by finding the smallest possible change in each of the fitting parameters which would create a significant difference in the error value. However, this error analysis was not useful for the Shockley-Rheed function due to the band tailing and subsequent broadening of the spectral peak at lower energies.

In summary, the three major peaks analyzed for this sample appear to correspond, first, to a band-acceptor (or donor-acceptor) transition at the lowest energy, then, a bound exciton transition, and, finally, another bound exciton transition at the highest energy level. Overall the
crystal quality was fairly good considering the complex quaternary structure and the sharp bound exciton peaks. In conclusion, the program successfully simulated the Gaussian and Lorentzian peak intensity distributions, the temperature-related functions, and the incident intensity relationships and was useful in analyzing the sample spectra.

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References: