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TWO-PHOTON ABSORPTION IN BULK SEMICONDUCTORS AND QUANTUM WELL STRUCTURES AND ITS APPLICATIONS

by

HIMANSU SHEKHAR PATTANAIK
M.S. University of Central Florida, 2008

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Optics and Photonics: CREOL & FPCE at the University of Central Florida Orlando, Florida

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ABSTRACT

The purpose of this dissertation is to provide a study and possible applications of two-photon absorption (2PA), in direct-gap semiconductors and quantum-well (QW) semiconductor structures. One application uses extremely nondegenerate (END) 2PA, for mid-infrared (mid-IR) detection in uncooled semiconductors. The use of END, where the two photons have very different energies gives strong enhancement compared to degenerate 2PA. This END-2PA enhanced detection is also applied to mid-IR imaging and light detection and ranging (LIDAR) in uncooled direct-gap photodiodes. A theoretical study of degenerate 2PA (D-2PA) in quantum wells, QWs, is presented, along with a new theory of ND 2PA in QWs is developed.

Pulsed mid-IR detection of femtosecond pulses is investigated in two different semiconductor p-i-n photodiodes (GaAs and GaN). With the smaller gap materials having larger ND-2PA, it is observed that they have better sensitivity to mid-IR detection, but unwanted background from D-2PA outweighs this advantage. A comparison of responsivity and signal-to-background ratio for GaAs and GaN in END-2PA based detection is presented. END-2PA enhancement is utilized for CW IR detection in uncooled GaAs and GaN p-i-n photodiodes.

The pulsed mid-IR detection experiments are further extended to perform mid-IR imaging in uncooled GaN p-i-n photodetectors. A 3-D automated scanning gated imaging system is developed to obtain 3-D mid-IR images of various objects. The gated imaging system allows simultaneous 3-D and 2-D imaging of objects. The 3-D gated imaging system described in the dissertation could be used for examination of buried structures (microchannels, defects etc.) or laser written volumetric structures and could also be suitable for in-vivo imaging applications in
biology in the mid-IR spectral region. As an example, 3-D imaging of buried semiconductor structures is presented.

A theoretical study of D-2PA of QWs for transverse electric (TE) and transverse magnetic (TM) fields is carried out and an analytical expression for the D-2PA coefficient in QWs using second-order perturbation theory is derived. A theory for ND-2PA in QW semiconductor using second-order perturbation theory is developed for the first time and an analytical expression for the ND-2PA coefficient for TE, TM, and the mixed case of TE and TM is derived. The shape of the 2PA curve for the D-2PA and ND-2PA for QWs in the TE case is similar to that of bulk semiconductors. As governed by the selection rules both the D-2PA and ND-2PA curves for the TE case does not show a step-like signature for the density of states of the QWs whereas 2PA curve for the TM case shows such step like sharp features. The ND-2PA coefficient for TE, TM, and the mixed case is compared with that obtained for bulk semiconductors. Large enhancement in ND-2PA of QW semiconductors for the TM case over bulk semiconductors is predicted.
This dissertation is dedicated to my parents, my wife, and my brother extremely patient and supportive with me during all these years.
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<th>Description</th>
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<tr>
<td>2PA</td>
<td>Two-Photon Absorption</td>
</tr>
<tr>
<td>3PA</td>
<td>Three-Photon Absorption</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter ($10^{-2}$ m)</td>
</tr>
<tr>
<td>D-2PA</td>
<td>Degenerate Two-Photon Absorption</td>
</tr>
<tr>
<td>eV</td>
<td>Electron-Volt unit of energy</td>
</tr>
<tr>
<td>fs</td>
<td>Femtosecond ($10^{-15}$ s)</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>kHz</td>
<td>Kilohertz ($10^{3}$ Hz)</td>
</tr>
<tr>
<td>µJ</td>
<td>Microjoule ($10^{-6}$ J)</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer ($10^{-6}$ m)</td>
</tr>
<tr>
<td>ND-2PA</td>
<td>Nondegenerate Two-Photon Absorption</td>
</tr>
<tr>
<td>END-2PA</td>
<td>Extremely Nondegenerate Two-Photon Absorption</td>
</tr>
<tr>
<td>nJ</td>
<td>Nanojoule ($10^{9}$ J)</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer ($10^{-9}$ m)</td>
</tr>
<tr>
<td>NLA</td>
<td>Nonlinear Absorption</td>
</tr>
<tr>
<td>NLR</td>
<td>Nonlinear Refraction</td>
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<tr>
<td>OPA</td>
<td>Optical Parametric Amplifier</td>
</tr>
<tr>
<td>OPG</td>
<td>Optical Parametric Generator</td>
</tr>
<tr>
<td>pJ</td>
<td>Picojoule ($10^{12}$ J)</td>
</tr>
<tr>
<td>ps</td>
<td>Picosecond ($10^{12}$ s)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>QW</td>
<td>Quantum Well</td>
</tr>
<tr>
<td>SVEA</td>
<td>Slowly-Varying Envelope Approximation</td>
</tr>
<tr>
<td>TE</td>
<td>Transverse Electric</td>
</tr>
<tr>
<td>TM</td>
<td>Transverse magnetic</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>WLC</td>
<td>White-Light Continuum</td>
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CHAPTER 1: INTRODUCTION

The field of nonlinear optics describes the interaction between light and matter, where the light is of sufficiently high intensity to modify the optical properties of the material. Over the years there are many aspects of nonlinear light-matter interactions which have been explored experimentally and theoretically with a variety of proposed models. Considerable research has led to the development of optical devices based on nonlinear optics which once was more of a laboratory investigation subject but are now part of everyday life. There has been a continuous effort to find materials with large nonlinearities to improve the efficiency and performance of nonlinear optical devices.

The main purpose of this work to study and utilize the two-photon absorption (2PA) process in semiconductors for device applications. Multiphoton-processes are predicted by Dirac [1] and have been studied and understood after the seminal work of Göppert-Mayer [2]. 2PA processes occur by simultaneous annihilation of two-photons and exciting an electron transition to higher levels which is described by second-order perturbation theory. There are numerous applications of the two-photon absorption process like detection [3], optical limiting [4], microfabrication [5], two-photon fluorescence microscopy [6], [7] and optical switching [8]. Semiconductors are excellent nonlinear materials and show large third-order nonlinear properties. These third-order nonlinearities are well studied [9] and utilized in a variety of applications e.g. optical switching [8][10].

Applications related to two-photon absorption based devices require the availability of experimental data on semiconductors. There has been a considerable amount of work on 2PA of semiconductors to create an extensive database. Many theoretical models are presented and
further refined over the years to predict and explain the experimental data. The success of theoretical models is based on the formulations which provide a thorough explanation of the physical processes behind these phenomena. The availability of a large amount of data on 2PA of semiconductors led to the formulation of scaling laws which reasonably predict the degenerate and nondegenerate 2PA coefficient in direct-gap semiconductors [11]. The scaling laws showed that the large 2PA for degenerate 2PA (D-2PA) occurs for narrower bandgap materials as it depends on the inverse cube of the bandgap ($\propto E_{\text{gap}}^{-3}$). Due to this inverse cube band-gap dependence the large D-2PA coefficient for narrow bandgap materials e.g. InSb show orders of magnitude enhancement over wide bandgap materials e.g. GaN and GaAs. Thus for high 2PA coefficients we are limited to use only narrow bandgap materials and are restricted to applications that uses only mid-IR photons. The theory for nondegenerate 2PA (ND-2PA) using a 2-parabolic band model showed that these large 2PA coefficients can be obtained in wide bandgap materials provided we use two-photons of very different photon energies. The large increase in the 2PA coefficient for ND-2PA is similar to the intermediate state resonance enhancement (ISRE) seen in molecules[2]. In wide bandgap materials for ND-2PA the intermediate states can lie either in the valence band or conduction band and there are two-resonances that work: one when the energy of one of the photons becomes close to the bandgap which becomes resonant to the interband transitions and the second is where the other photon energy becomes resonant with the intraband transitions. In such an extreme nondegenerate (END) case when the two-photons are of very different energies the large 2PA values are accessible for wide bandgap materials in the near-IR and visible regions [12].

Large 2PA coefficients are attractive for quite a few applications. One application is absorption based all-optical switching [13]. A straightforward application is to use a mid-IR
pulse and turn on or turn off the detector response by irradiating with sub-bandgap photons. This led to the use of wide bandgap materials e.g GaN p-i-n photodiode, for the gated detection of femtosecond mid-infrared (mid-IR) pulses by Fishman et al [3]. Before this work, the detection using 2PA in semiconductors was limited to using degenerate [14] or slightly nondegenerate [15] 2PA and used a photomultiplier tube (PMT) or avalanche photodiode (APD). In this work the enhancement using nondegenerate ND 2PA is used to detect continuous wave (CW) IR radiation when keeping the detector on indefinitely by using a CW “gate” and detect IR radiation in the staring mode. Another application carried out in this thesis is gated scanning 3-D mid-IR imaging using extremely nondegenerate 2PA (END-2PA) in GaN photodiodes. To show the feasibility of the technique several fairly reflecting objects are scanned and 3-D images are obtained. Since going to the END case enhances the 2PA coefficient over the D-2PA coefficient in bulk materials, we investigated END-2PA enhancement in quantum well (QW) semiconductors due to their large density of states. The literature on 2PA of QW structures so far is directed only toward the study of D-2PA properties of QWs [16]–[20]. A theoretical study of D-2PA properties of QWs is derived here using second-order perturbation theory. Analytical expression for the D-2PA coefficient of QWs for the case where the two-photon are transverse electric (TE) polarized and the case where the two-photons are transverse magnetic (TM) polarized are derived. In this thesis our effort is to develop, for the first time, the theory for ND-2PA for QWs. The theoretical formulation is carried out using second-order perturbation theory. Three different cases TE, TM, and the mixed case of TE and TM of ND-2PA in QWs are investigated and analytical expressions for the ND-2PA coefficients for all the three cases are derived. The shape of the ND-2PA spectra as obtained from theory for the TE case in a QW semiconductor is similar to that for bulk semiconductors and not much enhancement of the ND-
2PA coefficient is seen over the ND-2PA coefficient values for bulk. Similarly, not much enhancement of the ND-2PA coefficient is obtained in the mixed case of TE and TM in a QW in comparison to bulk semiconductors. The theory for ND-2PA for the TM case in the QW predicts large enhancement over the bulk semiconductor values.

1.1. Dissertation outline

Chapter 2 provides a general background to understand the nonlinear response of bulk semiconductors. Bound electronic nonlinearities arising from $\chi^{(3)}$ emphasizing 2PA are discussed as they provide the background for detection using 2PA. Chapter 3 provides details of the laser systems. Chapter 4 provides a brief summary of different theoretical approaches for calculations of 2PA. Chapter 5 provides a detailed discussion of D-2PA and ND-2PA in direct-gap semiconductors. A brief review of previous theoretical and experimental results for direct-gap semiconductors is provided. Chapter 6 describes the pulsed and CW IR detection using END-2PA in uncooled GaN and GaAs p-i-n photodetectors. The parameters such as responsivity and signal-to-background ratio are discussed. With the END-2PA a gated scanning 3-D mid-IR imaging in an uncooled GaN p-i-n photodetector is performed in Chapter 7. The usefulness of this technique for obtaining images of buried structures is discussed. Chapter 8 provides the theoretical formulation for D-2PA and ND-2PA in QW semiconductors. For the first time a comprehensive theoretical approach for TE, TM and the mixed case of TE and TM of ND-2PA in QWs is presented. A comparison of 2PA in bulk and QW semiconductors is provided. Finally in Chapter 8 the work in this thesis is summarized and possible future work that can be carried out based on this work is discussed.
CHAPTER 2: NONLINEAR RESPONSE IN SEMICONDUCTORS

Nonlinear effects involves group of phenomenon which results from interaction of sufficient intense light fields with matter. Invention of ruby laser by Maiman led to interest in number of experiments and led to discovery of new phenomena which provided better understanding of the fundamentals of the light and matter interactions. The birth of the field of nonlinear optics came only after the invention of such highly coherent and intense light sources. The first nonlinear optical effect was observed by Franken et al, in 1961 using ruby laser [21], where they showed it is possible to generate a coherent output from a coherent input light source. In the experiment the group showed second harmonic generation at the ruby laser wavelength using crystalline quartz. Soon after the publication their result there were plethora experiments carried out using laser sources to study the nonlinear effects in different materials. The nonlinear effects can be observed in any medium provided the medium is driven enough by the intense fields to show such effects. So requirement of intense coherent sources such as laser is very essential.

The nonlinear response in a material system to an intense laser field give rise to nonlinear polarization which gives rise to new frequency components originally not present in the incident field. The new frequency components of polarization act as source of new frequencies of the electromagnetic field. The nonlinear interaction of the laser and the material can be described by Maxwell’s equations written as

\[ \nabla \cdot \mathbf{D} = \rho \]  \hspace{1cm} (2.1)

\[ \nabla \cdot \mathbf{B} = 0 \]  \hspace{1cm} (2.2)

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]  \hspace{1cm} (2.3)
\[ \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} \]  

(2.4)

Our interest in the solution lies in the region where there are no free charges, \( \rho = 0 \) and free currents, \( \mathbf{J} = 0 \). It is assumed that the medium is nonmagnetic, \( \mathbf{B} = \mu_0 \mathbf{H} \) and since the material is nonlinear the \( \mathbf{D} \) and \( \mathbf{E} \) are related by \( \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \), where in general \( \mathbf{P} \) depends nonlinearly upon the local value of the electric field strength. Under these assumptions taking the curl of Equation (2.3) we obtain

\[ \nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \mathbf{P}}{\partial t^2} \]  

(2.5)

The nonlinear polarization can be written as a convolution integral of the incident electric field and the susceptibility [22]

\[ \mathbf{P}(\mathbf{r}, t) = \varepsilon_0 \int_{-\infty}^{\infty} \chi^{(1)}(\mathbf{r} - \mathbf{r}', t - t') \mathbf{E}(\mathbf{r}', t') d\mathbf{r}' dt' \]

\[ + \varepsilon_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(2)}(\mathbf{r} - \mathbf{r}', t - t'; \mathbf{r} - \mathbf{r}'', t - t'') \]

\[ \times \mathbf{E}(\mathbf{r}', t') \mathbf{E}(\mathbf{r}'', t'') d\mathbf{r}' d\mathbf{r}'' dt' dt'' \]

\[ + \varepsilon_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(3)}(\mathbf{r} - \mathbf{r}', t - t'; \mathbf{r} - \mathbf{r}'', t - t''; \mathbf{r} - \mathbf{r'''}, t - t''') \]

\[ \times \mathbf{E}(\mathbf{r}', t') \mathbf{E}(\mathbf{r}'', t'') \mathbf{E}(\mathbf{r'''}, t''') d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' dt' dt'' dt''' \]

\[ + \ldots \]  

(2.6)

where \( \chi^{(n)} \) is the \( n \)th order susceptibility, \( \varepsilon_0 \) is the permittivity of free space. A convenient way to describe the nonlinear polarization is to shift the analysis into Fourier space by Fourier transforming the Equation (2.6) which turns the convolution into a simple product.
\[ P(\omega) = \varepsilon_0 \chi^{(1)}(\omega) E(\omega) \]
\[ + \varepsilon_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(2)}(\omega; \omega_q, \omega_p) E(\omega_q) E(\omega_p) \delta(\omega - \omega_q) \]
\[ - \omega_p d\omega_q d\omega_p \]
\[ + \varepsilon_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(3)}(\omega; \omega_r, \omega_q, \omega_p) E(\omega_r) E(\omega_q) E(\omega_p) \delta(\omega - \omega_r) \]
\[ - \omega_q - \omega_p d\omega_r d\omega_q d\omega_p + \cdots \] (2.7)

where \( E(\omega) \) and \( P(\omega) \) are Fourier transform of the real, time varying electric field \( E(t) \) and \( P(t) \) respectively. The susceptibilities \( \chi^{(n)} \) are complex quantities and provide information on optical properties of the medium and predict all nonlinear effects. In the present notation of \( \chi^{(n)} \), e.g. \( \chi^{(3)}(\omega; \omega_r, \omega_q, \omega_p) \) implies energy conservation of the input arguments, \( \omega = \omega_p + \omega_q + \omega_r \).

The linear and nonlinear terms in Equation (2.7) can be described by an appropriate model to a physical situation for calculation of susceptibility. Since we are interested in electronic nonlinearities simple anharmonic oscillator model can be used but for a proper calculation full quantum mechanical description is required. The quantum mechanical description requires interaction of electron and field by means of a perturbed Hamiltonian. In chapter 4 some specific cases of electron-field interaction will be discussed.

The power expansion of the polarization described in Equation (2.7) corresponds a local and instantaneous response. For bound electronic nonlinearities referred as pure \( \chi^{(n)} \) effects the response time is ultrafast (< fs) (faster than the pulse duration in measurement) but there are also other nonlinear effects which have varying magnitude of response times e.g. thermal effects (~ ns) and electrostriction (~ ns). In Equation (2.7) \( \chi^{(1)} \) corresponds to 1\(^{st} \) order susceptibility which give rise to the complex linear refractive index, \( \chi^{(2)} \) corresponds to 2\(^{nd} \) order susceptibility and
related to second harmonic generation, sum frequency generation, difference frequency generation, and optical rectification, etc, \( \chi^{(3)} \) corresponds to 3rd order susceptibility which can give rise to third-harmonic generation, four-wave mixing, coherent stokes raman scattering, coherent anti-stokes raman scattering, nonlinear refractive index \( (n_2) \), and two-photon absorption etc., \( \chi^{(5)} \) corresponds to three-photon absorption. Out of the mentioned effects of, \( \chi^{(3)} \) nonlinearity, the particular interest in this work is two-photon absorption which occurs at the incident optical frequency

Let us consider incident electric field consist of two copolarized monochromatic plane waves at frequency \( \omega_a \) and \( \omega_b \) given by

\[
E(r, t) = \hat{e} \frac{1}{2} E_a e^{(i k_a \cdot r - \omega_a t)} + \hat{e} \frac{1}{2} E_b e^{(i k_b \cdot r - \omega_b t)} + c.c
\]  

(2.8)

where \( E_a \) and \( E_b \) are complex electric field amplitudes, \( k_a \) and \( k_b \) are wave vectors, and \( \hat{e} \) unit vector in the polarization direction of the electric field, \( c.c \) represents complex conjugate of the 1st two terms. Using this expression for electric field in for the \( \chi^{(3)} \) term in Equation (2.7) the nonlinear polarization is obtained as

\[
P^{(3)}(\omega_a) = \hat{e} \frac{1}{2} p_a^{(3)} e^{(i k_a \cdot r - \omega_a t)} + c.c
\]  

(2.9)

The various terms in the expression for the nonlinear polarization are

- \( E^3(\omega_a) \) or \( E^3(\omega_b) \) corresponds to third-harmonic generation process with the energy conservation, \( \omega = 3\omega_a \) or \( \omega = 3\omega_b \).
- \( (|E(\omega_a)|^2 + |E(\omega_b)|^2)E(\omega_a) \) or \( (|E(\omega_a)|^2 + |E(\omega_b)|^2)E(\omega_b) \) corresponds to the intensity dependent terms, which contains the self-nonlinear terms \( \left( (|E(\omega_a)|^2 E(\omega_a)) \text{ or } (|E(\omega_b)|^2 E(\omega_b)) \right) \) acting on the same input frequency (two-
photon absorption ($\alpha_2$) and nonlinear refractive index ($n_2$)) and the cross-nonlinear terms acting on the other frequency \( \left( |E(\omega_b)|^2 E(\omega_a) \right) \) or \( \left( |E(\omega_a)|^2 E(\omega_b) \right) \) with the energy conservation, \( \omega = \omega_a + \omega_a - \omega_a = \omega_b + \omega_b - \omega_b \) or \( \omega = \omega_b + \omega_a - \omega_a = \omega_b + \omega_b - \omega_b \).

- \( E^2(\omega_a)(E(\omega_b) + E^*(\omega_b)) \) or \( E^2(\omega_b)(E(\omega_a) + E^*(\omega_a)) \) corresponds to coherent stokes raman scattering and coherent anti-stokes raman scattering with the energy conservation, \( \omega = 2\omega_a \pm \omega_b \) or \( \omega = 2\omega_b \pm \omega_a \).

Since our particular interest lies in the two-photon absorption terms, the nonlinear third-order polarization is written as

\[
P^{(3)}(\omega_a) = \frac{3}{4} \varepsilon_0 \chi^{(3)}(\omega_a; \omega_a, -\omega_b, \omega_a) |E(\omega_a)|^2 E(\omega_a)
+ \frac{6}{4} \varepsilon_0 \chi^{(3)}(\omega_a; \omega_b, -\omega_b, \omega_a) |E(\omega_b)|^2 E(\omega_a)
\]

\[
(2.10)
\]

and

\[
P^{(3)}(\omega_b) = \frac{3}{4} \varepsilon_0 \chi^{(3)}(\omega_b; \omega_b, -\omega_b, \omega_b) |E(\omega_b)|^2 E(\omega_b)
+ \frac{6}{4} \varepsilon_0 \chi^{(3)}(\omega_b; \omega_a, -\omega_b, \omega_b) |E(\omega_a)|^2 E(\omega_b)
\]

\[
(2.11)
\]

In Equation (2.10) and (2.11) intrinsic permutation symmetry is utilized which implies, the order in which fields are applied makes no physical difference to the final result. The first terms in Equation (2.10) and (2.11) corresponds to self-nonlinearities and the second terms in Equation (2.10) and (2.11) corresponds to cross-nonlinearities.

The expression for nonlinear polarization can be substituted in the wave propagation equation (Equation (2.5)) and with the slowly varying envelope approximation (SVEA), which
means the complex field amplitudes almost constant in space and time over one optical cycle, the propagation of the complex electric fields $E_a$ and $E_b$ is given by

$$\frac{\partial E_a(z, \omega_a)}{\partial z} = i \frac{\omega_a}{2 \varepsilon_0 n_a c} P_a^{(3)}(z, \omega_a) e^{i\Delta k z}$$

$$\frac{\partial E_b(z, \omega_b)}{\partial z} = i \frac{\omega_b}{2 \varepsilon_0 n_b c} P_b^{(3)}(z, \omega_b) e^{i\Delta k z}$$

(2.12)

(2.13)

where $\varepsilon_0$ is the permittivity of empty space, $n_a$ and $n_b$ are refractive indices at optical frequencies $\omega_a$ and $\omega_b$ respectively. Writing $E_a(z, \omega_a) = \rho_a(z)e^{i\phi_a^{NL}(z)}$ and $E_b(z, \omega_b) = \rho_b(z)e^{i\phi_b^{NL}(z)}$, the Equation (2.12) and Equation (2.13) becomes

$$\frac{\partial \rho_a(z)}{\partial z} + i \rho_a(z) \frac{\partial \phi_a^{NL}(z)}{\partial z} = i \frac{\omega_a}{2 n_a c} \chi^{(3)}(\omega_a; \omega_a, -\omega_a, \omega_a) \rho_a^3(z)$$

$$+ \frac{6}{4} \chi^{(3)}(\omega_a; \omega_b, -\omega_b, \omega_a) \rho_a^2(z) \rho_b(z)$$

(2.14)

$$\frac{\partial \rho_b(z)}{\partial z} + i \rho_b(z) \frac{\partial \phi_b^{NL}(z)}{\partial z} = i \frac{\omega_b}{2 n_b c} \chi^{(3)}(\omega_b; \omega_b, -\omega_b, \omega_b) \rho_b^3(z)$$

$$+ \frac{6}{4} \chi^{(3)}(\omega_b; \omega_a, -\omega_a, \omega_b) \rho_b^2(z) \rho_a(z)$$

(2.15)

where $\rho_{a,b}^2(z) = |E_{a,b}(z, \omega_{a,b})|^2 = (2/\varepsilon_0 n_{a,b} c) I_{a,b}(z)$, $I_a(z)$ and $I_b(z)$ are the irradiances, and $\phi_a^{NL}(z)$ and $\phi_b^{NL}(z)$ is the induced nonlinear phase change of the waves at frequency $\omega_a$ and $\omega_b$ respectively due to third-order susceptibility $\chi^{(3)}$. Since $\chi^{(3)}$ is a complex quantity it can be written as
\[ \chi^{(3)} = \chi^{(3)}_{\text{R}} + \chi^{(3)}_{\text{I}} \] (2.16)

The real part, \( \chi^{(3)}_{\text{R}} \) gives nonlinear refraction (NLR) and imaginary part, \( \chi^{(3)}_{\text{I}} \) gives nonlinear absorption (NLA). From Equation (2.14), the irradiance and nonlinear phase change of beam with frequency \( \omega_a \) is written as.

\[ \frac{\partial I_a(z)}{\partial z} = -\alpha^2(\omega_a; \omega_a)I^2_a(z) - 2\alpha^2(\omega_a; \omega_b)I_a(z)I_b(z) \] (2.17)

\[ \frac{\partial \phi^{\text{NL}}_a(z)}{\partial z} = k_{0,a}n_2(\omega_a; \omega_a)I_a(z) + 2k_{0,a}n_2(\omega_a; \omega_b)I_b(z) \] (2.18)

where \( k_{0,a} \) is the vacuum wave number, \( \alpha^2(\omega_a; \omega_a) \) and \( n_2(\omega_a; \omega_a) \) are the self-nonlinearities of the wave at \( \omega_a \), \( \alpha^2(\omega_a; \omega_b) \) and \( n_2(\omega_a; \omega_b) \) are the cross-nonlinearities of the wave at \( \omega_a \) due to \( \omega_b \). \( \alpha^2 \) and \( n_2 \) are related to \( \chi^{(3)} \) by

\[ \alpha^2(\omega_a; \omega_b) = \frac{3\omega_a}{2\varepsilon_0n_a n_b c^2} \chi^{(3)}_{\text{I}}(\omega_a; \omega_b, -\omega_b, \omega_a) \] (2.19)

\[ n_2(\omega_a; \omega_b) = \frac{3}{4\varepsilon_0n_a n_b c} \chi^{(3)}_{\text{R}}(\omega_a; \omega_b, -\omega_b, \omega_a) \] (2.20)

where \( n_2 \) is the nonlinear refractive index and \( \alpha^2 \) is the two-photon absorption coefficient (2PA). The parameters \( \alpha^2 \) and \( n_2 \) are calculated from quantum mechanical descriptions [11], [23]–[25] and are determined in experiments [12] using Equation (2.17) and (2.18) respectively.
CHAPTER 3: LASER SYSTEMS

The experiments carried out in this work use a femtosecond laser source. The main laser source is used to pump the tunable devices which are based on white light generation (WLC), optical parametric generation and amplification (OPG/OPA) to get broad range wavelengths. To extend the tunability range further, frequency doubling, difference frequency generation (DFG) are frequently employed using the output from main laser and the tunable devices.

In this chapter the laser system and the tunable parametric devices used in the experiments will be discussed in detail.

3.1. Laser systems and parametric devices

The femtosecond laser used in the experiment is a Clark MXR CPA-2010 system. The oscillator is an Erbium doped fiber ring laser operating at 1550 nm and at 27 MHz repetition rate. The pump source is an all solid-state fiber-coupled laser diode operating at 1550 nm. A temperature-stabilized periodically poled Lithium Niobate (PPLN) crystal acts as a frequency doubler and converts output of the oscillator to 775 nm. The output seed pulse at 775 nm is stretched using a reflection diffraction grating before the amplification stage to lower the peak power level and to prevent damage of the gain medium. The pulse entering the amplifier cavity is controlled by an electro-optics modulator (Pockel cell) which at a time allows a single pulse to enter the cavity. The gain medium is Ti:Sapphire crystal and it is pumped by a Q-switched frequency doubled Nd:YAG laser operating at 532 nm and 1kHz repetition rate. The amplification of the pulse takes place after multiple passes through the Ti:Sapphire gain cavity extracting the stored energy in the gain medium. Once the pulse energy amplified to the required...
level \((\approx mJ)\) the pulse is dumped out of the cavity by the pockel cell. The pulse is then compressed using a grating. This results in an output with energy \(\approx 1.03 \text{ mJ}\) per pulse at 1 \text{kHz} repetition rate and of pulse width \(\approx 150 \text{ fs(FWHM)}\). The process in which a short pulse is stretched then amplified and finally compressed is known as chirped pulse amplification (CPA).

![Layout of the Ti:Sapphire regenerative amplifier.](image)

Figure 3.1 Layout of the Ti:Sapphire regenerative amplifier. L-lens, M-mirror, PC-pockel cell, FR-Faraday rotator, B24-mirror, B25-mirror.

The parametric device used in the experiments is a TOPAS-C model by Light Conversion Ltd. It has a two stage parametric amplifier of white-light continuum. A full layout of TOPAS-C is shown in Figure 3.2. It consist of several subunits: 1) pump beam delivery and splitting optics (PO), 2) white-light continuum generator (WLG), 3) a pre-amplifier or first amplification stage (PA1), 4) a signal beam expander-collimator (SE) and 5) a power amplifier or second amplification stage (PA2).

In the laboratory the TOPAS-C is pumped by \(\approx 900 \mu\text{J}\) of 150 fs femtosecond pump pulse at 780 nm. As shown in Figure 3.2, ‘1’ denotes the input pump beam out of which \(1-3 \mu\text{J}\) is used as WLG pump beam ‘3’ and \(30-50 \mu\text{J}\) is used as the pump ‘4’ for the first amplification (PA1) stage. The whitelight continuum (WLC) is produced on a sapphire plate. The pump beam
‘4’ \((30 - 50 \mu J)\) along with WLC beam are focused into the pre-amplifier crystal. These two beams are synchronized and allowed to overlap inside the 1st nonlinear crystal (NC1) non-collinearly for parametric amplification. A non-collinear geometry is adopted for ease of separation of amplified signal beam ‘6’. A beam blocker is used thereafter to block the residual pump and idler beam. A lens telescope expands further the signal beam ‘6’ and collimate into the second amplification stage (PA2). The size of the pump beam ‘2’ is reduced by lens-mirror telescope to achieve the necessary pump intensity. Collimated pump and signal beams after the telescope are then overlapped collinearly into a 2nd nonlinear crystal (NC2). As a result the TOPAS-C produces collinear well collimated signal and idler beams. As per the requirement additional frequency mixers at TOPAS-C output can be incorporated facilitating the tuning range into visible, ultra violet and/or infrared.

Figure 3.2 Layout of TOPAS-C. 1-Input pump beam, 2-PA2 pump beam, 3-WLG pump beam, 4-PA1 pump beam, 5-White-light beam, 6-signal beam. M-mirror, DM-dichroic mirror, A-aperture, L-lens, VF-variable filter, TD-time delay, NC-nonlinear crystal, and BS-beam splitter.

To achieve the wavelength tuning in the pre-amplifier stage the delay of the white light pulse is changed with respect to the first pump pulse and the crystal angle is adjusted for optimal phase-matching. A well-defined sequence is followed for wavelength tuning in the power-
amplifier. First the pre-amplifier wavelength is adjusted, then 2\textsuperscript{nd} crystal angle and signal delay is adjusted with respect to the 2\textsuperscript{nd} pump beam. A programmable computer controlled “translation and rotation stages” are incorporated within the TOPAS C for fast and precise control of movement of crystal and delay lines during tuning of output wavelength.
CHAPTER 4: THEORETICAL APPROACHES FOR CALCULATING TWO-PHOTON ABSORPTION

Theories are developed to understand the underlying physics behind a particular phenomenon. The correctness of the particular theory lies in the fact that, how accurately it predicts the experimental observations. Based on the experiments further improvements of the particular theory are done or new theories are developed to match the experimental data. Sometimes the lack of sophistication in experiments undermines a particular theory and need to wait for further advancements in experimental techniques and tools to verify the usefulness of the particular theory.

The theoretical models for two-photon absorption were predicted way before the possibility of its experimental measurements. It’s only the invention of laser that led to measurement and verification of theoretical approaches for such an ultrafast process. The advancement in the development of highly stable tunable short pulse sources led to the prediction of theory with many degrees of accuracy and better agreement with the experiments. The predicted enhancement in 2PA [11], [23] for extreme nondegenerate cases were measured and verified only after availability of ultrashort laser systems.

In this chapter main theoretical approaches for calculating two-photon absorption rates in semiconductor are discussed. One of such theoretical model will be used in Chapter 8 for development of theory D-2PA and ND-2PA in infinitely high QWs.
4.1. Electron-field interaction

The optical process such as one-photon absorption and emission in bulk semiconductor and QW structures is described by interaction of these physical systems with the electric field of the incident light where the interaction between the electrons and the photons in the semiconductor is described by a total Hamiltonian \((H)\) [26]

\[
H = \frac{1}{2m_0} (p - eA)^2 + V(r)
\]  

(4.1)

where \(m_0\) is the free electron mass, \(e\) is the electronic charge, \(A\) is the vector potential of the electromagnetic field, \(V(r)\) is the potential, and \(p\) is the momentum of the electron. The Hamiltonian in Equation (4.5) can be expanded to

\[
H = \frac{p^2}{2m_0} + V(r) - \frac{e}{2m_0} (p.A + A.p) + \frac{e^2 A^2}{2m_0} = H_0 + H_{int}
\]  

(4.2)

where is \(H_0\) the unperturbed Hamiltonian and \(H_{int}\) is the interaction Hamiltonian given as

\[
H_0 = \frac{p^2}{2m_0} + V(r)
\]  

(4.3)

\[
H_{int} \approx - \frac{e}{m_0} A.p
\]  

(4.4)

In deriving Equation (4.4) Coulomb gauge, \(\nabla.A = 0\) has been used such that \(p.A = A.p\). The last term \(e^2 A^2/2m_0\) is smaller than terms linear in \(p\), since \(|eA| \ll |p|\) for most practical intensities and the term \(e^2 A^2/2m_0\) can be ignored. The form of interaction Hamiltonian described in Equation (4.4) will be used for calculation of two-photon absorption (2PA) coefficient of QWs in Chapter 8.
4.2. Perturbation theory approach

The phenomenon of 2PA is described by interaction of electrons and intense laser fields. Perturbation theory approach is one of the method of calculating 2PA coefficient ($\alpha_2$). For an $n$ level system described by an unperturbed time independent Hamiltonian $\hat{H}_0$, the time independent Schrödinger equation is written as $\hat{H}_0|\Psi_n\rangle = E_n|\Psi_n\rangle$, where $E_n$ and $|\Psi_n\rangle$ are the eigenvalues and eigenstates of the unperturbed system respectively. The temporal evolution of the system at a later time $t$ is given by $|\Psi(t)\rangle$ which satisfies the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle \quad (4.5)$$

$|\Psi(t)\rangle$ can be written as a linear superposition of the eigenstates

$$|\Psi(t)\rangle = \sum_n c_n |\Psi_n\rangle e^{-iE_n t/\hbar} \quad (4.6)$$

where $c_n$ are the complex amplitudes, and $|c_n|^2$ gives the probability of finding the system in $|\Psi_n\rangle$. With the small perturbation $\hat{H}_{int}(t)$ the coefficients $c_n$ becomes time dependent. Thus $|\Psi(t)\rangle$ is written as

$$|\Psi(t)\rangle = \sum_n c_n(t) |\Psi_n\rangle e^{-iE_n t/\hbar} \quad (4.7)$$

The time-dependent Schrödinger equation then becomes

$$i\hbar \frac{\partial}{\partial t} \sum_n c_n(t) |\Psi_n\rangle e^{-iE_n t/\hbar} = (\hat{H}_0 + \hat{H}_{int}(t)) \sum_n c_n(t) |\Psi_n\rangle e^{-iE_n t/\hbar} \quad (4.8)$$

Taking the inner product with $|\Psi_m\rangle e^{-iE_m t/\hbar}$ on both sides using the orthonormality condition for eigenstates, Equation (4.8) becomes
\[
\frac{i\hbar}{\partial t} c_m(t) = \sum_n c_n(t) \langle \Psi_m | \hat{H}_{\text{int}}(t) | \Psi_n \rangle e^{i(E_m - E_n)t/\hbar}
\]  

(4.9)

Equation (4.9) allows us to calculate the probability of finding the system in a state \( m \) at an arbitrary time \( t \) by calculating the probability \( |c_m(t)|^2 \). For a system with many eigenstates finding a solution for \( |c_m(t)|^2 \) becomes very difficult. To simply the problem \( c_m(t) \) expanded in a power series \( c_m(t) = c_m^0(t) + c_m^1(t) + c_m^2(t) + \cdots \), where \( c_m^1(t) \) and \( c_m^2(t) \) are 1\(^{st} \) and 2\(^{nd} \) order term corresponds to corrections to unperturbed solution of Equation (4.5). The approach described is generic for any kind of perturbation, which in our case is the electromagnetic field.

The 1\(^{st} \) order term \( c_m^1(t) \) describes transitions between two electronic states due to one-photon. The 2\(^{nd} \) order term \( c_m^2(t) \) describes two-photon transitions between the two electronic states. Similarly higher order terms describe multi-photon transitions. The transition rate \( W \) as described by Fermi’s Golden rule from an initial state \( |\Psi_i \rangle \) to a final state \( |\Psi_f \rangle \) is given by

\[
W_{n}^{i\rightarrow f} = \frac{d|c_f^n(t)|^2}{dt}
\]  

(4.10)

where \( c_f^n(t) \) denotes the \( n \)th order corrections for \( n \)-photon transitions. For two-photon transitions involving two different photon energies \( \hbar \omega_1 \) and \( \hbar \omega_2 \) the transition rate from an initial state \( |\Psi_i \rangle \) to final state \( |\Psi_f \rangle \) is given by given by

\[
W_2 = \frac{2\pi}{\hbar} \left| \sum_j \left[ \frac{\langle \Psi_f | H_{2\text{int}} | \Psi_j \rangle \langle \Psi_j | H_{1\text{int}} | \Psi_i \rangle}{E_{ji}(\mathbf{k}) - \hbar \omega_1} + \frac{\langle \Psi_f | H_{1\text{int}} | \Psi_j \rangle \langle \Psi_j | H_{2\text{int}} | \Psi_i \rangle}{E_{ji} - \hbar \omega_2} \right] \right|^2 \delta(E_f - E_i - \hbar \omega_1 - \hbar \omega_2)
\]  

(4.11)
where the summation is over all the intermediate states $|\Psi_j\rangle$. The two-photon transition rate is related to 2PA coefficient by the relation

$$\alpha_2(\omega_1; \omega_2) = \frac{\hbar \omega_1 W_2}{2I_1 I_2}$$

where $I_1$ and $I_2$ represent irradiance of beams at photon energy $\hbar \omega_1$ and $\hbar \omega_2$ respectively. The expression in Equation (4.12) is used in chapter 8 for calculation of ND-2PA coefficient in QWs.
CHAPTER 5: TWO-PHOTON ABSORPTION IN SEMICONDUCTORS

Two-photon absorption (2PA) is a $\chi^{(3)}$ process which occurs in semiconductors through annihilation of two-photons of the same photon energy (Degenerate (D)) or different photon energies (nondegenerate (ND)) creating an electron-hole pair. D-2PA properties of semiconductors have been extensively studied both theoretically and experimentally [12]. In early years, due to the lack of laser sources at different wavelengths, 2PA spectra of semiconductors were only available in limited spectral ranges. There were also discrepancies in the published D-2PA data. The advent of sophisticated experimental techniques and laser systems and the availability of broadband continuum sources have led to extensions of the spectral range in the published data [11], [27], [28]. The large amount of experimental data also helped refinements in the earlier theoretical models for D-2PA and established scaling rules which provided accurate prediction of D-2PA in semiconductors [11].

5.1. Degenerate two-photon absorption (D-2PA)

Chapter 4 describes various methods for the theoretical calculation of the 2PA spectra in direct-gap semiconductors. In condensed materials such as semiconductors the electronic levels form continuous bands and the initial and final states for transitions lie within the valence and conduction bands respectively. The two-photon transition rate as obtained from second order perturbation theory is

$$W^D_2 = \frac{2\pi}{\hbar} \sum_{vc} \left| \sum_i \langle c | \hat{H}_{int} | i \rangle \langle i | \hat{H}_{int} | v \rangle \right|^2 \delta(E_{cv}(k) - \hbar\omega)$$  (5.1)
where \( v \) and \( c \) represent valence band and conduction band respectively, \( i \) represents intermediate states, \( \hat{H}_{int} \) is the electron-field interaction Hamiltonian, \( E_{cv}(k) \) is the energy difference between the valence and conduction bands. The summation is over all possible intermediate states \( i \) and over all possible transitions starting from filled states in the valence band to empty states in the conduction band, i.e. a sum over electronic wave vector \( (k) \) and the bands. Since in the semiconductors there are no states within the gap, it is shown by Wherrett et al [24] that the transitions that dominate the two-photon transition process are for the case where the intermediate states lie within the valence and conduction bands. This leads to two-photon transition processes in semiconductors described as an interband transition (valence to conduction band) followed by an intraband (self) transition, or vice versa as shown in Figure 5.1.

![Figure 5.1 Transition paths shown for 2PA in semiconductors correspond to interband (line) and intraband (circle), or vice versa.](image)

For this 2-parabolic band model the D-2PA coefficient is obtained as

\[
\alpha_2^D(\omega) = K \frac{\sqrt{E_p}}{n^2 E_{gap}^3} F_2^D \left( \frac{\hbar \omega}{E_{gap}} \right)
\]

(5.2)
where $\alpha_2^D(\omega)$ is the D-2PA coefficient for optical frequency $\omega$, $E_{gap}$ is the bandgap energy, $E_p$ is the Kane energy, and $K = 3100 \, cmGW^{-1}eV^{5/2}$ is a material independent constant, $n$ is the refractive index at frequency $\omega$. The theory predicted well the experimental results as shown in Figure 5.2 [4], [11].

![Figure 5.2 Scaled 2PA coefficient vs. bandgap energy($E_{gap}$) taken from reference [11].](image)

The solid line fit has a slope ‘$-3$’.

In Figure 5.2 a comparison of scaled values of $\alpha_2^D$ is shown for different semiconductors which follow $E_{gap}^{-3}$ dependence. Figure 5.2 suggested that the D-2PA coefficient values measured in wide-bandgap semiconductors can be increased by orders of magnitude in narrow gap semiconductors e.g InSb and InAs [27], [29], [30]. Such increase in D-2PA coefficient can be seen by looking at the two-photon transition rate equation
\[ W_{2}^{D} \propto \left| \frac{M_{cv} M_{vv}}{-\hbar \omega} + \frac{M_{cc} M_{cv}}{\hbar \omega} \right|^2 \]  

(5.3)

where \( M_{vv,cc} \) and \( M_{cv} \) are intraband and interband transition matrix elements respectively. For similar systems e.g zinc blende structures, the transition matrix element mainly depends on the symmetry properties of the bands involved [31]. From Equation (5.3) it is observed that for narrow gap semiconductors the orders of magnitude increase in D-2PA (\( \alpha_{2}^{D} \)) coefficient is expected to be obtained for long wavelength photons. For example for large gap semiconductors such as ZnO (3.2 eV), the D-2PA coefficient \( \alpha_{2}^{D} = 5 \text{ cm/GW} \) at 532 nm [28] and for narrow gap semiconductors such as InSb, the D-2PA coefficient \( \alpha_{2}^{D} = 2 \text{ cm/MW} \) in the range 8 \( \mu \text{m} \) to 12 \( \mu \text{m} \) [12], [32].

5.2. Nondegenerate two-photon absorption (ND-2PA)

The high value of nonlinearities obtained in narrow gap semiconductors is limited in operation to the mid-infrared (mid-IR) region and hence not accessible in the near-infrared (near-IR) or visible region due to linear absorption. It is also possible to obtain such high nonlinearities in wide-bandgap semiconductors if the two-photons are of very different energies. For this nondegenerate case it has been shown that, for extreme nondegenerate (END) case there is orders of magnitude enhancement in the nondegenerate two-photon absorption (ND-2PA) coefficient over the D-2PA coefficient in direct-gap semiconductors [12], [23] The increase in ND-2PA coefficient for END case can be understood qualitatively from the nondegenerate two-photon transition rate obtained from second order perturbation theory.
\[ W_{2}^{ND} = \frac{2\pi}{\hbar} \frac{2}{V} \sum_{vc} \left[ \sum_{i} \left( \frac{\langle c | H_{2\text{int}} | i \rangle \langle i | H_{1\text{int}} | v \rangle}{E_{iv}(\mathbf{k}) - \hbar \omega_{1}} + \frac{\langle c | H_{1\text{int}} | i \rangle \langle i | H_{2\text{int}} | v \rangle}{E_{iv}(\mathbf{k}) - \hbar \omega_{2}} \right) \right]^{2} \delta(E_{cv}(\mathbf{k}) - \hbar \omega_{1} - \hbar \omega_{2}) \]  

where 1 and 2 represent indices for the two different photons, \( v \) and \( c \) represents valence band and conduction band respectively, \( i \) represents intermediate states, \( \hat{H}_{\text{int}} \) is the electron-field interaction Hamiltonian, \( E_{cv}(\mathbf{k}) \) is the energy difference between the valence and conduction bands, \( \hbar \omega_{1} \) and \( \hbar \omega_{2} \) are the photon energies. The summation is over all possible intermediate states \( i \) and over all possible transitions starting from filled states in the valence band to empty states in the conduction band, i.e. a sum over electronic wave vector (\( \mathbf{k} \)) and the bands. As discussed in the D-2PA section for semiconductors the intermediate states lie within the valence and conduction bands. In END-2PA there are actually two resonances which lead to divergence of the expression in Equation (5.4). The large energy photon becomes close to one-photon resonant and the smaller photon energy becomes near resonant to self-transitions, i.e. zero energy resonance. The nondegenerate two-photon transition paths in semiconductors are similar to the degenerate processes described as an interband transition (valence to conduction band) followed by an intraband (self) transition, or vice versa as shown in Figure 5.3. For a 2-parabolic band model the intermediate state can either be in the valence band \( (E_{iv}(\mathbf{k}) = 0) \) or conduction band \( (E_{iv}(\mathbf{k}) = \hbar \omega_{1} + \hbar \omega_{2}) \) and the nondegenerate transition rate can be written explicitly by considering all the possible transition paths (Figure 5.3) for the system [12]

\[ W_{2}^{ND} \propto \left| \frac{M_{cv}^{2} M_{vv}^{1}}{-\hbar \omega_{1}} + \frac{M_{cv}^{1} M_{cv}^{2}}{-\hbar \omega_{2}} + \frac{M_{cc}^{2} M_{cv}^{1}}{\hbar \omega_{1}} + \frac{M_{cc}^{1} M_{cv}^{2}}{\hbar \omega_{2}} \right|^{2} \]  

(5.5)
where $M_{vv}^{1,2}$ and $M_{cc}^{1,2}$ are intraband and $M_{cv}^{1,2}$ are interband transition matrix elements respectively given by $M_{ji}^{1,2} = \langle j | H_{\text{int}} | i \rangle$.

![Diagram](image)

Figure 5.3 Transition paths shown for ND-2PA in semiconductors correspond to interband (line) and intraband (circle), or vice versa.

An interesting fact observed from Equation (5.5) is that each of the transition paths shown in Figure 5.3 yields a term that diverges when one of the photon energies of the two-photon pair becomes small. In END-2PA as one of the photon energies becomes small the enhancement observed is similar to intermediate state resonance enhancement observed in molecular systems [33], [34].

In chapter 4 a couple of approaches have been discussed for calculations of the ND-2PA coefficient. ND-2PA coefficients ($\alpha_{2}^{ND}$) can be derived by directly calculating the two-photon transition rate ($\alpha_{2}^{ND}$) from second-order perturbation theory (Equation (5.5)) by using the relation

$$\alpha_{2}^{ND}(\omega_1; \omega_2) = W_{2}^{ND} \frac{\hbar \omega_1}{2 I_1 I_2}$$  \hspace{1cm} (5.6)

A simple 2-parabolic band model can be used to find an expression for $\alpha_{2}^{ND}$, which has predicted well the shape of the ND-2PA curve and is scaled to match the experimental results.
Better accuracy can be obtained by employing a complex 4-band model (heavy-hole, light-hole, split-off) which didn’t require scaling and successfully predicted the experimental results for structures exhibiting zincblende symmetry [23], [35]. Another approach discussed in reference [11] is the work based on Keldysh’s tunneling theory which uses a scattering matrix formalism with Volkov-type “dressed” electronic states in order to account for the effect of the electric field on the system [36] and used first-order perturbation theory to calculate the $\alpha_{2}^{ND}$. The results predicted by this method provide similar ND-2PA spectra as obtained by perturbation theory and $\alpha_{2}^{ND}$ values matching experimental results. The expression for the ND-2PA coefficient ($\alpha_{2}^{ND}$) for a 2-parabolic band model is written as

$$
\alpha_{2}^{ND}(\omega_{1}; \omega_{2}) = K \frac{\sqrt{E_{p}}}{n_{1}n_{2}E_{gap}^{3}} F_{2}^{ND} \left( \frac{\hbar \omega_{1}}{E_{gap}}, \frac{\hbar \omega_{2}}{E_{gap}} \right)
$$

(5.7)

where

$$
F_{2}^{ND}(x_{1}; x_{2}) = \frac{(x_{1} + x_{2} - 1)^{3/2}}{2^{7/2}x_{1}^{2/3}x_{2}^{2/3}} \left( \frac{1}{x_{1}} + \frac{1}{x_{2}} \right)^{2}
$$

(5.8)

$E_{gap}$ is the bandgap energy, $E_{p}$ is the Kane energy, and $K = 3100 \text{ cm} \text{GW}^{-1} \text{eV}^{5/2}$ is a material independent constant and $n_{1}$ and $n_{2}$ are the refractive indices at frequencies $\omega_{1}$ and $\omega_{2}$.

5.3. Theoretical and Experimental results

There are multiple methods of measuring ND-2PA e.g. pump-probe, 2-color Z-scan, four-wave mixing etc. The data presented in this chapter are taken from reference [12] obtained in a standard non-collinear pump-probe geometry. In the experiment the pump or the excitation beam was chosen to be the longer wavelength photons with photon energies less than 30% of the bandgap energy. This is to ensure that the pump is not depleted through 2PA or three-photon
absorption (3PA). 2PA or 3PA of the pump will create additional carriers which would cause extra loss and complicate the analysis of the experimental data. The propagation equation as obtained in Chapter 2 for the probe beam in the pump-probe experiment is written as

$$\frac{dI_p(\omega_p)}{dz} = -2\alpha_2^{ND}(\omega_p; \omega_e)I_p(\omega_p)I_e(\omega_e) - \alpha_{FCA}(\omega_p)I_p(\omega_p)$$  \hspace{1cm} (5.9)

where $I_e(\omega_e)$ is the irradiance of the excitation or the pump beam which is at the longer wavelength. $I_p(\omega_p)$ is the irradiance of the probe beam which is at the shorter wavelength. Thus absorption happening at the sample during the temporal overlap of pump and probe is solely due to ND-2PA with the loss of one-photon from each beam, which could be modeled for the propagation of the probe beam as per Equation (5.9). In Equation (5.9) the ND-2PA occurs through loss of one photon each from both the beams and the longer wavelength pump gives a higher magnitude of $\alpha_2^{ND}$ which scales with the photon energy as in Equation (5.7). From Equation (5.7) we can observe that the expression for $\alpha_2^{ND}(\omega_p; \omega_e)$ gives rise to a relation $\alpha_2^{ND}(\omega_p; \omega_e)/\alpha_2^{ND}(\omega_e; \omega_p) = \omega_p/\omega_e$. This tells us that even though the rate of photon loss is the same for both beams, the rate of energy loss is larger for the beam with higher photon energy [12]. Figure 5.4 shows semi-log plots of the calculated ND-2PA coefficient $\alpha_2^{ND}(\omega_p; \omega_e)$ for GaAs ($E_{gap} = 1.424$ eV). In Figure 5.4 (a), $\alpha_2^{ND}(\omega_p; \omega_e)$ is plotted against nondegeneracy ($\hbar \omega_p/\hbar \omega_e$) for which the sum of pump and probe photon energies are fixed and for each fixed value of ($\hbar \omega_p + \hbar \omega_e$), $\hbar \omega_p$ and $\hbar \omega_e$ are varied to vary the nondegeneracy ($\hbar \omega_p/\hbar \omega_e$). For higher nondegeneracy there is strong increase of $\alpha_2^{ND}(\omega_p; \omega_e)$ over the D-2PA coefficient ($\hbar \omega_p/\hbar \omega_e = 1$).
Figure 5.4 Semi-log plot of the calculated ND-2PA coefficient ($\alpha_2^{ND}$) showing the enhancement over the D-2PA coefficient: (a) $\alpha_2^{ND} \sim (\hbar \omega_p / \hbar \omega_e)$, where the sum of pump and probe photon energies are fixed and $\hbar \omega_p / \hbar \omega_e = 1$ corresponds D-2PA; (b) $\alpha_2^{ND} \sim (\hbar \omega_p + \hbar \omega_e) / E_{gap}$, for several pump photon energies and the probe photon energy is varied and the D-2PA curve corresponds to $\hbar \omega_p = \hbar \omega_e$.

In Figure 5.4 (b) $\alpha_2^{ND}(\omega_p; \omega_e)$ is plotted against the sum of pump and probe photon energies normalized to the bandgap. Each $\alpha_2^{ND}(\omega_p; \omega_e)$ curve corresponds to a particular pump photon energy and the probe photon energy is varied. For the D-2PA curve, $\hbar \omega_p = \hbar \omega_e$. As the pump photon energy decreases there is a strong increase of $\alpha_2^{ND}(\omega_p; \omega_e)$ over the D-2PA coefficient.

While there is some work carried out on nondegenerate 2PA and data exist from early experiments [31], data for 2PA in the extreme nondegenerate case were carried out only recently [12] where the predicted high enhancements in $\alpha_2^{ND}(\omega_p; \omega_e)$ in direct-gap semiconductors is verified experimentally. Figure 5.5 shows the results of END-2PA spectra taken from reference [12] for GaAs ($E_{gap} = 1.42 \text{ eV}$) and ZnSe ($E_{gap} = 2.67 \text{ eV}$) plotted against the sum of pump and probe photon energies normalized to the bandgap. The results in reference [12] for $\alpha_2^{ND}(\omega_p; \omega_e)$ is obtained through standard noncollinear pump-probe experiments. For
nondegeneracy, $\hbar \omega_e / \hbar \omega_p = 10$ for GaAs, $\alpha_2^{ND}(\omega_p; \omega_e)$ is $\approx 130$ times the D-2PA coefficient, $\alpha_2^D(\omega_e; \omega_e)$. Similarly for ZnSe for nondegeneracy $\hbar \omega_e / \hbar \omega_p \approx 13$, the $\alpha_2^{ND}(\omega_p; \omega_e)$ is $\approx 270$ times the D-2PA coefficient, $\alpha_2^D(\omega_e; \omega_e)$.

![Graphical representation](image)

Figure 5.5 Semi-log plot of END-2PA spectra (a) $\alpha_2^{ND} \sim (\hbar \omega_p + \hbar \omega_e) / 2E_{gap}$ for GaAs

(b) $\alpha_2^{ND} \sim (\hbar \omega_p + \hbar \omega_e) / 2E_{gap}$ for ZnSe. D-2PA spectra for GaAs and ZnSe is also shown for comparison [12]

The $\alpha_2^{ND}(\omega_p; \omega_e)$ values discussed here show similar order of magnitudes as obtained in a narrow gap semiconductor (e.g. InSb) for D-2PA but here we have to use two different wavelengths. Large $\alpha_2^{ND}(\omega_p; \omega_e)$ is obtained by probing closer to the bandgap but that effectively narrows the spectral range. The main limitation that can occur is the linear Urbach tail absorption of the probe, when the probe photon energy is close to the bandgap. Thus we need high quality samples.
CHAPTER 6: INFRARED (IR) DETECTION IN DIRECT-GAP SEMICONDUCTORS USING EXTREMELY NONDEGENERATE TWO-PHOTON ABSORPTION

Infrared (IR) detection using semiconductors in a linear detection mode annihilates a single photon and creates an electron-hole pair, which gives rise to the photocurrent in an external circuit. Semiconductors are also excellent nonlinear materials and show high third-order nonlinear properties, e.g. two-photon absorption (2PA) and nonlinear refraction of nonlinear index $n_2$. Both 2PA and $n_2$ are very well studied [9] and utilized in a variety of applications e.g. all-optical switching (AOS). Semiconductors have been utilized for direct detection in a nonlinear method through 2PA to create an electron-hole pair, which gives rise to a photocurrent. Direct detection by 2PA has been studied previously by many groups but nearly all previous studies have used two equal energy photons, i.e. degenerate, D-2PA [37] or use two-photons of only slightly different energies. In the scheme used by Roth et al [14] the two-photons are degenerate and Boitier et al [15], [38] discuss a case where two-photons are slightly nondegenerate. Roth et al showed a detection scheme of IR radiation using a CW beam at 1.5 $\mu$m in a GaAs PMT and a Silicon APD. The minimum power detectable using this scheme was 1.3 $\mu$W. Boitier et al [38] showed IR detection using CW beams in a GaAs PMT for a slightly nondegenerate scheme. Our previous work including this work is the first reported 2PA [3], [39]–[41] for the case where the two-photons are of very different energies. There has been an extensive study in the past both theoretical and experimental of 2PA in many direct-gap semiconductors [11], [12], [23]. The data predicts orders of magnitude enhancement in the 2PA coefficient ($\alpha_2$) for extremely nondegenerate (END) photons when compared to degenerate 2PA [12]. An important result with a direct application of these high 2PA values in the END cases is
to irradiate a semiconductor photodiode with sub-bandgap photon energy that essentially gates on and off the detection of an IR (or Mid IR) photon, i.e. the sum of the energies of the two photons is greater than the gap and therefore will create carriers via END 2PA. The IR or mid-IR pulse, which by itself does not produce any photodiode response. Based on this principle Fishman et al demonstrated a sensitive gated mid-IR (5.6 \mu m) detection method using femtosecond pulses using END-2PA [3]. The mid-IR pulse detection was carried out using an uncooled GaN p-i-n photodiode in a simple Transimpedance amplifier scheme. The minimum detectable energy of the pulse using the gated detection is \approx 100 \text{ pJ}. However the IR detection scheme based on the END two-photon absorption detection is always accompanied by unwanted D-2PA, producing additional photocarriers, which results in background with additional noise and possible detector saturation. In this chapter the previous work of gated detection of IR pulses is extended and carried out in a material of very different bandgap e.g. GaAs. The theoretical and experimental comparison of results of IR pulsed detection between GaN and GaAs will be presented, which will provide insight into two important characteristics such as responsivity and signal-to-background ratio in END-2PA based detection. It will also be demonstrated that the large enhancement in END-2PA enables detection of continuous wave (CW) IR detection in uncooled wideband-gap photodiodes.

6.1. IR detection in GaN and GaAs using END-2PA

In the END-2PA based detection methodology, the intense beam is called the “gate” beam and the weaker beam is called the “signal” beam. The intense pulse gates the detector ‘on’ by sensitizing the photodetector to the signal pulse as long as it is on via END-2PA. Figure 6.1
shows the scheme for gated IR detection using END-2PA in large bandgap photodiodes where simultaneous absorption of two largely different photon energies creates free electrons and holes in the conduction band and valence band respectively. The gate beam shown in Figure 6.1 could be of high or low energy photons. If the gate beam consists of high-energy photons it allows the detection of mid-IR photons using the large bandgap photodiode. Alternatively if the gate beam consists of low energy photons it allows the detection of sub-bandgap energy photons.

Figure 6.1 Diagram showing gated detection scheme for END-2PA. $\hbar \omega_g$ represents the strong gate beam and $\hbar \omega_s$ represents the weak signal beam.

For mid-IR pulsed detection since the gate pulse is of high photon energy it also creates carriers through D-2PA. Thus the signal obtained from the two-photon generated carrier density $N$ on the photodetector is given by [3]

$$\frac{dN}{dt} = \frac{dN_{ND}}{dt} + \frac{dN_D}{dt} + \frac{dN_U}{dt}$$

$$= 2\alpha_2^{ND}(\omega_s; \omega_g) \frac{I_g I_s}{\hbar \omega_s} + \alpha_2^{D}(\omega_g; \omega_g) \frac{I_g^2}{2 \hbar \omega_g} + \alpha_1^{U}(\omega_g) \frac{I_g}{\hbar \omega_g}$$

(6.1)
\[ \alpha_{2}^{ND}(\omega_s; \omega_g) = K \frac{\sqrt{E_p}}{n_s n_g E_{gap}^3} F_N^{ND} \left( \frac{\hbar \omega_s}{E_{gap}} ; \frac{\hbar \omega_g}{E_{gap}} \right) \]  
\[ \alpha_{2}^{D}(\omega_g; \omega_g) = K \frac{\sqrt{E_p}}{n_g^2 E_{gap}^3} F_N^{D} \left( \frac{\hbar \omega_g}{E_{gap}} \right) \]  

with \( F_N^{ND}(x_1; x_2) = \frac{(x_1 + x_2 - 1)^{1/2}}{2^7 x_1 x_2^2} \left( \frac{1}{x_1} + \frac{1}{x_2} \right)^2 \) and \( F_N^{D}(x) = \frac{(2x - 1)^{3/2}}{(2x)^5} \); \( N_{ND} \) and \( N_D \) are carrier densities due to ND-2PA, D-2PA respectively. \( N_U \) represents carrier density created due to any linear one-photon Urbach tail absorption (1PA) of the gate pulse. \( I_g, \hbar \omega_g \), and \( I_s, \hbar \omega_s \) are irradiances of the gate and signal beams respectively, \( \alpha_{2}^{ND}(\omega_s; \omega_g) \) is the ND-2PA coefficient for optical frequencies \( \omega_s \) and \( \omega_g \), \( \alpha_{2}^{D}(\omega_g; \omega_g) \) is the D-2PA coefficient for optical frequency \( \omega_g \), \( E_{gap} \) is the bandgap energy, \( E_p \) is the Kane energy, and \( K = 3100 \text{ cmGW}^{-1} eV^{5/2} \) is a material independent constant [28].

In END-2PA based detection the photocarriers created through D-2PA present a constant background and hence sets a limit for the minimum value of the ND-2PA signal to be detected.

In reference [3] The mid-IR pulsed detection experiment with extremely nondegenerate pairs of
photons is carried out with a GaN ($E_{gap}^{GaN} = 3.39 \text{ eV}$) p-i-n photodetector. The gate pulse is chosen to be a 390 nm femtosecond pulse (100 fs (FWHM)) and the signal pulse is a 5.6 $\mu$m femtosecond pulse (215 fs (FWHM)). The experimental setup is similar to the standard pump-probe geometry with pump (gate) and probe (signal) interacting noncollinearly on the photodetector (Figure 6.2). The signal on the photodetector is due to both the ND-2PA of the gate pulse and the signal pulse and the D-2PA of the gate pulse. To detect the ND-2PA signal the 1 kHz repetition rate mid-IR pulse is modulated at 283 Hz and discriminated against the unmodulated D-2PA background using synchronous detection [3]. Thus the signal detected is linear in the irradiance of each input beam

$$\frac{dN}{dt} = 2\alpha_2(\omega_s; \omega_g) \frac{l_g l_s}{h\omega_s} = 2 \frac{K\sqrt{E_p}}{n_sn_g E_{gap}^2} F_2^{symm} \left( \frac{\hbar\omega_s}{E_{gap}}, \frac{\hbar\omega_g}{E_{gap}} \right) l_g l_s$$

(6.4)

with $F_2^{symm}(x_1; x_2) = \frac{(x_1 + x_2 - 1)^{3/2}}{2^7 x_1 x_2} \left( \frac{1}{x_1} + \frac{1}{x_2} \right)^2$. The term $F_2^{symm}(x_1; x_2)$ is introduced to show although enhancement in ND-2PA coefficient is not symmetric in input frequencies the detected carrier generation is symmetric in these frequencies, hence the signal enhancement is the same, both for detection of mid-IR and sub-bandgap light. The signal output at the detector is a cross-correlation of the gate pulse and the signal pulse. Figure 6.3 shows results of mid-IR pulsed detection using END-2PA where the output voltage from the GaN detector is plotted against the pulse energy of 5.6 $\mu$m. The plotted voltage values are the zero delay signals between the gate pulse and the signal pulse. As seen from Figure 6.3 the output voltage increases linearly with the increase of the input pulse energy of the mid-IR beam at a constant value of the gate pulse energy as per Equation (6.4). The signals with gated detection in GaN for several values of gate
pulse energies are compared with the output voltage for mid-IR detection from a commercially available liquid-nitrogen-cooled-mercury-cadmium-telluride (MCT) detector.

![Graph showing output voltage vs. input signal pulse energy for different pulse energies and a MCT detector.](image)

Figure 6.3 Linear-linear plot of the output voltage of a GaN p-i-n photodiode versus 5.6 μm(215 fs) input signal pulse energy with 390 nm(100 fs) temporally overlapped gate pulses of the four energies indicated in the figure [3]. The output of the MCT detector is also plotted.

The signal with the gated detection is comparable or even better than results obtained using MCT detector for pulsed detection. The high sensitivity for the pulsed case in using END-2PA technique is attributed to the fact that the infrared signal pulse to be detected is gated with a high photon energy gate pulse so we need to know when to look for the signal pulse. This makes this technique uniquely suitable for LIDAR applications.

To study the similar gated detection with a material of different bandgap, we carried out mid-IR pulsed END detection experiment with a GaAs p-i-n photodetector. The gate pulse is chosen to be of a 920 nm femtosecond pulse (168 fs (FWHM)) and the signal pulse to be a 7.5 μm femtosecond pulse (280 fs (FWHM)). Figure 6.4 shows the results for the detection of
mid-IR pulses of wavelength 7.5 μm. Similar to previous results with GaN, a linear increase of
the signal with the increase of the pulse energy at 7.5 μm is observed.

Figure 6.4 Linear-linear plot of the output voltage of a GaAs p-i-n photodiode versus 7.5 μm(280 fs) input signal
pulse energy with 920 nm(168 fs) temporally overlapped gate pulse [3].

One of the main parameters in the gated detection experiments is the responsivity for different
gate pulse energies. Comparing Equation (6.4) with the carrier generation equation for direct
detection through a one-photon process

$$\frac{dN}{dt} = \alpha_1 \frac{I}{h\omega}$$

(6.5)

we see that for END-2PA detection there is an effective absorption coefficient $2\alpha_2 I_g$. As
observed from the experiments and theory, the signal linearity at the output of the detector is
preserved for a constant gate pulse irradiance. So the responsivity or the quantum efficiency can
be directly controlled via the gate pulse irradiance. For gated detection it is important to know
how one particular material compares to another in terms of responsivity. Based on the band gap
dependence of the two-photon absorption coefficient (Equation (6.2) and Equation (6.3)), it is known that both degenerate two-photon absorption (D-2PA) and extremely nondegenerate two-photon absorption (END-2PA) scales inversely with the bandgap cubed \( (E_{\text{gap}})^{-3} \). So it is expected that detection based on END two-photon absorption should be more sensitive in narrower gap-semiconductors. However the IR detection scheme based on END-2PA is always accompanied by unwanted D-2PA, producing additional photocarriers, which results in a background with additional noise and possible detector saturation. Looking at Equation (6.1) it seems that both \((dN/dt)_{ND}\) and \((dN/dt)_{D}\) scale as \( E_{\text{gap}}^{-4} \) but in the extremely nondegenerate case, since the photon energies are very different and one of the photon energies is close to the bandgap, the two signals don’t scale identically [39]. This can be seen by representing the two photon energies as \( \hbar \omega_s = \Omega \), the IR photon energy and \( \hbar \omega_g = E_g - \delta \) (the gate photon energy), where \( \delta \) is the detuning from the bandgap as shown in Figure 6.5.

![Figure 6.5 Schematic representation of the transition in END-2PA process characterized by small detuning energy (δ).](image)

With these substitutions the expression for the carrier generation due to ND-2PA is written as

\[
\left( \frac{dN}{dt} \right)_{ND} = 2K\sqrt{E_p} \left( \frac{\Omega}{E_{\text{gap}} - E_{\text{gap}}} \right)^{3/2} \left( \frac{E_{\text{gap}}}{\Omega} + \frac{E_{\text{gap}}}{E_{\text{gap}} - \delta} \right)^2 l_g l_s \tag{6.6}
\]
\[
\left( \frac{dN}{dt} \right)_{ND} = 2 \frac{K \sqrt{E_p}}{27 n_g n_s} \frac{(\Omega - \delta)^{3/2}}{E_{gap}^{3/2}} \frac{E_{gap}}{\Omega^2 E_{gap}^2} \left( 1 - \frac{\delta}{E_{gap}} \right) \left( \frac{E_{gap}}{\Omega} + \frac{1}{\frac{\delta}{E_{gap}}} \right)^2 I_g I_s
\]

With the approximations \( \Omega \ll E_{gap} \Rightarrow E_{gap}/\Omega \gg 1 \) and \( \delta \ll E_{gap} \Rightarrow 1 - \delta/E_{gap} \approx 1 \), Equation (6.6) becomes

\[
\left( \frac{dN}{dt} \right)_{ND} \approx 2 \frac{K \sqrt{E_p}}{27 n_g n_s} \frac{(\Omega - \delta)^{3/2}}{E_{gap}^{3/2}} \frac{E_{gap}}{\Omega^2 E_{gap}^2} \left( \frac{E_{gap}}{\Omega} + 1 \right)^2 I_g I_s
\]

(6.7)

Similarly the carrier generation due to D-2PA is written as

\[
\left( \frac{dN}{dt} \right)_{D} = \frac{K \sqrt{E_p}}{27 n_g^2} \left( \frac{1 - 2\delta}{E_{gap}} \right)^{3/2} \frac{E_{gap}}{E_{gap} - \delta})^4 \left( \frac{E_{gap}}{E_{gap} + \delta} \right)^2 I_g I_s
\]

(6.8)

With the approximation \( \delta \ll E_{gap} \Rightarrow 1 - \delta/E_{gap} \approx 1 \), Equation (6.6) becomes

\[
\left( \frac{dN}{dt} \right)_{D} \approx \frac{K \sqrt{E_p}}{27 n_g^2} \frac{1}{E_{gap}^4} I_g^2
\]

(6.9)

Now taking the ratio of \( (dN/dt)_{ND} \) and \( (dN/dt)_{D} \) we obtain

\[
\left. \frac{(dN/dt)_{ND}}{(dN/dt)_{D}} \right|_{exact} = \frac{n_g}{n_s} \left( \frac{\Omega - \delta}{E_{gap} - 2\delta} \right)^{3/2} \left( \frac{E_{gap} - \delta}{\Omega^2} \right) \left( 1 + \frac{E_{gap} - \delta}{\Omega} \right)^2 \frac{I_s}{I_g}
\]

(6.10)

With similar approximations \( \Omega \ll E_{gap} \Rightarrow E_{gap}/\Omega \gg 1 \) and \( \delta \ll E_{gap} \Rightarrow 1 - \delta/E_{gap} \approx 1 \) we obtain the following expression for \( (dN/dt)_{ND}/(dN/dt)_{D} \)

\[
\left. \frac{(dN/dt)_{ND}}{(dN/dt)_{D}} \right|_{approx.} = \frac{n_g}{n_s} \left( \frac{\Omega - \delta}{\Omega^4} \right)^{3/2} \left( E_{gap} \right)^{5/2} \frac{I_s}{I_g}
\]

(6.11)
From Equation (6.11) we observe that even though the signals \((dN/dt)_{ND}\) and \((dN/dt)_D\) scale as \(E_{gap}^{-3/2}\) and \(E_{gap}^{-4}\) respectively, their ratio scales as \(E_{gap}^{5/2}\). From the bandgap scaling of \((dN/dt)_{ND}\) (Equation (6.7)) it is expected that responsivity will be higher for larger bandgap materials. The ratio \((dN/dt)_{ND}/(dN/dt)_D\) (Equation (6.11)) is the signal-to-background ratio and hence is expected to be higher for smaller bandgap materials. In the END-2PA detection scheme the most significant contribution to the noise comes from the fluctuations of the laser pulses contributing to the background D-2PA signal. Even though the signal is discriminated against using synchronous detection, the noise from the background D-2PA of the gate pulse cannot be discriminated and hence affects the signal-to-noise ratio (SNR). The signal-to-background ratio thought does not provide a direct estimation of the SNR but it provides a qualitative idea about how the SNR depends on bandgap\((E_{gap})\). Thus the SNR is expected to be higher for larger bandgap materials considering the amplitude noise contribution of the gate laser in the D-2PA background signal as the dominant contribution to the total noise. This agrees with our experimental results given below.

To obtain the responsivity dependences on bandgap scaling we compared the ND-2PA signals for GaN and GaAs for similar gate irradiances \(\approx 2 \text{ GW/cm}^2\) as shown in Figure 6.6 (a). An order of magnitude increase in the ND-2PA signal voltage is observed for GaAs in comparison to GaN showing higher responsivity for GaAs than GaN. This increase is as expected from Equation (6.7). To calculate the signal to background ratio we show the cross-correlation measurements of the IR pulse and the gate pulse with the separately recorded D-2PA background of the gate pulse for similar signal irradiances \(\approx 0.06 \text{ GW/cm}^2\). As shown in Figure 6.6 (b) at zero delay the voltage is due to the sum of the ND-2PA and D-2PA signals of the gate...
pulse. The signals in regions where the pulses do not overlap temporally correspond to the background D-2PA signal of the gate. The signal-to-background ratio for GaN is $\approx 4.7$ and for GaAs is $\approx 3.2$. The lower ratio for GaAs is due to the larger contribution of the D-2PA of the gate pulse.

Figure 6.6 (a) Comparison of output voltages for GaN and GaAs for similar gate irradiances, (b) Cross-correlation measurements of gate pulse and signal pulse on photodetectors: 920 nm gate (1 $GW/cm^2$) and 7.5 $\mu$m signal ($\approx 0.06 GW/cm^2$) for GaAs and 390 nm gate and 5.6 $\mu$m signal ($\approx 0.06 GW/cm^2$) for GaN.

As observed from theory (Equation (6.4)) and experimental results (Figure 6.3 and Figure 6.4) the responsivity or the quantum efficiency is directly controlled by the gate pulse irradiance. The responsivity increases linearly with an increase in gate pulse irradiance. One possible concern as we go to high gate pulse irradiances is the amount of charge carriers created through D-2PA. Therefore we should choose the gate irradiance level for which the current through D-2PA should not lead to saturation effects. This effect is seen in Figure 6.7 which shows log-log plot of the ND-2PA and D-2PA output voltage for GaAs and GaN for detection of the signal pulse at 920 nm using 7.5 $\mu$m gate pulses and 390 nm using 5.6 $\mu$m gate pulses respectively. The voltage plot due to ND-2PA has slope 1 whereas the voltage plot due to D-2PA has slope 2. Thus
as we increase the input energies at 920 nm and 390 nm the D-2PA curve approaches the ND-2PA. But this approach of D-2PA toward ND-2PA happens at lower input energies for GaAs due to the relative scaling of ND-2PA and D-2PA to $E_{gap}$ (Equation (6.11)).

Figure 6.7 Detection of 920 nm signal pulse by GaAs (7.5 μm gate pulse of $\approx 0.5 \text{ GW/cm}^2$) and of 390 nm signal pulse by GaN (5.6 μm gate pulse of $\approx 0.5 \text{ GW/cm}^2$).

Figure 6.8 (a) Comparison of nondegenerate and degenerate carrier contributions to the photodetector output.

To compare the signal-to-background ratio for GaN and GaAs we compare the ratio of output signal of ND-2PA and the D-2PA to the theoretical curves (calculated using Equation (6.11))
with the experimental parameters. Figure 6.8 shows the ratio of nondegenerate and degenerate carrier contributions to the photodetector output voltage for GaN and GaAs for detection of subband gap radiation for 920 nm signal pulses using 7.5 μm gate pulses for GaAs and 390 nm signal pulses using 5.6 μm gate pulses. The δ for GaN is ≈ 0.1 and for GaAs is ≈ 0.07. Here the D-2PA signal is due to the D-2PA absorption of 390 nm and 920 nm signal pulse for GaN and GaAs respectively. The ratio of the output signal scales as $E_{gap}^{5/2}$ showing experimental agreement with the predicted Equation (6.11) and so is larger for GaN. Also the ratio of output signals scales inversely with the input energy. This inverse variation is due to the linear dependence of the ND-2PA signal on irradiance whereas the D-2PA scales quadratically with irradiance for all direct gap semiconductors [3].

6.2. CW IR detection in GaN and GaAs using END-2PA

In previous section we discussed the case where END 2PA enables mid-IR pulsed detection in uncooled wide-bandgap photodiodes. For pulsed beams a variable delay line is added between the gate beam and the signal beam. The sensitivity of the method is attributed to the fact mid-IR signal pulse is synchronous to the gate pulse where we need to know when to look for the signal pulse. Due to enhancement in the 2PA for extreme nondegenerate photon pairs, it is also possible to use CW beams and detect a CW “signal” beam using a CW “gate” in staring mode [40], [41]. This section describes CW IR detection in uncooled GaN and GaAs p-i-n photodiodes using END-2PA based gated detection technique.
Figure 6.9 shows the configuration for CW IR detection using END-2PA. We carried out experiments for CW IR detection with commercially available GaAs \((E_{gap}^{GaAs} = 1.41 \, eV)\) and GaN \((E_{gap}^{GaN} = 3.39 \, eV)\) p-i-n photodiodes. For GaN the CW “gate” beam is a laser diode source emitting at wavelength 405 nm \((3.06 \, eV = 0.9E_{gap}^{GaN})\) and for GaAs the CW “gate” beam is a laser diode source emitting at wavelength 976 nm \((1.27 \, eV = 0.9E_{gap}^{GaAs})\). The detected IR radiations are from a laser diode sources emitting CW light at near-IR wavelength of 1550 nm \((0.9 \, eV = 0.24E_{gap}^{GaN})\) and at mid-IR wavelength 4890 nm \((0.25 \, eV = 0.18E_{gap}^{GaAs})\) for GaN and GaAs respectively. The 1550 nm source is a DFB InGaAs laser and the 4890 nm source is a quantum cascade laser (QCL). Here the nondegeneracy is not as extreme as reported in pulsed cases. The carrier generation equation as defined before is

\[
\frac{dN}{dt} = \frac{dN_{ND}}{dt} + \frac{dN_D}{dt} + \frac{dN_U}{dt}
\]

\[
= 2\alpha_{2}^{ND}(\omega_s; \omega_g) \frac{l_g l_s}{h \omega_s} + \alpha_{2}^{P}(\omega_g; \omega_g) \frac{l_g^2}{2h \omega_g} + \alpha_{1}^{U}(\omega_g) \frac{l_g}{h \omega_g}
\]

In comparison to the pulsed case, for CW case it is the Urbach tail that leads to a large background signal and the D-2PA is not detectable. Although 405 nm and 976 nm are well below the band edges, the Urbach tail absorption still produces a linear signal with power that is
comparable to the ND-2PA signal of interest. As shown in Figure 6.9 to detect the IR radiation we modulate the IR beams at 250 Hz to suppress detection of any unmodulated signal resulting from the linear absorption of CW “gate” laser wavelengths below the bandgap, i.e. from the Urbach tail absorption, as well as any degenerate 2PA. Figure 6.10 and Figure 6.11 shows the results for CW IR detection with GaN and GaAs p-i-n photodiodes respectively. We observe a linear variation of the ND-2PA signal as the power of the IR beams is increased at a particular value of the CW “gate” laser power as expected from Equation (6.4).

Figure 6.10 Log-log plot of the output voltage of GaN versus power of 1550 nm IR beam at the high energy photon wavelength of 405 nm.

From Figure 6.10 the obtainable minimum detectable power 1550 nm beam with GaN was \( \approx 60 \, \mu W \) for 405 nm laser power of \( \approx 0.22 \, mW \). Similarly the minimum detectable power of the 4890 nm beam observed with GaAs is \( \approx 300 \, \mu W \) for 976 nm laser power of \( \approx 20 \, mW \). The dark current observed in both the detectors is around \( \approx 10 \, \mu V \). We could not go to higher powers of the 405 nm laser as it led to the saturation of the ND 2PA voltage. Also higher powers of CW “gate” can lead to thermal damage of the detector material due to Urbach tail absorption. One
possible way to increase the responsivity to have long interaction lengths between the gate and signal beam which could approach the quantum efficiency of photodetectors based on one-photon absorption.

![Graph showing the output voltage of GaAs versus power of 4890 nm IR beam and data points for different laser powers at 976 nm.]

Figure 6.11 Log-log plot of the output voltage of GaAs versus power of 4890 nm IR beam at the high energy photon wavelength of 976 nm

The results shown Figure 6.10 and Figure 6.11 show that nondegenerate two-photon detection is a viable method for IR detection with uncooled semiconductor detectors where both beams are CW. In the case of gated detection of IR pulses using ND-2PA the background current is primarily due to the D-2PA absorption of the CW “gate” laser whereas in the case of detection of CW IR radiation the background current is primarily due to one-photon Urbach tail absorption below the bandgap. For CW detection, reduction of the background requires using a longer wavelength gate laser so that the Urbach tail is reduced but this also reduces the ND-2PA coefficient and may improve the signal-to-background ratio for CW IR detection.
CHAPTER 7: IR IMAGING IN DIRECT-GAP SEMICONDUCTORS USING EXTREMELY NONDEGENERATE TWO-PHOTON ABSORPTION

The work described in Chapter 6 shows END-2PA is a viable method for mid-IR pulsed detection in uncooled p-i-n photodetectors. In this gated detection method for a particular direct-gap material the gate photon energy determines the spectral range of IR detection. So the same detector material can be used for near-IR as well as mid-IR detection by choosing the appropriate gate photon energy for END-2PA. Also with the choice of direct-gap semiconductor material the detection can be further extended to a broad spectral range. The method described is simple and the process is automatically phase matched so detection for a different wavelength does not require any modification of the detection system similar to direct detection systems through linear absorption. The mid-IR spectral region is very interesting to probe as there are numerous emerging applications of mid-IR wavelength sources since this is the molecular fingerprint spectral region (C-H, N-H, C=O, C-C, CH3, etc.) exhibiting well-defined absorption bands attributed to specific absorbing molecules [42]–[44]. This spectral region for sensing is important for human breath analysis, tissue spectroscopy (collagens, lipids, proteins, glycogens, etc.), and for monitoring of e.g., glucose, water and air pollutants, pharmaceuticals, toxic agents, etc [42]–[46]. There are also important applications in the area of spectral imaging and detection of mid-IR wavelengths: optical coherence tomography has been shown in the mid-IR region for noninvasive monitoring of the structure and biochemical content of engineered tissue during the growth cycle[47], 3-D multispectral stand-off imaging is shown for target discrimination [45], Mid-IR imaging is used as a relevant technique complementing near-IR imaging of biological tissues, etc. [44]. There are two basic modes of carrying out mid-IR spectroscopy and imaging, i)
transmission mode and ii) reflection mode. The reflection mode has potential for clinical diagnostic applications in imaging as it allows in-vivo operation on biological samples. There has been considerable work in near-IR and mid-IR diffuse reflectance imaging [44]. The complementary information of mid-IR reflectance imaging in comparison to near-IR imaging lies in the fundamental difference in the optical properties of the biological samples between these two spectral regions. For most biological tissues, the mid-IR region has an absorption coefficient much larger than the near-IR regions due to the presence of the absorption bands mentioned earlier. But mid-IR beams reflected from biological tissues are scattered much less owing to the wavelength dependence of Rayleigh-like scattering (\(\propto \lambda^{-4}\)) of biological tissues in the mid-IR region. For the near-IR region the scattering is more Mie-like, resulting in greater scattering in the near-IR hence penetrating less deeply into the biological tissues. There is also potential interest in characterization and detection of microstructures manufactured in industrial ceramics e.g. alumina and zirconia for application in microfluidic devices for microreactors, fuel cells, and medical devices, etc. [48]. Su et al. [48] showed an optimal wavelength within the 1.3 \(\mu m\) to 6 \(\mu m\) range for inspection of micromanufacturing of alumina and zirconia based devices. These devices, though not limited to alumina and zirconia, need a mid-IR based imaging system for characterization of internal features. In most of the experiments related to mid-IR imaging, the detection system is a liquid nitrogen cooled HgCdTe (MCT) detector based on linear absorption of the mid-IR light [44]–[47], [49]. Apart from using MCT detectors there are other methods possible for detection of mid-IR light. Frequency up-conversion is one such technique which uses the \(\chi^{(2)}\) nonlinearity of the medium to up-convert IR photons to high energy photons via sum-frequency generation to be detected by high quantum efficiency detectors. Recently Dam et al. [42] showed a highly sensitive field deployable upconversion
device which can acquire mid-IR images between 2.85 and \( \sim 5 \, \mu m \). The system can acquire images of thermal light sources at room temperature and is the first mid-IR single photon imaging device applied to high-resolution spectral imaging. There are few reports of IR detection using D-2PA mainly because of the relatively low quantum efficiency of the process in comparison to linear absorption in a lower bandgap semiconductor photodiode. The reports available have therefore used a photomultiplier tube (PMT) or avalanche photo diode (APD) [14], [15].

The IR up-conversion technique has been shown to be highly efficient with conversion efficiencies now approaching unity, but requires a separate detector and fabrication of periodically poled upconversion crystals for phase matching which can restrict imaging performance [50]–[56]. IR detection described in Chapter 6 using END-2PA is much simpler where the detector element itself is the active material for 2PA. In chapter 6 the discussed mid-IR pulsed detection [3] at 5.6 \( \mu m \) using an uncooled p-i-n GaN photodiode surpassed the response of a HgCdTe detector when using femtosecond IR in combination with 390 nm subgap femtosecond gating pulses. In this chapter the work of mid-IR femtosecond pulse detection is extended to show scanning 3-D mid-IR imaging in an uncooled GaN photodiode using END-2PA. This work demonstrates the feasibility of mid-IR imaging using this technique with uncooled wide-gap commercial photodiodes. To show this proof of principle we have carried out mid-IR imaging on fairly reflecting objects.
7.1. Experimental methods

The experimental configuration for mid-IR pulsed detection is modified to be used for imaging as shown in Figure 7.1. Imaging of IR (both near-IR and mid-IR) scattered from surfaces was performed using a commercial GaN p-i-n photodetector. The IR signal pulse is focused on the object after passing through a chopper and the collected scattered light from the object is focused onto the GaN photodetector.

![Diagram](image)

Figure 7.1 Experimental configuration for 3-D scanning gated IR imaging.

The gate and signal pulses were produced using various nonlinear frequency conversion devices pumped by a regeneratively amplified, 1kHz repetition rate, Ti:Sapphire laser system (ClarkMXR, CPA 2010) producing 780 nm femtosecond pulses ($\approx 1.03 \text{ mJ and } \approx 150 \text{ fs (FWHM)}$). The detailed description of the laser system is provided in chapter 3. The TOPAS-C, Light Conversion Ltd. was used to obtain signal (1100 nm – 1550 nm) and idler (1550 nm – 2640 nm) pulses. The near-IR pulse (1600 nm) is obtained from the idler of the OPG/OPA and the mid-IR pulse (4.93 μm) is obtained by difference frequency generation (DFG) of the signal (1340 nm) and idler (1840 nm) pulses. The pulse widths as measured by
autocorrelation (or cross-correlation) were determined to be $79\, fs (FWHM)$ and $305\, fs (FWHM)$ for $1600\, nm$ and $4.93\, \mu m$ respectively assuming Gaussian temporal profiles which well fit the measured correlation functions shown in Figure 7.2.

![Figure 7.2 Measured pulsewidth of the femtosecond IR pulses.](image)

The GaN p-i-n photodetector ($E_{gap} = 3.43\, eV, \lambda_{gap} = 362\, nm$) purchased from SVT Associates Inc., has an active area of $0.5\, mm^2$ and an intrinsic layer of thickness $0.5\, \mu m$. The p and n-GaN region have thicknesses of $0.5\, \mu m$ and $2\, \mu m$ respectively. The detector was used in the photoconductive mode, with a preamplifier gain factor of 28. The reverse bias voltage was $-2.5\, V$. The gate pulse at $390\, nm$ ($\equiv 0.93E_{gap}$) was obtained by frequency doubling of a portion of the $780\, nm$ Ti: Sapphire output using a BBO crystal. The experiments were carried out in the standard pump-probe geometry with pump and probe (gate and signal) interacting noncollinearly ($< 10^\circ$) on the photodetector. The output voltage from the detector is due to both the ND-2PA of the gate and signal and the D-2PA of the gate. To detect only the IR we modulate the $1\, kHz$ repetition rate IR pulse at $285\, Hz$ and use synchronous detection to record the ND-2PA signal. Thus the signal detected is linear in the irradiance of each input beam [3] as given by following equations:
\[
\frac{dN}{dt} = 2\alpha_2(\omega_s; \omega_g) \frac{I_g I_s}{\hbar \omega_s} = 2 \frac{K \sqrt{E_p}}{n_g n_g} \frac{1}{E_{gap}^4} F^{\text{symm}}_2 \left( \frac{\hbar \omega_s}{E_{gap}} ; \frac{\hbar \omega_g}{E_{gap}} \right) I_g I_s
\]  
(7.1)

with

\[
F^{\text{symm}}_2(x_1; x_2) = \frac{(x_1 + x_2 - 1)^{3/2}}{2^7 x_1^2 x_2^2} \left( \frac{1}{x_1} + \frac{1}{x_2} \right)^2
\]  
(7.2)

The ND-2PA signal results when the IR pulse and the 390 nm gate pulse temporally and spatially overlap at the detector similar to the one described in reference [3].

To obtain the image, the object is raster scanned in the x and y directions (Figure 7.1) and for each (x, y) coordinate the ND-2PA signal from the GaN detector is measured as a function of the relative time delay between the IR pulse and the gate pulses yielding their cross-correlation. The output of the GaN photodetector is fed into a lock-in amplifier and the signal from the lock-in amplifier is stored on a PC using National Instruments (NI) data acquisition card (DAQ). The raster scanning translation stage of the object and the delay stage movements and the recording of cross-correlation data is automated and controlled using Labview software through the NI DAQ card to take data for further processing to obtain the image. The recorded signal contains two imaging modalities which provide two different types of information about the object: 1) A 3-D image is obtained by noting the position of the cross-correlation signal for each (x, y) coordinate, which provides depth information about the object 2) A 2-D image is obtained by recording the photodetector output magnitude at the peak of the cross-correlation curve for each (x, y) coordinate.
7.2. Experimental results

To demonstrate the technique we raster scanned several objects starting from objects with simple surface profiles. The signal pulse was first chosen to be in the near-IR region at 1600 nm. We chose a reflective object as shown in Figure 7.3 (a) to have a large signal-to-noise ratio (SNR) at the photodetector.

![Image](a) Photograph of the object “7”. Area of the raster scanning is shown by dotted line. (b) Cross-correlation of the IR pulse and the gate pulse for two different positions of the object.

The object is made of steel with depressed regions on it. To obtain the image, the object is raster scanned in x and y (Figure 7.1) and for each \((x, y)\) coordinate the cross-correlation signals were recorded. Figure 7.3 (b) shows the cross correlation curves for two different positions on the object. The 3-D image of the object is constructed by noting the peak of the cross-correlation curve for each \((x, y)\) coordinate, which corresponds to various levels of depth of the object in the z-direction (Figure 7.4 (a)). The 2-D image of the object is shown in Figure 7.4 (b) is obtained by recording the magnitude of the peak of the cross-correlation curve for each \((x, y)\) coordinate. The depth resolution on this object \(\approx 5 \mu m\).
To show the usefulness of this technique we scanned a more complex object for which we chose the US 10 cents coin commonly referred to as “dime” (Figure 7.5 (a)). Here the object was scanned with a grid spacing of 250 \( \mu m \times 500 \mu m \) using the 1600 nm signal pulse. From the near IR image of the dime (Figure 7.5 (b)) we can clearly see the surface features of the object.

A similar experimental configuration is used to carry out mid-IR imaging with a 4.93 \( \mu m \) signal pulse. In this setup the near IR beam is replaced by the mid-IR beam. The purpose of choosing 4.93 \( \mu m \) for mid-IR imaging is low atmospheric transmission loss and the availability of a PbSe photodetector, which is sensitive to 4.93 \( \mu m \) for characterization of the mid-IR beam. As before in (Figure 7.3 (a)) for the mid-IR imaging we chose an object (Figure 7.6 (a)) made of
steel with depressed regions on it (“80”). Figure 7.6 shows the 3-D image and 2-D image obtained from the cross-correlation curve as described before. Here the object is raster scanned with a finer grid spacing (80 μm × 80 μm). The 3-D image here is obtained from the peak positions of the cross-correlation signal. From Figure 7.6 we can clearly see the “80” engraved on the object.

Figure 7.6 (a) Photograph of the objet “80”, (b) 3-D reflectance image of the object, (c) 2-D reflectance of the object.

The 3-D images obtained in this work with the ND-2PA technique so far is a surface 3-D image where the object was not moved in the z-direction and the object is opaque for the particular wavelength used, thus scattering most of the incident light which is collected to obtain a 3-D image. Imaging of laser written volumetric structures or any other buried structures could also be obtained using this technique provided the substrate material is transparent to the
wavelength of the signal pulse. To demonstrate the image acquisition of buried structures we chose the object to be a GaAs semiconductor structure (Figure 7.7 (a)) of depth $\approx 21 \mu m$ as measured by a profilometer. The image is obtained by raster scanning the structure with light incident from the substrate side (Figure 7.7 (b))

![Figure 7.7 (a) Photograph of the GaAs semiconductor structure showing the scanned area, (b) Sketch describing the raster scanning carried out from the substrate side.](image)

![Figure 7.8 (a) 3-D image of the GaAs semiconductor structure showing scanned area obtained by raster scanning from substrate side.](image)

Figure 7.8 shows 3-D image of the GaAs semiconductor structure obtained scanning from the substrate side. The cross-correlation signals at the point A and B are shown in Figure 7.9 (a). It is observed in Figure 7.9 (a) that the cross-correlation signals are shifted by the optical path length
within the structure. Thus the height of the scanned profile determined by a portion of the structure from the substrate side is \( \approx 69 \pm 6 \mu m \). This can be visible by the line scan shown in Figure 7.9 (b) showing the optical path length within the structure. The height of the structure is then obtained by dividing the optical path length by the refractive index of the GaAs at 4.93 \( \mu m \), which gives the height of the structure \( = 21 \pm 2 \mu m \). The depth resolution is found by how well we can determine the peak of the correlation function in time. In the case of Figure 7.8 we find the resolution to be is less than the vacuum wavelength used. This ‘superresolution’ in depth is due to the nonlinear detection method used and is limited by the pulsewidth and SNR in the cross correlation data. This enables us in obtaining post-fabrication imaging of buried structures such as the semiconductor structures or any laser written volumetric structures as described elsewhere [57].

![Figure 7.9](image)

Figure 7.9 (a) Cross-correlation at the position A and B of Figure 7.8, (b) Line scanning showing the depth, obtained by scanning from substrate side.
7.3. Resolution

The spatial resolution here in the obtained images is determined by digitized raster scanning resolution but the ultimate spatial resolution is determined by the minimum spot size obtained through the imaging optics for the signal pulse. The longitudinal (depth) resolution is defined by the accuracy determination of the zero delay positions. The error in determination of zero delay positions occurs due to noise in the cross-correlation curve which limits the depth resolution.

To experimentally determine the longitudinal resolution various semiconductor structures are fabricated from GaAs substrate with different depths of \( \approx 3 \, \mu m, \approx 6 \, \mu m, \approx 11 \, \mu m, \approx 21 \, \mu m, \) and \( \approx 31 \, \mu m \). Each structure is coated with gold to maximize the reflectivity for better SNR. The depths are measured by an alpha stepper profilometer. Figure 7.10 shows a photograph and sketch of one such structure and Figure 7.11 (a), (b), and (c) show line scans of \( 11 \, \mu m, 21 \, \mu m, \) and \( 31 \, \mu m \) structures respectively. From the line scans the measured depth profiles obtained show a clear profile of the \( \approx 11 \, \mu m, \approx 21 \, \mu m, \) and \( \approx 31 \, \mu m \) structures. The \( \approx 3 \, \mu m \) and \( \approx 6 \, \mu m \) structures are not resolvable due to noise present on the cross-correlation curve. The estimated depth resolution is \( < 11 \, \mu m \) but not better than \( 6 \, \mu m \).

![Figure 7.10](image1.png)

(a) Photograph of the GaAs semiconductor structure, (b) Sketch of the raster scanning carried out on the front side.
The percentage of noise in the cross-correlation curve is obtained by \( \sigma = \frac{1}{SNR} \). Considering the cross-correlation curves to be Gaussian the output cross-correlation signals are represented as \( I = I_0 e^{-\left(\frac{t}{\tau_{FWHM}}\right)^2} \) with zero noise, and \( I = I_0 (1 + \sigma) e^{-\left(\frac{t}{\tau_{FWHM}}\right)^2} \) with noise \( \sigma \).

The error in determination of zero delay is obtained as

\[
\Delta z = \pm \frac{1}{2\ln 2} \sqrt{\ln(1 + \sigma)} \tau_{FWHM} c
\]

(7.3)

where \( \tau_{FWHM} \) is the full width half maximum (FWHM) of the cross-correlation curve, \( c \) is the velocity of light. In the experiments the noise on the cross-correlation curves are \( \approx 2\% \) and the FWHM of the cross-correlation curve \( \approx 350 \) fs. From the Equation 7.3 for noise \( \sigma = 2 \% \), on the cross-correlation signal gives \( \Delta z \approx 8 \mu m \).
7.4. Discussion

The method described here is an experimental investigation of how the END-2PA in wide-gap semiconductor photodetectors can be explored for imaging in the mid-IR as well as in the near IR region. It is worth mentioning that the detector element used in the experiment is not intended for an END-2PA process, which generally needs thicker elements for longer interaction of the gate and the signal pulse for ND-2PA. The design of such thick p-i-n detector elements need considerable research to make an efficient detector for END-2PA. One possible solution is a waveguide p-i-n photodetector.

The time taken for the scanning is fairly long, but this idea could be taken for further research to find a solution for this issue. Assuming depth variations within the spot size is negligible, the longitudinal (depth) resolution is limited by the noise present on the cross-correlation curve and depends width of the cross-correlation curve.

Another useful application could be in the area which currently uses optical coherence tomography (OCT) in the mid-IR region. OCT is mainly concerned with determining structural differences between tissues than tissue spectroscopy. There is little research being carried out in this area of spectroscopy. In reference [47] a mid-IR OCT system is described in which a signal and reference beam interfere at the MCT detector. The system is designed to characterize bioengineering tissue in terms of their structure and biochemical composition. The OCT is an interferometric setup and uses signal and reference beams which interfere at the detector, hence requires very sensitive alignment and is prone to vibrations. The imaging technique described here using ND-2PA is more robust in comparison to an interferometric setup and could be used in areas which need a mid-IR OCT.
Another useful application as described in the experimental setup section is the imaging of buried structures in bulk IR transmissive materials such as semiconductors and certain ceramics. Nondestructive 3-D imaging of laser written volumetric structures could be performed provided the substrate is transparent to the wavelength of the incident IR-beam. In reference [57] the authors showed a nondestructive 3-D imaging using optical coherence microscopy (OCM) of the laser written structures. The technique facilitates real time monitoring of the 3-D structures created in fused silica and hence provide quantitative assessment of the features for better control of the writing process. Our technique could be useful for similar applications but for post fabrication 3-D imaging as real time monitoring is not possible with the present technique. As an example we have shown here post fabrication imaging of a semiconductor device structures as described in the experimental section. But the main advantage of this system is that the imaging can be carried out at a variety of wavelengths in the mid-IR and near-IR with appropriate gate wavelength and choice of direct-gap material without any modification to the detection and imaging systems. The method described here is nondestructive and suitable for in-vivo applications in biology. Each of the application described here needs its own optical system design and development for its application to obtain its full potential.
CHAPTER 8: TWO-PHOTON ABSORPTION IN QUANTUM WELL STRUCTURES

Quantum wells (QW) are thin layered semiconductor heterostructures, which are obtained by sandwiching a thin layer of semiconductor material between two other semiconductor ‘barrier’ layers. Their special properties are derived from the ability to control the charge carriers (electrons and hole). The quantum confinement results in a modulated step-like density of states which show enhanced linear and nonlinear properties near resonance. Due to several superior properties, QW semiconductor devices are often preferred over devices based on bulk semiconductors. Figure 8.1 shows a sketch of a QW structure, where the $xy$ plane denotes the plane of the QW and $z$ is the confinement or growth direction. Due to confinement in a QW, the plane wave type envelope function of the electron in the bulk semiconductor is modulated along the confinement direction and the resulting shape depends on the type of QW.

Figure 8.1 Sketch of a finite QW structure showing electric vector polarization for TE and TM case.
In Figure 8.1 the QW shown is of the rectangular type. A QW with an infinitely high barrier has its electron and hole wave functions confined completely between the barriers. But in practice all QWs have finite barriers and the electron and hole wave function penetrates into the barrier layer. In a QW because of the confinement, the electron energy is quantized in the confinement direction. Figure 8.2 shows $E$ vs $k$ diagram of a QW showing valence and conduction subbands labelled by index ‘$n$’. In Figure 8.2 solid lines and dashed lines in the valence band represent heavy-holes and light-holes respectively. Since in QWs the degeneracy between the heavy-holes and the light-holes is lifted, distinct features are observed in the absorption spectra of QWs for heavy-hole-electron and light-hole-electron transitions.

QWs are anisotropic because their optical properties largely depend on the polarization of the incident light. If we look into a waveguide with QW layers in it (Figure 8.3), there are two distinct optical polarization directions when light propagates along the waveguide. In
correspondence with transverse electric (TE) polarization of the incident beam propagation along
the waveguide, the electric field vector always lies in the plane \((\hat{e} \equiv \hat{x} \text{ or } \hat{y})\) of the QW layers.
When a QW is irradiated by light, the absorbed photons excite electrons from valence subbands
to conduction subbands. The absorption process between the valence band and conduction band
in a QW is governed by a set of selection rules and depends on the transition matrix elements of
the initial and final subbands.

![Figure 8.3 Sketch of a ridge waveguide with QW core region.](image)

For one-photon absorption in the TE case, because of the selection rules associated with the
unit cell wave functions, we get nonzero one-photon absorption only for transitions between the
valence subbands and conduction subbands having the same index such that \(\Delta n = 0\). In one-photon absorption for the TE case both heavy-hole-electron and light-hole-electron transitions
are allowed, so we observe two sets of peaks in the absorption curve. The heavy hole gives a
dominant contribution when we look at the optical absorption in the TE case. Similarly in
correspondence with the transverse magnetic (TM) polarization of the incident beam propagating
along the waveguide, the electric field vector always lies in the confinement direction i.e. the
plane \((\hat{e} \equiv \hat{z})\) of the QW layers. For one-photon absorption in the TM case the selection rule also
allows transitions between subbands of the same index \(\Delta n = 0\). But here only light-hole-electron
transitions are allowed. The selection rule is a consequence of defining the symmetry axis in the
material, and in the case of a quantum well it is in the growth direction of the quantum well.
Similar selection rules could also be obtained by applying a uniaxial stress to a bulk semiconductor.

Two-photon absorption (2PA) properties of quantum wells (QW) are important in investigating the electronic properties of these structures e.g. valence and conduction band offsets, exciton binding energies etc. Determination of these properties are possible, due to the different selection rules in two-photon transitions as compared with 1-photon transitions, hence involving initial and final states where transitions are otherwise forbidden.

Two-photon absorption in a QW has different selection rules for TE and TM polarizations, and there are actually three possible polarization cases; TE-TE, TM-TM and TE-TM for the two photons. In the TE-TE case the 2PA occurs only for transitions between the valence subbands and conduction subbands of same index ‘n’ such that \( \Delta n = 0 \). In the TM-TM case only transitions with odd \( \Delta n \) contribute to the two-photon absorption. In this chapter a brief review of previous 2PA work in QWs is discussed. A theory for D-2PA in QWs with analytical expressions for the D-2PA coefficient, \( \alpha_{2D}^D \) are presented using second-order perturbation theory. For the first time a theory for ND-2PA in QWs is developed and analytical expressions for the ND-2PA coefficient, \( \alpha_{2D}^{ND} \) are derived using second-order perturbation theory.

8.1. Previous work on 2PA of QWs

Quantum wells possess a large density of states, hence nonlinear properties are greatly enhanced near the resonance. Two-photon absorption of QW structures have attracted interest for many researchers because of their potential application in a variety of optical devices [58]–[60]. The literature so far is directed toward the study of D-2PA properties of QWs. These theoretical
studies and experimental studies on D-2PA properties of QWs are primarily investigated in the vicinity of the middle of the bandgap aiming for applications based on low D-2PA and hence large nonlinear refraction (NLR) owing to a large figure of merit (FOM) for all-optical switching applications [16], [61]–[63]. The performance of nonlinear optical devices based on NLR is determined by the ratio of NLR to nonlinear absorption rather than on the absolute value of NLR. Therefore both for fundamental science and application purposes, understanding the nonlinear properties of these QW structures is invaluable. The theoretical work by Spector et al [18] and Pasquarello and Quattropani [19] are the very first ones in predicting the spectral shape of D-2PA QW. These groups have disagreements in the predicted spectra and the choice of gauge. The D-2PA theory by Shimizu et al [20] considered excitonic effects and their predictions confirmed by experimental observations [61], [64], [65]. Xia et al [17] discussed the D-2PA properties of QWs both in the presence or absence of an external electric field. Khurgin et. al. [16] developed analytical expressions for the polarization dependent D-2PA in QWs. In this work we have revisited the paper by Khurgin et al. and in our derivation of analytical expressions for D-2PA coefficients we have made several corrections to the D-2PA coefficients derived by Khurgin et. al. While there is some amount of theoretical and experimental work on D-2PA of QWs, no work has been carried out on nondegenerate (ND) 2PA in QWs. In ND-2PA the energy of the individual photons may approach intermediate-state resonances, thus leading to an enhancement of ND-2PA over the D-2PA. As discussed in Chapter 5, in bulk semiconductors, the enhancement due to ND-2PA has been predicted theoretically [11], [23] and verified experimentally [12]. For bulk semiconductors the theoretical predictions for ND-2PA are obtained considering a two parabolic-band model where the dominant transitions for 2PA were shown to be a combination of interband (allowed) and intraband (forbidden) (Chapter 5). These
intermediate-state resonance enhancements become very significant when one of the photons of the pair has energy very small and the other photon has energy approaching the bandgap energy (Chapter 5). In such a case the two photons are of extremely different photon energies which lead to orders of magnitude enhancement of ND-2PA over D-2PA. This orders of magnitude increase has been measured in multiple direct-gap semiconductors including GaAs and ZnSe [12]. Based on the extremely nondegenerate, END, enhancements in 2PA, Fishman et al. showed sensitive detection of mid-infrared (IR) femtosecond pulses in an uncooled p-i-n GaN photodiode [3]. In Chapter 6 the END-2PA in bulk semiconductors is further extended for detection of continuous wave infrared, IR, in uncooled GaAs p-i-n photodiodes [40], [66]. QWs have shown superior properties in comparison to bulk semiconductors due to their large density of states. It is expected that ND-2PA will be even enhanced more near resonance in comparison to bulk semiconductors due to the larger density of states at the band edge. It is apparent that, similar to one-photon absorption, QWs will show different optical properties depending upon whether the incident radiation has its electric vector in the TE polarization mode or in the TM polarization mode.

8.2. Theoretical approach for calculating 2PA in QW

The accurate calculation of 2PA coefficients in semiconductors requires using a realistic band structure near the center of the Brillouin zone which takes care of band nonparabolicity and degeneracy of valence bands [23]. The model used is very successful in studying linear optical processes in bulk and QW semiconductors and is adopted from the classic paper by Kane [67]. The motion of the electron in a periodic potential
\[ V(r) = V(r + R) \]  

(8.1)

where \( R = n_1a_1 + n_2a_2 + n_3a_3 \), and \( a_1, a_2, a_3 \), are the three lattice vectors, and \( n_1, n_2, n_3 \), are integers, is governed by the Schrödinger equation

\[
\left[ \frac{p^2}{2m_0} + V(r) \right] \psi_{nk}(r) = E_n(k)\psi_{nk}(r) \tag{8.2}
\]

where \( \psi_{nk}(r) \) and \( E_n(k) \) are the wave function and the energy of the electron in the eigenstate of the \( nt \)th band, \( m_0 \) is the rest mass of the electron, \( k \) is the electron wave vector. In the reduced zone scheme the solution of Equation (8.2) is expressed in terms of Bloch function as

\[
\psi_{nk}(r) = e^{i k \cdot r} u_{nk}(r) \tag{8.3}
\]

Substituting Equation (8.3) in Equation (8.2) we obtain

\[
\left[ \frac{p^2}{2m_0} + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar}{m_0} k \cdot p + V(r) \right] u_{nk}(r) = E_n(k)u_{nk}(r) \tag{8.4}
\]

The above equation can be expanded near \( k_0 \) in the band structure and with \( k_0 = 0 \), Equation (8.4) is expanded near \( E_n(0) \),

\[
\left[ H_0 + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar}{m_0} k \cdot p \right] u_{n0}(r) = E_n(0)u_{n0}(r) \tag{8.5}
\]

where

\[
H_0u_{n0}(r) = E_n(0)u_{n0}(r) \tag{8.6}
\]

\[
H_0 = \frac{p^2}{2m_0} + V(r) \tag{8.7}
\]

In Equation (8.6), \( u_{n0}(r) \) are Bloch periodic functions at \( k = 0 \) i.e. at the \( \Gamma \) point of a direct gap semiconductor. Once we solve Equation (8.6) and find the eigenvalues, \( E_n(0) \), and the corresponding eigenfunctions, \( u_{n0}(r) \), then we can treat the terms \( \hbar^2 k^2 / 2m_0 \) and \( (\hbar/m_0) k \cdot p \)
in Equation (8.5) as perturbations and solve using the standard nondegenerate perturbation theory to find the new eigenvalues and eigenfunctions. The new eigenvalues, $E_n(k)$, and the eigenfunctions, $u_{nk}(r)$, will account for band dispersion and will be expressed in terms of known eigenvalues, $E_n(0)$, and eigenfunctions, $u_{n0}(r)$. This method of calculating the band dispersion with known eigenfunctions and eigenvalues at $k = 0$ is described as $k.p$ theory [67].

It is important to understand the symmetry properties as it will be helpful in understanding the evolution of the band structure. The symmetry properties near the band edge in Equation (8.6) are obtained from group theory. For semiconductors if we think of putting atoms together to form a crystal, the conduction band possesses s-orbital like spherical symmetry and the valence band possesses p-orbital like symmetry near the band edge. The eigenfunctions corresponding to the conduction band are denoted by $S \uparrow$ and $S \downarrow$ for the two spin states and the eigenfunctions corresponding to the valence bands are denoted by $X \uparrow$, $X \downarrow$, $Y \uparrow$, $Y \downarrow$, $Z \uparrow$, and $Z \downarrow$.

Now, considering the perturbation due to the spin orbit interaction

$$H_{SO} = \frac{\hbar}{4m_0^2c^2} \sigma \cdot [\nabla \times \mathbf{p}]$$

(8.8)

and using the Schrödinger equation for the Bloch function $\psi_{nk}(r)$ we obtain

$$\left[ \frac{\mathbf{p}^2}{2m_0} + V(r) + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar}{m_0} k \cdot \mathbf{p} + \frac{\hbar}{4m_0^2c^2} \sigma \cdot [\nabla \times \mathbf{p}] \right] \psi_{nk}(r) = E_n(k)\psi_{nk}(r)$$

(8.9)

Equation (8.9) in terms of the cell periodic function $u_{nk}(r)$ is obtained as

$$\left[ \frac{\mathbf{p}^2}{2m_0} + V(r) + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar}{m_0} k \cdot \mathbf{p} + \frac{\hbar}{4m_0^2c^2} \sigma \cdot [\nabla \times \mathbf{k}] \right] u_{nk}(r) = E_n(k)u_{nk}(r)$$

(8.10)
The 6th term in Equation (8.10) is a \( k \) –dependent spin-orbit interaction term, which is small in comparison to the 5th term because the crystal momentum \( \hbar k \) is very small compared with the atomic momentum \( p \) in the far interior of the atom where most of the spin-orbit interaction occurs and hence can be neglected. Thus, the general form of the Hamiltonian for the electron in a periodic cell structure including the spin-orbit interaction and the \( k.p \) interaction between the valence band and the conduction band is written as

\[
H = \frac{p^2}{2m_0} + V(r) + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar}{m_0} k \cdot p + \frac{\hbar}{4m_0^2 c^2} \sigma \cdot \nabla \times p
\]  

(8.11)

where \( \sigma \) and \( p \) are spin and momentum operators respectively. The eigenfunctions of the spin-orbit interaction Hamiltonian are nothing but eigenstates of the total angular momentum \( j \) and its z component \( j_z \). The angular momentum \( j \) is the sum of the orbital angular momentum (\( l \)) and the spin angular momentum (\( s \)). Considering the similarity to atomic wave functions the conduction band with \( s \)-like symmetry states correspond to \( l = 0 \) and the valence bands with \( p \)-like symmetry has \( l = 1 \). Thus, three \((2l + 1)\) valence band states can therefore be chosen to be the eigenstates of the z-component of \( l \). Hence these correspond to \( l_z = -1, 0, \) and \( 1 \). Therefore, for the conduction band \( j \) is \( 1/2 \) and for the valence band \( j \) can take values \( 3/2 \) or \( 1/2 \). The eigenfunctions of \( j \) and \( j_z \) for the valence states are given by

\[
|jm\rangle = \begin{cases} 
\begin{pmatrix} 3 \\ \frac{3}{2} \\ \frac{3}{2} \end{pmatrix}, \begin{pmatrix} 3 \\ \frac{3}{2} \\ -\frac{3}{2} \end{pmatrix} & \text{corresponds to the heavy-hole (hh) band} \\
\begin{pmatrix} 3 \\ \frac{1}{2} \\ \frac{3}{2} \end{pmatrix}, \begin{pmatrix} 3 \\ \frac{1}{2} \\ -\frac{1}{2} \end{pmatrix} & \text{corresponds to the light-hole (lh) band} \\
\begin{pmatrix} 1 \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 \\ \frac{1}{2} \\ -\frac{1}{2} \end{pmatrix} & \text{corresponds to the split-off (so) band}
\end{cases}
\]  

(8.12)
The spin-orbit interaction presented in Equation (8.11) lifts the triple degeneracy of the valence bands by splitting the \( j = 3/2 \) states from the \( j = 1/2 \) states. The split-off band is shifted by an energy \( \Delta \) at \( k_0 = 0 \) from the top of the valence band.

For a \( \mathbf{k} \) vector oriented along the \( z \) direction and using the basis functions

\[
| \uparrow \rangle, \quad \frac{X - iY}{\sqrt{2}} \uparrow, \quad | \downarrow \rangle, \quad \frac{X + iY}{\sqrt{2}} \uparrow \tag{8.13}
\]

and

\[
| \uparrow \rangle, \quad \frac{X + iY}{\sqrt{2}} \downarrow, \quad | \downarrow \rangle, \quad \frac{X - iY}{\sqrt{2}} \downarrow \tag{8.14}
\]
yielding a total of eight basis functions. Therefore, the Hamiltonian can be represented by an \( 8 \times 8 \) interaction matrix written as

\[
\begin{bmatrix}
\mathcal{H} & 0 \\
0 & \overline{\mathcal{H}}
\end{bmatrix}
\]

where

\[
\mathcal{H} = \begin{bmatrix}
E_s & 0 & kP & 0 \\
0 & E_p - \Delta/3 & \sqrt{2} \Delta/3 & 0 \\
kP & \sqrt{2} \Delta/3 & E_p & 0 \\
0 & 0 & 0 & E_p + \Delta/3
\end{bmatrix} \tag{8.15}
\]

where \( P \) is the Kane momentum parameter defined below and \( \Delta \) the spin-orbit split-off energy, defined as

\[
P = -i \frac{\hbar}{m_0} \langle S|p_z|Z \rangle = -i \frac{\hbar}{m_0} \langle S|p_z|X \rangle = -i \frac{\hbar}{m_0} \langle S|p_z|Y \rangle \tag{8.16}
\]

and

\[
\Delta = \frac{3\hbar i}{4m_0^2 c^2} \left( X \left| \frac{\partial V}{\partial x} p_y - \frac{\partial V}{\partial y} p_x \right| Y \right) \tag{8.17}
\]

and \( E_s \) and \( E_p \) are the two eigenvalues obtained solving for Equation (8.6) for \( E_n(0) \). \( E_s \) corresponds to the conduction band and \( E_p \) corresponds to the valence band.
For \( k \) oriented in an arbitrary direction the Hamiltonian becomes complicated but can be transformed to the same form of Equation (8.15) through a rotation of the basis functions. The new set of functions are given by

\[
\begin{bmatrix}
X' \\
Y' \\
Z'
\end{bmatrix} = \begin{bmatrix}
\cos \theta \cos \phi & \cos \theta \sin \phi & -\sin \theta \\
-\sin \phi & \cos \phi & 0 \\
\sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta
\end{bmatrix} \begin{bmatrix}
X \\
Y \\
Z
\end{bmatrix}
\]  

(8.18)

and

\[
\begin{bmatrix}
\uparrow' \\
\downarrow'
\end{bmatrix} = \begin{bmatrix}
e^{-i\phi/2} \cos \frac{\theta}{2} & e^{i\phi/2} \sin \frac{\theta}{2} \\
e^{-i\phi/2} \sin \frac{\theta}{2} & e^{i\phi/2} \cos \frac{\theta}{2}
\end{bmatrix} \begin{bmatrix}
\uparrow
\end{bmatrix}
\]  

(8.19)

The spherical symmetry function is invariant under rotation, \( S' = S \). The angles \( \theta \) and \( \phi \) described here are the usual polar angles of the \( k \) vector with respect to the crystal symmetry axes \( x, y, \) and \( z \). The expression for \( k \) for any direction is given by

\[
k = k \sin \theta \cos \phi \, \hat{x} + k \sin \theta \sin \phi \, \hat{y} + k \cos \theta \, \hat{z}
\]  

(8.20)

The secular equation \( \det[H' - E'I'] \) resulting from Equation (8.15) has four double roots (eigenvalues)

\[
E' = 0
\]  

(8.21)

\[
E'(E' - E_g)(E' + \Delta) - k^2 P^2 (E' + \frac{2}{3} \Delta) = 0
\]  

(8.22)

where \( E_s = E_g \) and \( E_p = -\Delta/3 \) and \( E' = E_n(k) - \hbar^2 k^2 / 2m_0 \).

The doubly degenerate electronic wave functions obtained from the first \( 4 \times 4 \) matrix (Equation (8.13))

\[
\Phi_{hh,\alpha} = \left\{ \frac{X' + iY'}{\sqrt{2}} \right\}
\]  

(8.23)
\[ \Phi_{n,\alpha} = a_n |iS \downarrow\rangle + b_n \left| \frac{X' - iY'}{\sqrt{2}} \uparrow\right\rangle + c_n |Z' \downarrow\rangle \]  
(8.24)

and the second 4 × 4 matrix (Equation (8.14)),

\[ \Phi_{nh,\beta} = \left| \frac{X' - iY'}{\sqrt{2}} \downarrow\right\rangle \]  
(8.25)

\[ \Phi_{n,\beta} = a_n |iS \uparrow\rangle + b_n \left| - \frac{X' + iY'}{\sqrt{2}} \downarrow\right\rangle + c_n |Z' \uparrow\rangle \]  
(8.26)

where \( \alpha \) and \( \beta \) denote the degenerate up and down spin states. The index \( n \) refers to the conduction (c), light-hole (lh), or split-off (so) band. The expression for \( a, b, \) and \( c \) are obtained as

\[ a_n = kP(E_n' + \frac{2}{3}\Delta)/N \]

\[ b_n = \frac{\sqrt{2}}{3}\Delta(E_n' - E_g)/N \]  
(8.27)

\[ c_n = (E_n' - E_g)(E_n' + \frac{2}{3}\Delta)/N \]

where \( N \) is the normalizing factor which gives \( a_n^2 + b_n^2 + c_n^2 = 1 \). In the limit of small \( k \) (\( k^2 \to 0 \)), Equation (8.27) becomes

\[ a_c = 1, \quad b_c = c_c = 0 \]

\[ a_{lh} = 0, \quad b_{lh} = 1/\sqrt{3}, \quad c_{lh} = \sqrt{2}/3 \]  
(8.28)

\[ a_{so} = 0, \quad b_{so} = \sqrt{2}/3, \quad c_{so} = -1/\sqrt{3} \]

From this formulation we can define the wave functions at the band edges for the electron wave vector \( k \) oriented in an arbitrary direction as written below
Conduction Band

\[ |iS \downarrow\rangle \quad \text{and} \quad |iS \uparrow\rangle \]  \hspace{1cm} (8.29)

Heavy-hole Band

\[
\left| \frac{3}{2}, \frac{3}{2} \right\rangle = -\frac{1}{\sqrt{2}} |(X' + iY') \uparrow\rangle
\]
\[
= -\frac{1}{\sqrt{2}} \left[ (\cos \theta \cos \phi - i \sin \phi)X + (\cos \theta \sin \phi + i \cos \phi)Y \\ - \sin \theta Z \right] |\uparrow\rangle
\]  \hspace{1cm} (8.30)

Light-hole Band

\[
\left| \frac{3}{2}, \frac{1}{2} \right\rangle = -\frac{1}{\sqrt{6}} |(X' + iY') \uparrow\rangle + \sqrt{\frac{2}{3}} |Z' \uparrow\rangle
\]
\[
= -\frac{1}{\sqrt{6}} \left[ (\cos \theta \cos \phi - i \sin \phi)X + (\cos \theta \sin \phi + i \cos \phi)Y \\ - \sin \theta Z \right] |\uparrow\rangle + \sqrt{\frac{2}{3}} \left[ \sin \theta \cos \phi X + \sin \theta \sin \phi Y + \cos \theta Z \right] |\downarrow\rangle
\]  \hspace{1cm} (8.31)

Split-off Band

\[
\left| \frac{1}{2}, \frac{1}{2} \right\rangle = \frac{1}{\sqrt{3}} |(X' + iY') \uparrow\rangle + \frac{1}{\sqrt{3}} |Z' \uparrow\rangle
\]
\[
= \frac{1}{\sqrt{6}} \left[ (\cos \theta \cos \phi - i \sin \phi)X + (\cos \theta \sin \phi \pm i \cos \phi)Y \\ - \sin \theta Z \right] |\downarrow\rangle + \sqrt{\frac{2}{3}} \left[ \sin \theta \cos \phi X + \sin \theta \sin \phi Y + \cos \theta Z \right] |\uparrow\rangle
\]  \hspace{1cm} (8.32)

The wave functions for other spin polarizations can be written simultaneously using Equation (8.25) and (8.26). There are a couple of approaches commonly used for calculating the D-2PA
coefficient \( (\alpha_2^D) \), which have been discussed in detail in Chapter 4. One of the methods for calculating \( \alpha_2^D \) is through the two-photon transition rate via second-order perturbation theory. Second-order perturbation theory has been employed for calculating both \( \alpha_2^D \) and the ND-2PA coefficient \( (\alpha_2^{ND}) \) for bulk semiconductors. Reasonable predictions have been shown for these coefficients using a 2-parabolic-band model which is confirmed by experimental results.\[ref\] For better accuracy a more complex 4-band model can be employed which has been discussed for zinc blende symmetry semiconductors [23]. For calculations of the of three-photon absorption (3PA) coefficient using third-order perturbation theory the use of this complex 4-band structure is required due to the many different possible transition paths involved which leads to quantum interference. The predicted spectra agree both in shape and magnitude (within a factor of 3). In this chapter the D-2PA coefficient in QWs is calculated using the two-photon transition rate obtained from second-order perturbation theory. A 2-parabolic band model is used to describe the two-photon transitions between the QW valence and conduction subbands.

8.2.1. Theory for degenerate two-photon absorption (D-2PA) in quantum wells

To calculate the D-2PA coefficient \( (\alpha_2^D) \) an ideal infinitely high barrier QW is considered. The width of the QW is \( d \), with \( x, y \) being the plane of the quantum well and \( z \) is the growth axis (Figure 8.1). QWs have one dimensional confinement that lifts the degeneracy of the heavy-hole and light-hole subbands at the band edge and both conduction band and valence and valence bands split into many subbands. These subbands have confinement energies evaluated as

\[
E_{v,n} = \frac{n^2 \pi^2 \hbar^2}{2m_{\perp} d^2}
\]  

(8.33)
where $\nu = c, hh, lh$ represents conduction, heavy-hole, and light-holes, respectively, $m_{\nu,\perp}$ is the longitudinal effective mass given by

$$m_{c,\perp} = m_c$$

(8.34)

$$m_{hh,\perp} = \frac{m_0}{\gamma_1 - 2\gamma_2}$$

(8.35)

$$m_{lh,\perp} = \frac{m_0}{\gamma_1 + 2\gamma_2}$$

(8.36)

where $m_c$ and $m_0$ are the effective mass of the electron in the conduction band and the free electron mass, respectively. $\gamma_1$ and $\gamma_2$ denote the Luttinger parameters [68].

The in-plane dispersion in the plane of the QW is given by

$$E_{\nu,\parallel} = \frac{\hbar^2 k_{\parallel}^2}{2m_{\nu,\parallel}}$$

(8.37)

where $k_{\parallel}$ is the lateral quasi-momentum and $m_{\nu,\parallel}$ is the lateral effective mass given by

$$m_{c,\parallel} = m_c$$

(8.38)

$$m_{hh,\parallel} = \frac{m_0}{\gamma_1 + \gamma_2}$$

(8.39)

$$m_{lh,\parallel} = \frac{m_0}{\gamma_1 - \gamma_2}$$

(8.40)

Following the envelope approximation the wave function describing the subbands in a QW can be written as

$$|\nu,n\rangle = u_0 \psi_n(z)e^{ik_{\parallel}r_{\parallel}}$$

(8.41)

where $r_{\parallel} = x\hat{x} + y\hat{y}$. For QWs with an infinitely high potential the envelope wave function is given by
\[ \Psi_n(z) = \frac{2}{d} \sin \left( \frac{n\pi z}{d} \right) \]  

(8.42)

and \(u_v\) are the Bloch wave functions near the Brillouin zone center given by Equation (8.29) - (8.32). Using second-order perturbation theory the degenerate two-photon absorption rate is expressed as

\[ W_2^D = \frac{2\pi^2}{\hbar V} \sum_{vc} \left| \sum_i \frac{\langle c | \hat{H}_{\text{int}} | i \rangle \langle i | \hat{H}_{\text{int}} | v \rangle}{E_{iv}(\bm{k}) - \hbar \omega} \right|^2 \delta(E_{cv}(\bm{k}) - 2\hbar \omega) \]  

(8.43)

where \(\hat{H}_{\text{int}} = -\frac{e}{m_0} \bm{A}(\bm{r}, t) \cdot \bm{p}\) represents the electron-field interaction Hamiltonian related to solids. \(|v\rangle\), \(|c\rangle\), and \(|i\rangle\) represent the valence band (initial state), conduction band (final state), and intermediate states respectively. \(V\) is the volume and the expression includes the spin degeneracy. \(E_{cv}(\bm{k})\) is the energy difference between the valence band and conduction band. The transition rate is summed over all possible intermediate states \(i\) and the sum over all possible transitions from a filled state in the valence band to an empty state in the conduction band.

### 8.2.2. D-2PA in QWs for TE-TE polarization

As mentioned before, QWs are anisotropic, hence the 2PA transition rate depends on the direction of polarization of the incident light. For light polarized in the plane of the quantum well \(\hat{e} \equiv \hat{x}\) or \(\hat{y}\) (referred as TE) the selection rules obey the condition \(\Delta n = 0\), where \(n\) represents the subband index for valence subband or conduction subband [19], [20], [64], [69]. For the TE-TE case the intermediate states lie in the subbands and the intraband transition occurs within the
subbands. Every two-photon transition occurs between the subbands of the same index in the valence band and the conduction band respectively.

Figure 8.4 shows various possible transition paths possible for 2PA of the TE-TE polarized light which correspond to interband transitions from valence subbands to conduction subbands and hole (or electron) intrasubband transitions. For the two-photon transition, if the intermediate state \(i\) in the valence band then \(E_{iv}(k\parallel) = E_v(k\parallel) - E_v(k\parallel) = 0\) and if \(i\) in the conduction band then \(E_{iv}(k\parallel) = E_{cv}(k\parallel) = E_c(k\parallel) - E_v(k\parallel) = 2\hbar\omega\), where \(k\parallel\) stands for the electron momentum in the quantum well plane.

The transition rate for the TE-TE polarized case in QWs is modified as

\[
W_{2D}^{\parallel} = \frac{2\pi 2}{\hbar V} \sum_{v} \sum_{n} \sum_{k\parallel} \left| \langle c,n | \hat{H}_{int} | v,n \rangle \langle v,n | \hat{H}_{int} | v,n \rangle \right| \frac{1}{\hbar\omega} \\
+ \frac{1}{\hbar\omega} \left| \langle c,n | \hat{H}_{int} | c,n \rangle \langle c,n | \hat{H}_{int} | v,n \rangle \right|^2 \delta(E_{cv}(k\parallel) - 2\hbar\omega)
\]

where the 1st summation corresponds to sum over the 2PA contributions of light-holes and heavy-holes, the 2nd summation corresponds to two-photon transitions summed over subbands of the same index, and the 3rd summation corresponds to the sum over electronic wave vectors in
the plane of the quantum well. For TE-TE polarized light there are contributions to 2PA both from heavy-holes and light-holes and the intersubband matrix elements exist only for transitions within one subband, given by
\[ \langle v|p|v\rangle = \hbar \frac{m_0}{m_{v,\parallel}} k_{\parallel} \text{ and } \langle c|p|c\rangle = \hbar \frac{m_0}{m_{c,\parallel}} k_{\parallel} \] (8.45)
and the transition matrix elements for the intersubband matrix elements is given by
\[ \langle c|p|v\rangle = p_{cv} \] (8.46)
Substituting the values of transition matrix elements from Equation (8.45) and Equation (8.46) and subband energies from Equation (8.33) and transforming the summation over the in-plane wave vector \( k_{\parallel} \) into an integration over the kinetic energy and using the momentum gauge for the interaction Hamiltonian Equation (8.44) is simplified to
\[ W^D_{2\parallel} = \sum_v a_v |p_{cv}|^2 \frac{4}{\hbar^5} \frac{e^4 A_0^4}{16 m_0^2} \left( \frac{m_0}{\omega} \right)^2 \frac{1}{d} \sum_n \left( 2\hbar \omega - E_{c,n} - E_{v,n} - E_g \right) \Theta(2\hbar \omega - E_{c,n} - E_{v,n} - E_g) \] (8.47)
where the \( a_v \)'s are the coefficients obtained by averaging over the electronic wave-vector \( k_{\parallel} \) and are equal to 1/4 for heavy holes and 1/12 for light holes. The D-2PA coefficient can be obtained from the transition rate as
\[ \alpha = W^D_{2} \frac{2\hbar \omega}{I^2} \] (8.48)
where \( I \) is the irradiance of the incident beam, \( n_\omega \) is the refractive index, \( \varepsilon_0 \) is the permittivity of free space,
\[ I = \frac{n_\omega c \varepsilon_0 \omega^2 A_0^2}{2} \] (8.49)
The momentum matrix element \(|p_{cv}|^2\) is related to the Kane energy parameter \( E_p \) by [26]
\[ E_p = 2|p_{cv}|^2/m_0 \]  

(8.50)

From Equation (8.47) after the summation and using the relation in Equation (8.48) we obtain the following expression for the D-2PA coefficient for the TE-TE polarized light, \( \alpha^D_{2\|} \):

\[
\alpha^D_{2\|} = 2 \left( \frac{16\alpha}{n_r} \right)^2 \frac{2E_p(E_{v,11})^2}{m_0E_g^5} \left[ \frac{1}{4\mu_{hh,\perp}} F(\zeta_{hh}) + \frac{1}{12} F(\zeta_{lh}) \right] \left( \frac{E_g}{2\hbar\omega} \right)^5
\]

(8.51)

where

\[
\zeta^D_v = \frac{2\hbar\omega - E_g}{E_{v,11}}
\]

(8.52)

\[
E_{v,11}^\perp = E_c^\perp + E_{lh} \frac{\hbar^2\pi^2}{2\mu_{hh,\perp} d^2}
\]

(8.53)

\[
F(\zeta_v) = \left( \zeta_v N_v - \frac{1}{3} N_v^3 - \frac{1}{2} N_v^2 - \frac{1}{6} N_v \right)
\]

(8.54)

\[
N_v = \text{Int} \left( \sqrt{\zeta^D_v} \right)
\]

(8.55)

where \( \alpha = e^2/4\pi\hbar c = 7.297 \times 10^{-3} \) is the fine structure constant, \( N_v \) is the number of two-photon transitions between the valence and conduction subbands.

### 8.2.3. D-2PA in QW for TM-TM polarization

For light polarized along the growth direction of the QW, \( \hat{\epsilon} \equiv \hat{z} \) (referred as TM) the selection rule obeys the condition \( \Delta n = odd \) [19], [20], [64], [69]. For the TM-TM case the intermediate state lies in the subbands and the intraband transitions occurs either between two conduction subbands or valence subbands. Figure 8.5 shows the various transition paths possible for 2PA of TM-TM polarized light which correspond to interband transitions from valence subbands to conduction subband and hole (or electron) intersubband transitions.
Figure 8.5 Transition paths for D-2PA in TM-TM case

Considering two-photon transitions between the \( n \)th and \( n' \)th subbands where \( n' = n \pm 1 \), for the summation over intermediate states (1) if \( i \) is in \( n' \)th the valence subband

\[
E_{iv} - \hbar \omega = E_{th,n'} - E_{th,n} - \hbar \omega = - \left[ \hbar \omega + \frac{(n'^2 - n^2)\pi^2 \hbar^2}{2m_{th,\perp} d^2} \right]
\]  
(8.56)

(2) if \( i \) is in \( n \)th the conduction subband \( E_{iv}(k_\parallel) = E_{e,n}(k_\parallel) - E_{th,n}(k_\parallel) \)

\[
E_{iv} = E_{e,n}(k_\parallel) - E_{th,n}(k_\parallel) = E_g + \frac{n^2 \pi^2 \hbar^2}{2m_{e,\perp} d^2} + \frac{n'^2 \pi^2 \hbar^2}{2m_{th,\perp} d^2} - \hbar \omega
\]

\[
= \hbar \omega - \frac{(n'^2 - n^2)\pi^2 \hbar^2}{2m_{e,\perp} d^2}
\]  
(8.57)

The transition rate for TM-TM polarized light is given by

\[
W_2^D|_\perp = \frac{2\pi}{\hbar V} \sum_{n} \sum_{k_\parallel} \left| \frac{\langle c, n' | \tilde{H}_{\text{int}} | c, n \rangle \langle c, n | \tilde{H}_{\text{int}} | v, n \rangle}{\hbar \omega - \frac{(n'^2 - n^2)\pi^2 \hbar^2}{2m_e d^2}} \right|^2 
\]

\[
- \frac{\langle c, n' | \tilde{H}_{\text{int}} | v, n' \rangle \langle v, n' | \tilde{H}_{\text{int}} | v, n \rangle}{\hbar \omega + \frac{(n'^2 - n^2)\pi^2 \hbar^2}{2m_{e,\perp} d^2}} \right|^2 \delta(E_{ev}(k_\parallel) - 2\hbar \omega)
\]  
(8.58)
We calculate the two-photon transitions in the TM-TM case only considering $\Delta n = \pm 1$. Higher odd $\Delta n$ values are ignored as their contribution is small[16]. Disregarding transitions between light-holes and heavy-holes [11] it can be seen from using Equation (8.41) that for TM-TM polarized light, contributions to 2PA occurs only for light-hole and electron pair. The intersubband matrix elements for the TM polarized light are given by

$$
\langle \nu, n'|p|\nu, n \rangle = -i \hbar \frac{m_0}{m_{v,\perp}} \frac{4n'n}{d(n'^2 - n^2)} \hat{z} \quad \text{and} \quad \langle c, n'|p|c, n \rangle = -i \hbar \frac{m_0}{m_{c,\perp}} \frac{4n'n}{d(n'^2 - n^2)} \hat{z}
$$

(8.59)

where $n' = n \pm 1$. Using the interaction Hamiltonian, $\hat{H}_{int} = -\frac{e}{m_0} A(r, t) \cdot \hat{p}$ and following a similar method for simplification, to Equation (8.58) as carried out for the TE-TE case we obtain

$$W_{2D}^{\perp} = \left[ \frac{2\pi e^4 A_0^8}{\hbar} \mu_{th,\parallel} \frac{\hbar^2 m_0^2}{2d^2} \frac{2}{3} |p_{cv}|^2 \sum_n \left[ \frac{4(n \pm 1)n}{1 \pm 2n} \right]^2 \right] \left[ \frac{\hbar \omega}{\mu_{th,\perp}} \left[ \frac{\hbar \omega - (1 \pm 2n)\pi^2 \hbar^2}{2m_c d^2} \right] \left[ \frac{\hbar \omega + (1 \pm 2n)\pi^2 \hbar^2}{2m_{th,\perp} d^2} \right] \right]^2 \theta(2\hbar \omega - E_g)$$

(8.60)

$$- E_{c,n \pm 1} - E_{th,n}$$

Simplifying Equation (8.60) and using the relation in Equation (8.48) we obtain the following expression for the D-2PA coefficient for the TM-TM polarized light $\alpha_2^{D \perp}$

$$\alpha_2^{D \perp} = \frac{1}{3} \left( \frac{32 \alpha}{\pi n_r} \right)^2 2 E_p \left( E_{th,11} \right)^2 \frac{d\mu_{th,\parallel}}{\hbar} \left( \frac{E_g}{2\hbar \omega} \right)^5 \left[ F(N_1) + F(N_2) \right]$$

(8.61)

where
\[ F(N_{1(2)}) = \sum_{n} [(2n + 1) \left( \frac{1}{2n + 1} \right) \left( \frac{h\omega - \frac{(1 + 2n)\pi^2\hbar^2}{2m_{c(\perp)}}}{h\omega + \frac{(1 + 2n)\pi^2\hbar^2}{2m_{th,\perp}d^2}} \right) \left( \frac{h\omega + \frac{(1 + 2n)\pi^2\hbar^2}{2m_{th,\perp}d^2}}{h\omega - \frac{(1 + 2n)\pi^2\hbar^2}{2m_{c(\perp)}}} \right)]^2 \] (8.62)

and

\[ N_{1(2)} = \text{Int} \left[ \zeta_{th} - \frac{\mu_{th,\perp}}{m_{c(\perp)}} \left( \frac{\mu_{th,\perp}}{m_{c(\perp)}} \right)^{1/2} - \frac{\mu_{th,\perp}}{m_{c(\perp)}} \right] \] (8.63)

where \( N_{1} \) is the number of all possible two-photon transitions from the \( nth \) light-hole subband to the \((n + 1)th\) conduction subband and there are \( N_{2} \) possible two-photon transitions from the \((n + 1)th\) light-hole subband to the \( nth \) conduction subband.

![Figure 8.6 D-2PA coefficient (\( \alpha_{2}^{D} \)) for bulk GaAs and GaAs QW (TE-TE and TM-TM) of width 10 nm.](image)

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Figure 8.6 shows results for the D-2PA coefficient plotted against the two-photon energy \((2\hbar\omega)\) for the TE-TE and TM-TM cases calculated for an infinitely high barrier in a GaAs QW of thickness 10 nm along with the D-2PA coefficient for bulk GaAs calculated using the relation [11], [24]

\[
\alpha_2^D = \left(\frac{16\alpha}{n_r}\right)^2 \pi E_p \frac{\hbar^2}{m_0} \frac{2^{3/2}\mu_r^{1/2}}{E_g^{7/2}} F(x) \tag{8.64}
\]

where

\[
F(x) = \left(\frac{2x-1}{2x}\right)^{3/2} \quad \text{and} \quad x = \frac{\hbar\omega}{E_g} \tag{8.65}
\]

In Equation (8.64), \(E_p\) is the Kane energy and \(\mu_r\) is the reduced mass of electron and hole. The D-2PA coefficient \(\alpha_2^D|_\parallel\) increases continuously with photon energy \(\hbar\omega\) and has kinks in the D-2PA curve as we cross the transition from the \(n^\text{th}\) valence subband to the \(n^\text{th}\) conduction subband. The continuous increase of \(\alpha_2^D|_\parallel\) from one band to the other band is due to the linear dependence of the intraband transition matrix elements on the in-plane wave vector \((\mathbf{k})\) (Equation (8.45)). When the two-photon energy increases just past the \(n^\text{th}\) transition energy the in-plane wave vector is zero so we don’t observe a step-like increase in the \(\alpha_2^D|_\parallel\) for the TE-TE case as observed in the TE case for one-photon absorption in QWs. In the TM-TM case the D-2PA coefficient \(\alpha_2^D|_\perp\) is more structured and shows features of the step-like density of states of a QW corresponding to each band-to-band transition. The fact that the \(\alpha_2^D|_\perp\) in the TM-TM case shows step-like features is due to the reason that the intraband matrix elements are \(\mathbf{k}\) independent (Equation (8.59)).
Figure 8.7 D-2PA coefficient in bulk GaAs and GaAs QW’s of different widths in TE-TE case.

Figure 8.7 shows the D-2PA coefficient evaluated for two different thicknesses for TE-TE case along with that for bulk GaAs. For the bulk case the $\alpha_2^D$ is plotted against the two-photon energy normalized to the bandgap ($E_g$), whereas for the QW the $\alpha_2^D_{||}$ is plotted against the two-photon energy normalized by $E_g + E_{hh,11}$ for the TE-TE case and $\alpha_2^D_{\perp}$ is plotted against the two-photon energy normalized by $E_g + E_{th,11}$ for the TM-TM case. The D-2PA curve in the bulk can be explained by the effective interplay of the density of states and the detuning term $E_{iv}(k) - \hbar\omega$.

As we go higher in two-photon energy ($2\hbar\omega$), the $\alpha_2^D$ value increases for photon energies ($\hbar\omega$) close to the middle of the bandgap, goes through a maximum and decreases for higher values of photon energies close to the bandgap. The initial increase in $\alpha_2^D$ for midgap photon energies is attributed to the dominant contribution of the increased density of states and the decrease for close to bandgap photon energies is attributed to the dominant contribution of the increase in the detuning term $E_{iv}(k) - \hbar\omega$ (Equation (8.43)). For the QW we observe that $\alpha_2^D_{||}$
in the TE-TE case decreases with the decrease in the QW width \( (d) \). The decrease in \( \alpha_2^D \parallel \) can be explained due to increase in the effective gap energy due to confinement.

Figure 8.8 D-2PA coefficient in bulk GaAs and GaAs QW’s of different widths in TM case.

For the QW in the TM case (Figure 8.8) we observe an increase in \( \alpha_2^D \perp \) values with a decrease in the QW width \( (d) \). This is due to modulation of the 2PA curve by the step-like feature of the density of states, as observed in the TM-TM case. The arrows in the Figure 8.8 represent the labeled valence band to conduction band transition energies. As discussed earlier for the TE-TE case only \( \Delta n = 0 \) and for the TM-TM case only \( \Delta n = \pm 1 \) are considered. In the TE-TE case, the kinks corresponding to creation of a light hole and electron pair is not visible due to the presence of heavy holes. In the TM-TM case, the first transition starts at the 2\textsuperscript{nd} light-hole subband to 1\textsuperscript{st} electron subband. In the limiting case of an infinitely wide QW, both \( \alpha_2^D \parallel \) in the TE-TE case and \( \alpha_2^D \perp \) in the TM-TM case approaches the bulk value \( \alpha_2^D \) as seen in Figure 8.7 and Figure 8.8.
8.2.4. Theory for nondegenerate two-photon absorption (ND-2PA) in quantum wells

For nondegenerate two-photon absorption, the transition rate as obtained from second order perturbation theory where each photon of energy \( \hbar \omega_1 \) and \( \hbar \omega_2 \) is absorbed is given by

\[
W_{2}^{ND} = \frac{2\pi}{\hbar} \frac{2}{V} \sum_{vc} \left[ \sum_{i} \left( \frac{\langle c | H_{2_{int}} | i \rangle \langle i | H_{1_{int}} | v \rangle}{E_{iv}(\mathbf{k}) - \hbar \omega_1} \right) \right] \delta(E_{cv}(\mathbf{k}) - \hbar \omega_1 - \hbar \omega_2) \tag{8.66}
\]

where \( \hat{H}_{1_{int}} = -\frac{e}{m_0} A_1(\mathbf{r}, t) \hat{p} \) and \( \hat{H}_{2_{int}} = -\frac{e}{m_0} A_2(\mathbf{r}, t) \hat{p} \) represents the electron-field interaction Hamiltonian related to solids.

8.2.5. ND-2PA in QWs for TE-TE polarization

Considering the selection rules for TE (i.e. TE-TE) polarized light, the transition rate can be further simplified as

\[
W_{2}^{ND}_{\parallel} = \frac{2\pi}{\hbar} \frac{2}{V} \sum_{vc} \sum_{n} \sum_{k_1} \left| \langle c, n | \hat{H}_{2_{int}} | v, n \rangle \langle v, n | \hat{H}_{1_{int}} | v, n \rangle \right| \frac{\langle c, n | \hat{H}_{2_{int}} | v, n \rangle \langle v, n | \hat{H}_{1_{int}} | v, n \rangle}{-\hbar \omega_1} \delta(E_{cv}(\mathbf{k}_{\parallel}) - \hbar \omega_1 - \hbar \omega_2) \tag{8.67}
\]

Similar to the Equation (8.44) in \( W_{2}^{D}_{\parallel} \) the 1st summation corresponds to a sum over 2PA contributions of light-holes and heavy-holes, the 2nd summation corresponds to two-photon
transitions summed over subbands of the same index, and the 3\textsuperscript{rd} summation corresponds to a sum over electronic wave vectors in the plane of the quantum well. As we know, there are contributions both from heavy-holes and light-holes to 2PA for TE-TE polarized light and the intersubband matrix elements exist only for transitions within a single subband. Substituting values for the transition matrix elements (Equation (8.45)) and subband energies (Equation (8.37)) and transforming the summation over the in-plane wave vector $\mathbf{k}_\parallel$ into an integration over the kinetic energy, we obtain

$$W_{2}^{ND}|\parallel = \sum_{v} a_v \frac{4}{\hbar^5} \frac{e^4 A_{01}^2 A_{02}^2}{16 m_0^2} |p_{cv}|^2 \frac{1}{d} \left( \frac{1}{\omega_1} + \frac{1}{\omega_2} \right)^2 \sum_{n} (\hbar \omega_1 + \hbar \omega_2 - E_{e,n} - E_{v,n} - E_g)$$

where the $a_v$'s are the coefficients obtained by averaging over the polarization of light and are equal to 1/4 for heavy holes and 1/12 for light holes. The ND-2PA coefficient for TE-TE polarization is obtained from the transition rate as

$$\alpha_{2}^{ND}(\omega_1, \omega_2)|\parallel = W_{2}^{ND}|\parallel \frac{\hbar \omega_1}{2I_1 I_2}$$

where $I_1$ and $I_2$ are the irradiances of the beams with photon energies $\hbar \omega_1$ and $\hbar \omega_2$ respectively.

$$I_1 = \frac{n_{\omega_1} c \varepsilon_0 \omega_1^2 A_{01}^2}{2}$$

$$I_2 = \frac{n_{\omega_1} c \varepsilon_0 \omega_2^2 A_{02}^2}{2}$$

After the summations in Equation (8.68) and substituting $E_p$ from Equation (8.50) into Equation (8.69), we obtain the following expression for the ND-2PA coefficient for TE-TE polarized light $\alpha_{2}^{ND}|\parallel$.
\[ \alpha_{2}^{ND}(\omega_1, \omega_2)_{||} = 2 \frac{(16\alpha)^2}{n_{\omega_1} n_{\omega_1}} \frac{2E_p(E_{th,11})^2}{m_0 E_g^5} \frac{d\mu_{th,\perp}}{4 \mu_{th,\perp}} \left[ \frac{1}{\mu_{th,\perp}} F(\zeta_{hh}) \right] \]

\[ + \frac{1}{12} F(\zeta_{lh}) \left( \frac{\hbar}{E_g} \frac{\hbar \omega_1}{E_g} \right)^2 \left( \frac{E_g}{\hbar \omega_1} + \frac{E_g}{\hbar \omega_2} \right)^2 \]  

(8.72)

where for the nondegenerate case

\[ \zeta_{v}^{ND} = \frac{\hbar \omega_1 + \hbar \omega_2 - E_g}{E_{v,11}} \]  

(8.73)

The expression for \( E_{v,11} \), \( F(\zeta_{v}) \), and \( N_v \) in the nondegenerate case has the same form as in Equation (8.53), Equation (8.54), and Equation (8.55) but with the substitution of \( \zeta_{v}^{ND} \) given by Equation (8.73). Here \( N_v \) is the number of nondegenerate two-photon transitions between the valence and conduction subbands.

8.2.6. ND-2PA in QW for TM-TM polarization

Considering the selection rules for TM (i.e. TM-TM) polarized light, the transition rate for ND-2PA is given by
\[ W_{2}^{ND} \big|_{\perp} = \frac{2\pi e^{4} A_{01}^{2} A_{02}^{2}}{\hbar 16 m_{0}^{4}} \sum_{n} \sum_{k_{i}} \left[ \langle c, n' | \hat{A}_{2\text{int}} | v, n' \rangle \langle v, n' | \hat{A}_{1\text{int}} | v, n \rangle \right] \]

\[ - \left[ \hbar \omega_{1} + \frac{(n'^{2} - n^{2}) \pi^{2} \hbar^{2}}{2m_{th, \perp} d^{2}} \right] \]

\[ + \frac{\langle c, n' | \hat{A}_{1\text{int}} | v, n' \rangle \langle v, n' | \hat{A}_{2\text{int}} | v, n \rangle}{\hbar \omega_{2} + \frac{(n'^{2} - n^{2}) \pi^{2} \hbar^{2}}{2m_{c, \perp} d^{2}}} \]

\[ + \frac{\langle c, n' | \hat{A}_{2\text{int}} | c, n \rangle \langle c, n | \hat{A}_{1\text{int}} | v, n \rangle}{\hbar \omega_{2} - \frac{(n'^{2} - n^{2}) \pi^{2} \hbar^{2}}{2m_{c, \perp} d^{2}}} \]

\[ + \frac{\langle c, n' | \hat{A}_{2\text{int}} | c, n \rangle \langle c, n | \hat{A}_{1\text{int}} | v, n \rangle}{\hbar \omega_{1} - \frac{(n'^{2} - n^{2}) \pi^{2} \hbar^{2}}{2m_{c, \perp} d^{2}}} \]

\[ + \frac{\langle c, n' | \hat{A}_{2\text{int}} | c, n \rangle \langle c, n | \hat{A}_{1\text{int}} | v, n \rangle}{\hbar \omega_{1} - \frac{(n'^{2} - n^{2}) \pi^{2} \hbar^{2}}{2m_{c, \perp} d^{2}}} \]

\[ \delta (E_{cv}(k_{\parallel}) - \hbar \omega_{1} - \hbar \omega_{2}) \quad (8.74) \]

Substituting intersubband and interband transition matrix elements from Equation (8.46) and Equation (8.59), Equation (8.74) becomes

\[ W_{2}^{ND} \big|_{\perp} = \frac{2\pi e^{4} A_{01}^{2} A_{02}^{2}}{\hbar 16 m_{0}^{4}} \sum_{n} \sum_{k_{i}} \left[ \frac{\hbar^{2} m_{0}^{2}}{(\mu_{th, \perp})^{2} d^{2}} \left[ \frac{4(n \pm 1)n}{1 \pm 2n} \right]^{2} \frac{2}{3} |p_{cv}|^{2} \right] \]

\[ \times \left[ \frac{\hbar \omega_{1}}{\hbar \omega_{1} - \frac{(1 \pm 2n) \pi^{2} \hbar^{2}}{2m_{c, \perp} d^{2}}} \right] \left[ \frac{1}{\hbar \omega_{1} + \frac{(1 \pm 2n) \pi^{2} \hbar^{2}}{2m_{th, \perp} d^{2}}} \right] \]

\[ + \left[ \frac{\hbar \omega_{2}}{\hbar \omega_{2} - \frac{(1 \pm 2n) \pi^{2} \hbar^{2}}{2m_{c, \perp} d^{2}}} \right] \left[ \frac{1}{\hbar \omega_{2} + \frac{(1 \pm 2n) \pi^{2} \hbar^{2}}{2m_{th, \perp} d^{2}}} \right] \]

\[ \delta (E_{cv}(k_{\parallel}) - \hbar \omega_{1} - \hbar \omega_{2}) \quad (8.75) \]
where \( n' \) is substituted as \( n \pm 1 \). The summation over \( n \) corresponds to allowed two-photon transitions between valence subbands \( n \) and conduction subbands \( n \pm 1 \). Simplifying Equation (8.75) we obtain

\[
W_{2}^{ND} |_{\perp} = \frac{2\pi e^{4}A_{01}^{2}A_{02}^{2}}{\hbar 16m_{0}^{4}} \frac{\hbar^{2}m_{0}^{2}}{(\mu_{\text{th,}})^{2} d^{2} \pi \hbar^{2} d^{2}} \frac{\mu_{\text{th,}}}{3} \left[ F(N_{1}) + F(N_{2}) \right]
\]

where \( F(N_{1}) \) and \( F(N_{2}) \) are given by

\[
F(N_{1(2)}) = \left[ (2n + 1) - \frac{1}{(2n + 1)} \right]^{2}
\]

\[
= \frac{1}{(2n + 1)} \left[ \frac{\hbar \omega_{1}}{\hbar \omega_{1} - (1 + 2n)\pi^{2}\hbar^{2}} \right]^{2}
\]

\[
= \frac{1}{(2n + 1)} \left[ \frac{\hbar \omega_{2}}{\hbar \omega_{2} - (1 + 2n)\pi^{2}\hbar^{2}} \right]^{2}
\]

The ND-2PA coefficient for TM-TM polarized light is obtained from the transition rate as

\[
\alpha_{2}^{ND} (\omega_{1}, \omega_{2}) |_{\perp} = W_{2}^{ND} |_{\perp} \frac{\hbar \omega_{1}}{2I_{1}I_{2}}
\]

where \( I_{1} \) and \( I_{2} \) are given in Equation (8.70) and Equation (8.71) respectively. Substituting \( E_{p} \) from Equation (8.50) and \( W_{2}^{ND} |_{\perp} \) from Equation (8.76) into Equation (8.69), we obtain the following expression for the ND-2PA coefficient for TM-TM polarized light \( \alpha_{2}^{ND} |_{\perp} \)
\[ \alpha_{2}^{ND}(\omega_1, \omega_2) \parallel = \frac{1}{3} \frac{32\alpha}{\pi} \frac{2E_p(E_{th,11})^2}{E_g^3} \frac{\mu_{th,||} \hbar d}{m_0} \sum_n [F(N_1) + F(N_2)] \left( \frac{1}{2^7 \hbar \omega_1} \left( \frac{\hbar \omega_2}{E_g} \right)^2 \right) \]

(8.79)

Figure 8.9 and Figure 8.10 show results for the ND-2PA coefficient of bulk GaAs with infinitely high barriers for a GaAs QW having different widths for both the TE-TE and TM-TM case, calculated at optical frequencies \( \omega_1 \) and \( \omega_2 \). The ND-2PA coefficient of bulk GaAs is calculated using the relation [11][23]

\[ \alpha_{2}^{ND}(\omega_1, \omega_2) = \frac{(16\alpha)^2}{n_{\omega_1} n_{\omega_2}} \frac{1}{5} \frac{1 \pi E_p \hbar^2 2^{3/2} m_r^{1/2}}{m_0 E_g^{7/2}} F(x_1, x_2) \]

(8.80)

where

\[ F(x_1, x_2) = \frac{(x_1 + x_2 - 1)^{3/2}}{2^7 x_1 x_2^2} \left( \frac{1}{x_1} + \frac{1}{x_2} \right)^2 \text{ and } x_1 = \frac{\hbar \omega_1}{E_g}, x_2 = \frac{\hbar \omega_2}{E_g} \]

(8.81)

For the bulk case the \( \alpha_{2}^{ND} \) is plotted against the sum of the two-photon energies normalized to the bandgap \( E_g \), whereas for the QW the \( \alpha_{2}^{ND} \parallel \) is plotted against two-photon energies normalized to \( E_g + E_{th}^{11} \) for the TE-TE case and \( \alpha_{2}^{ND} \parallel \) is plotted against two-photon energies normalized to \( E_g + E_{th}^{11} \) for the TM-TM case. As the linear absorption in QW for TE case starts at \( E_g + E_{th}^{11} \) and for TM case starts at \( E_g + E_{th}^{11} \) so the sum of two-photon energies are normalized to \( E_g + E_{th}^{11} \) for TE case and to \( E_g + E_{th}^{11} \) for TM case respectively. Due to the large energy difference of photon pairs in the nondegenerate case for a bulk semiconductor there is an orders of magnitude increase in \( \alpha_{2}^{ND}(\omega_1, \omega_2) \) over \( \alpha_{2}^{D} \). This enhancement of \( \alpha_{2}^{ND}(\omega_1, \omega_2) \) has been measured for
direct-gap semiconductors [12] and could be used for different applications such as mid-infrared (mid-IR) detection [3] and imaging [70].

Figure 8.9 Non-degenerate 2PA coefficient in bulk GaAs and GaAs QW’s of different widths in TE-TE case

In a standard experimental setup, the measurement of $\alpha_{2}^{ND}(\omega_1, \omega_2)$ carried out in [12] uses a pump-probe geometry where the strong beam is called the pump and the weak beam, for which the transmission is monitored, is called the probe. In Figure 8.9 and Figure 8.10 the photon with energy $h\omega_2$ is the pump and the photon with energy $h\omega_1$ is the probe. In reference [12] the pump photon is at the long wavelength to avoid any 2PA or three-photon absorption (3PA) caused by the pump itself. In all the plots the 2PA coefficients are plotted against photon energies which are shown scaled to the respective one-photon transition energies. This allows comparing the ND-2PA coefficient for the bulk and QW semiconductors on the same scale and it also makes the comparison to the respective D-2PA coefficient values easier.
Figure 8.10 Non-degenerate 2PA coefficient in bulk GaAs and GaAs QW’s of different widths in TM-TM case.

The enhancement in $\alpha_{2}^{ND}(\omega_1, \omega_2)$ is explained by the resonant terms in the denominator of Equation (8.66) which makes $\alpha_{2}^{ND}(\omega_1, \omega_2)$ diverge when the energy of one of the photons becomes goes to zero and the energy of the other photon becomes more nearly resonant to the bandgap of the semiconductor. Figure 8.9 and Figure 8.10 are generated with pump photon energy $\hbar \omega_2 \approx 0.12E_g$, corresponding to a wavelength of 7.5 $\mu$m and varying the probe photon energy $\hbar \omega_1$ for $\alpha_{2}^{ND}(\omega_1, \omega_2)$. For the QW in the TE-TE case $\alpha_{2}^{ND}|_{\parallel}$ shows similar continuous transitions from the $n$th valence subband to the $n$th conduction subband as in D-2PA. The transition paths for ND-2PA in the TE-TE and TM-TM cases are shown in Figure 8.4 and Figure 8.5 respectively. In Figure 8.9 $\alpha_{2}^{ND}|_{\parallel}(\omega_1, \omega_2)$ for QW widths of 10 nm and 5 nm is shown. We observe an increase in $\alpha_{2}^{ND}|_{\parallel}(\omega_1, \omega_2)$ over the bulk values for larger confinements attributed to the nondegenerate enhancement in QWs. For $(\hbar \omega_1 + \hbar \omega_2)/E_g = (\hbar \omega_1 + \hbar \omega_2)/E_g + E_{hh}^{11} = 1.02$, $\alpha_{2}^{ND}|_{\parallel}(\omega_1, \omega_2)$ for a QW of width of 10 nm is $\approx 2$ times the bulk $\alpha_{2}^{ND}(\omega_1, \omega_2)$ and for a QW of width of 5 nm is $\approx 3.4$ times the bulk $\alpha_{2}^{ND}(\omega_1, \omega_2)$. Similar to the $\alpha_{2}^{D}|_{\parallel}$ curve there is a
continuous increase of $\alpha_2^{ND}(\omega_1, \omega_2)$ due to the linear dependence of the intraband transition matrix elements on the in-plane wave vector ($k$) (Equation (8.45)) and the signature step-like density of states feature of a QW is not observed.

For ND-2PA in the TM-TM case (Figure 8.10) $\alpha_2^{ND}(\omega_1, \omega_2)$ shows more structured features as in the D-2PA case due to similar selection rules and transition paths. For $(\hbar \omega_1 + \hbar \omega_2)/E_g = 1.02$ in the bulk case $\alpha_2^{ND}(\omega_1, \omega_2) \approx 75 \text{ cm/GW}$ and for $(\hbar \omega_1 + \hbar \omega_2)/E_g + E_{th}^{12} = 1.02$ in a QW of width 10 nm, $\alpha_2^{ND}(\omega_1, \omega_2) \approx 2600 \text{ cm/GW}$. For the QW in the TM case the first 2PA transition starts at $E_g + E_{th}^{12}$ so the ratio of $(\hbar \omega_1 + \hbar \omega_2)$ and $E_g + E_{th}^{12}$ is taken to compare the ND-2PA coefficient values of the bulk and QW on the same scale. For a QW of width 10 nm in the TM-TM case there is a two orders of magnitude increase in $\alpha_2^{ND}(\omega_1, \omega_2)$ over the bulk $\alpha_2^{ND}(\omega_1, \omega_2)$ value.

![Figure 8.11 ND-2PA coefficient in bulk GaAs and GaAs QW of width 10 nm.](image)

Figure 8.11 shows a comparison of bulk and QW for the TM-TM case for different values of $\hbar \omega_2$. By comparison of $(\hbar \omega_1 + \hbar \omega_2)/E_g = 1.03$ in the bulk case to $(\hbar \omega_1 + \hbar \omega_2)/E_g + E_{th}^{12} = 1.03$. For the QW in the TM case the first 2PA transition starts at $E_g + E_{th}^{12}$ so the ratio of $(\hbar \omega_1 + \hbar \omega_2)$ and $E_g + E_{th}^{12}$ is taken to compare the ND-2PA coefficient values of the bulk and QW on the same scale. For a QW of width 10 nm in the TM-TM case there is a two orders of magnitude increase in $\alpha_2^{ND}(\omega_1, \omega_2)$ over the bulk $\alpha_2^{ND}(\omega_1, \omega_2)$ value.
1.03, we can see for $\hbar \omega_2 = 7 \, \mu m$ there is a several orders of magnitude increase in $\alpha_2^{ND}|_\perp(\omega_1, \omega_2)$ over the bulk $\alpha_2^{ND}(\omega_1, \omega_2)$.

Figure 8.12 and Figure 8.13 describes different scenarios of $\alpha_2^{ND}|_\perp(\omega_1, \omega_2)$. In Figure 8.12 $\alpha_2^{ND}|_\perp(\omega_1, \omega_2)$ is plotted for a QW of width 10 nm for different $\hbar \omega_2$ values and as each $\hbar \omega_2$, $\hbar \omega_1$ is varied. Whereas in Figure 8.13 $\alpha_2^{ND}|_\perp(\omega_1, \omega_2)$ is plotted for QWs of different widths with a constant $\hbar \omega_2$ and varying $\hbar \omega_1$.

![Figure 8.12](image_url)

Figure 8.12 ND-2PA coefficient ($\alpha_2^{ND}|_\perp$) in a GaAs QW of width 10 nm for various pump photon energies. The inset shows the zoomed in circled section.
Figure 8.13 ND-2PA coefficient ($\alpha_{ND}^2|_\perp$) in a GaAs QW of different widths for a constant pump photon energy.

As observed in Figure 8.12 as we decrease the photon energy $\hbar \omega_2$ we observe a strong increase in $\alpha_{ND}^2|_\perp(\omega_1, \omega_2)$. But as the photon energy $\hbar \omega_2$ is further decreased $\hbar \omega_2(8 \mu m)$, such high values as happened for the C2LH1 transition for $\hbar \omega_2(7 \mu m)$ is not accessible. This is also observed in Figure 8.13 as we decrease the QW width from 10 nm to 8 nm. As the confinement increases there is a strong enhancement of $\alpha_{ND}^2|_\perp(\omega_1, \omega_2)$ at the C1LH2 transition, but the C2LH1 transition is not accessible for the particular photon energy $\hbar \omega_2(5 \mu m)$. The range over which the pump ($\hbar \omega_2$) and probe $\hbar \omega_1$ photon energies can vary depends on the quantum well width and gives a limitation to for extreme nondegenerate cases for QWs with large confinement. The photon energy of the pump is given by the condition

$$\hbar \omega_2 > E_{th}^{12} - E_{th}^{11}$$

(8.82)

The range of probe photon energies is given by

$$E_g + E_{th}^{12} - \hbar \omega_2 < \hbar \omega_1 > E_g + E_{th}^{11}$$

(8.83)
8.2.7. ND-2PA in QW for mixed case of TE and TM (TE-TM)

So far the cases of ND-2PA in QWs examined are where the two-photons have the same polarization. It would be an interesting case to investigate the mixed case of ND-2PA where one of the incident beams is TE polarized and the other beam is TM polarized. Let the TE polarized beam have photon energy $\hbar \omega_1$ and the TM polarized beam have photon energy $\hbar \omega_2$. The transition paths for ND-2PA for TE-TM case are shown in Figure 8.14

Figure 8.14 (a) Transitions shown here corresponds to an interband transition from valence subbands to conduction subband and hole (or electron) intersubband transitions and (b) Transitions shown here corresponds to interband transitions from valence subbands to conduction subband and hole (or electron) intrasubband transitions.

In Figure 8.14 (a) the transition path is shown only for light-hole contributions to the 2PA as the heavy-hole interband transition is not excited by TM polarized light. In Figure 8.14 (b), the transition paths shown have both light-hole and heavy-hole contribution to the 2PA. Considering the two-photon transition paths shown in Figure 8.14 (following the appropriate selection rules) the transition rate for ND-2PA for TE-TM case is given by
\[ W_{2}^{ND} \mid \text{mixed} = \frac{2\pi e^{4}A_{01}^{2}A_{02}^{2}}{16m_{e}^{4}} \sum_{n} \left[ \sum_{k_{1}} \hat{m}_{2} \cdot \hat{e}_{1} \cdot \hbar \frac{m_{0}}{m_{v,\parallel}} k_{\|} \right]^{2} \delta(E_{cv}(k_{\|}) - \hbar \omega_{1} - \hbar \omega_{2}) \]

\[ + \frac{\hat{e}_{1} \cdot \hbar \frac{m_{0}}{m_{e}} k_{\|} \hat{m}_{2} \cdot \hat{p}_{cv}}{\hbar \omega_{1}} \left[ \frac{\hbar}{\hbar \omega_{1} - \left( \frac{(n^{2} - n^{2})\pi^{2} \hbar^{2}}{2m_{e,\perp} d^{2}} \right)} \right]^{2} \delta(E_{cv}(k_{\|}) - \hbar \omega_{1} - \hbar \omega_{2}) \quad (8.84) \]

where \( \hat{e}_{1} \) and \( \hat{m}_{2} \) represent polarization of TE and TM beams respectively, and the summation over \( v \) corresponds to the contribution of light holes and heavy holes to ND-2PA. Following the procedure as carried in the derivation of the ND-2PA coefficient for the TE-TE and TM-TM cases the \( \alpha_{2}^{ND}(\omega_{1}, \omega_{2}) \mid \text{mixed} \) is given by

\[ \alpha_{2}^{ND}(\omega_{1}, \omega_{2}) \mid \text{mixed} = \frac{\alpha^{2}}{n_{r1}n_{r2}} \frac{E_{p}}{m_{0} \pi^{2} E_{g}^{3}} \left( E_{nh}^{11} \right)^{2} \left[ E_{g} \frac{\mu_{nh,\perp}}{\hbar \omega_{1}} \frac{\pi^{2}}{E_{g}^{3}} \frac{1}{3} F(\zeta_{lh}) \right] \]

\[ + \frac{4\hbar^{2} d}{\pi^{2}} \left[ \frac{1}{6} \mu_{lh,\parallel} \sum_{n} \left[ F_{lh}(N_{1}) + F_{lh}(N_{2}) \right] \right] \]

\[ + \left( \frac{\mu_{lh,\perp}}{\mu_{hh,\perp}} \right)^{2} \frac{1}{2} \mu_{hh,\parallel} \sum_{n} \left[ F_{hh}(N_{1}) + F_{hh}(N_{2}) \right] \right] \left[ \frac{E_{g}^{3}}{(\hbar \omega_{1})(\hbar \omega_{2})^{2}} \right] \quad (8.85) \]

where \( N_{1} \) and \( N_{2} \) are given by Equation (8.77) and \( F_{lh}(N_{1(2)}) \) and \( F_{hh}(N_{1(2)}) \) are given by
\[ F_{lh}(N_{1(2)}) = \left(2n + 1\right) \]

\[ - \frac{1}{(2n + 1)} \left[ \frac{\hbar \omega_2}{\hbar \omega_2 - \frac{(1 + 2n)\pi^2 \hbar^2}{2m_{c(h,\perp)}d^2}} \right]^{2} \]

(8.86)

\[ F_{hh}(N_{1(2)}) = \left(2n + 1\right) \]

\[ - \frac{1}{(2n + 1)} \left[ \frac{\hbar \omega_2}{\hbar \omega_2 - \frac{(1 + 2n)\pi^2 \hbar^2}{2m_{c(h,\perp)}d^2}} \right]^{2} \]

(8.87)

In Figure 8.15 the ND-2PA coefficients evaluated for bulk GaAs and GaAs QW’s for the TM-TM case and the TE-TM case are shown. For the bulk case the \( \alpha_{2}^{ND} \) is plotted against the sum of two-photon energies normalized to the bandgap \( (E_g) \), whereas for the QW the \( \alpha_{2}^{ND}|_{\perp} \) is plotted against the sum of two-photon energies normalized to \( E_g + E_{lh}^{11} \) for the TM case and \( \alpha_{2}^{ND}|_{mixed} \) is plotted against the sum of two-photon energies normalized to \( E_g + E_{hh}^{11} \) for the mixed case.
From Figure 8.15 we observe that ND-2PA in the mixed case is also structured as for the TM-TM case. Here the 1st transition starts when the sum of two-photon energies becomes greater than $E_g + E_{th}^{11}$. For $(\hbar \omega_1 + \hbar \omega_2)/E_g = 1.02$ in the bulk case $\alpha_2^{ND}(\omega_1, \omega_2) \approx 75 \text{ cm/GW}$ and for $(\hbar \omega_1 + \hbar \omega_2)/E_g + E_{th}^{11} = 1.02$ in the QW of width 10 nm, $\alpha_2^{ND}|_{\text{mixed}}(\omega_1, \omega_2) \approx 100 \text{ cm/GW}$. Since the 1st 2PA transition starts at $E_g + E_{th}^{11}$ the ratio of $(\hbar \omega_1 + \hbar \omega_2)$ and $E_g + E_{th}^{11}$ is taken to compare the ND-2PA coefficient values of the bulk and QW for the TE-TM case on the same scale. As we see, the values of ND-2PA in the QW for the TE-TM case and bulk case are almost equal and is not significantly enhanced. As we go deeper into the band the ND-2PA in the bulk case is even larger than the ND-2PA in the TE-TM case for the QW. For a better understanding of ND-2PA in the TE-TM case, $\alpha_2^{ND}|_{\text{mixed}}(\omega_1, \omega_2)$ for QWs of different widths is plotted with the bulk ($\alpha_2^{ND}$) and TM-TM cases for ($\alpha_2^{ND}|_\perp$) of a QW of width 10 nm in Figure 8.16. For a QW of width 5 nm at $(\hbar \omega_1 + \hbar \omega_2)/E_g + E_{th}^{11} = 1.02$, $\alpha_2^{ND}|_{\text{mixed}}(\omega_1, \omega_2) \approx$
Comparing $\alpha_{2}^{ND}|_{mixed}$ value with the bulk $\alpha_{2}^{ND}$ value of 75 cm/$GW$ at $(h\omega_{1} + h\omega_{2})/E_g = 1.02$.

Figure 8.16 ND-2PA coefficient of bulk GaAs and GaAs QW of width 10 nm for TM-TM and TE-TM case.

We observe two-orders of increase in magnitude over bulk values. This enhancement comes only for strong confinement in the TE-TM case. To obtain the enhancement of ND-2PA in the TE-TM case over the bulk we need to carefully design the QW.

In the calculation of the all the viewgraphs discussed in this chapter the values of various parameters considered are $E_p = 25 eV$ (GaAs), $K = 3100 \text{ cm}\text{GW}^{-1}eV^{5/2}$, $\gamma_1 = 6.8$, and $\gamma_2 = 1.9$. $\gamma_1$ and $\gamma_2$ value are taken from reference [26]

8.3. Possible applications of ND-2PA enhancement in QW

One of the straightforward application of the extreme nondegenerate case over the degenerate case in bulk semiconductors is IR detection using uncooled wide bandgap
photodiodes [3], [39]. For pulsed IR detection, a gate pulse of photon energy slightly less than the bandgap energy is used to sensitize the photodiode during which the IR pulse is detected. Similarly for CW IR detection a “CW” gate is used to sensitize the photodiode continuously for the CW IR radiation to be detected [40], [41]. Based on this enhancement, Fishman et al showed gated detection of sub–100 pJ mid-infrared radiation using an uncooled GaN detector. In the ND-2PA coefficient definition $\alpha_{2}^{ND}(\omega_1, \omega_2)$, the beam with photon energy $\hbar \omega_2$ is defined here as the pump to monitor the transmission of the probe with photon energy $\hbar \omega_1$ where $\alpha_{2}^{ND}(\omega_1, \omega_2)$ is defined by the Equation (8.80). If we consider photon energy $\hbar \omega_1$ as the pump and monitor the transmission of the probe at the photon energy $\hbar \omega_2$, then the ND-2PA coefficient is defined by switching the frequencies, i.e., $\alpha_{2}^{ND}(\omega_2, \omega_1)$. Through Equation (8.80) this leads to a relation $\alpha_{2}^{ND}(\omega_1, \omega_2)/\alpha_{2}^{ND}(\omega_2, \omega_1) = \omega_1/\omega_2$. This tells us that if we use the lower photon energy as the pump then we see maximum depletion of the probe at the given irradiance level. For gated IR detection using the ND-2PA, the signal measured at the output of the photodetector is proportional to the photo-generated carrier density ($N_{ND}$), and is given by [3]

$$\frac{dN_{ND}}{dt} = 2 \frac{\alpha_{2}^{ND}(\omega_1; \omega_2)}{\hbar \omega_1} I_2 I_1 = 2 \frac{\alpha_{2}^{ND}(\omega_2; \omega_1)}{\hbar \omega_2} I_1 I_2$$  (8.88)

where $I_1$ and $I_2$ are the respective irradiances. From Equation (8.88) we observe the signal or the carrier generation enhancement is proportional to $\alpha_{2}^{ND}(\omega_1; \omega_2)/\hbar \omega_1$ or $\alpha_{2}^{ND}(\omega_2; \omega_1)/\hbar \omega_2$ and is the same for the measured signal at the output of the photodetector for $\hbar \omega_1$ and $\hbar \omega_2$.

The large enhancement shown for ND-2PA in the QW for the different cases can also be used for IR detection using wide bandgap QW semiconductors. For IR detection purposes it is
more instructive to compare the carrier generation enhancement in different scenarios of ND-2PA in QWs with ND-2PA in bulk semiconductors.

Figure 8.17 Theoretical predicted carrier generation enhancement for ND-2PA: (a) bulk semiconductors, (b) W semiconductors for TE-TE and TM-TM case.

Figure 8.17 (a) shows a plot of $\alpha_2^{ND}(\omega_1; \omega_2)/\hbar\omega_1$ as a function of the normalized photon energies $\hbar\omega_1/E_g$ and $\hbar\omega_2/E_g$. Similar plots are shown for ND-2PA in a GaAs QW of width 10 nm for TE and TM cases. Figure 8.17 (b) shows a plot of $\alpha_2^{ND}\parallel(\omega_1; \omega_2)/\hbar\omega_1$ as a function of the normalized photon energies $\hbar\omega_1/(E_g + E_{hh}^{11})$ and $\hbar\omega_2/(E_g + E_{hh}^{11})$ for the TE-TE case and Figure 8.17 (c) shows plot a of $\alpha_2^{ND}\perp(\omega_1; \omega_2)/\hbar\omega_1$ as a function of the normalized photon energies.
energies $\hbar \omega_1 / (E_g + E_{1h}^{11})$ and $\hbar \omega_2 / (E_g + E_{1h}^{11})$ for the TM-TM case. The shaded triangular area corresponds to regions where 2PA occurs. The dotted line corresponds to the degenerate case and the arrows show the extreme nondegenerate case. These plots enable us to determine the experimental conditions for detection using extremely nondegenerate photon pairs in bulk and QW semiconductors. It is also visible from Figure 8.17 that the maximum enhancement of ND-2PA coefficient is observed in the TM-TM case of a QW. In the TM-TM case the arrows shown in Figure 8.17(c) corresponds to a photon energy ratio, $\hbar \omega_1 / \hbar \omega_2 = 11$. Comparing with the same photon energy ratio in the bulk we see the carrier generation enhancement is $\approx 20$ times its bulk value. Such an increase in the amount of carrier generation in QWs could lead to an increase in quantum efficiency of END-2PA detection based devices with QWs as their active regions.
CHAPTER 9: CONCLUSION

9.1. Summary

The purpose of this thesis work is to provide a study and understanding of D-2PA and ND-2PA in bulk and QW semiconductors and to identify possible applications using END-2PA enhancement.

The gated mid-IR pulsed detection experiments with extremely nondegenerate photon pairs is carried out with uncooled GaN and GaAs p-i-n photodetectors. The sensitivity of the method is attributed to the time gating of the mid-IR pulse with the sub-bandgap pulse. The responsivity or the quantum efficiency of the method is dependent on the gate pulse irradiance and can be controlled by changing the gate pulse irradiance. The carriers created independently by the gate pulse is a possible concern even though the END-2PA signal is discriminated through the synchronous detection technique. The photocurrent at the output of the detector due to the gate pulse varies quadratically with the irradiance of the gate pulse. Hence, in the experiment, amplitude noise present in the gate pulse gives the dominant noise contribution to this gated detection system. Also for high gate pulse irradiances the photocarriers created due to the gate pulse can saturate the detector. The saturation effect due to D-2PA can be understood by the signal-to-background ratio discussed in Chapter 6 for GaN and GaAs. So there is a trade-off between the responsivity and the background signal/noise. It is observed in Chapter 6 that a higher responsivity is obtained in smaller bandgap semiconductors while a larger signal-to-background ratio is obtained in larger bandgap semiconductors by looking into the relative scaling of the ND-2PA to D-2PA signals. The enhancement in END-2PA enabled CW IR detection in uncooled GaN and GaAs p-i-n photodetectors; however, the sensitivity was low. The
minimum detectable power obtained was $\approx 60 \, \mu W$ at 1550 nm with GaN and was $\approx 300 \, \mu W$ at 4890 nm with GaAs. In this case the background current due to linear Urbach tail absorption of the CW “gate” is an issue. The low sensitivity can be improved using longer interaction lengths between the gate and the signal beam, i.e., a different detector geometry.

The advantage of IR detection using the END-2PA technique is that it is a direct detection technique where the detector element itself is the two-photon absorbing material. It is possible to detect both mid-IR and near-IR wavelengths with appropriate gate wavelength and choice of direct-gap material without any modification in the detection systems. The imaging experiments carried out in Chapter 7 show END-2PA is a viable method for scanning 3-D mid-IR imaging in uncooled GaN p-i-n photodiodes. With the END-2PA technique it is possible to obtain simultaneously both 3-D and 2-D images of the object. The ultimate spatial resolution of the mid-IR imaging using END-2PA is limited by the imaging optics but the longitudinal (depth) resolution does not depend on the wavelength but errors in determining the zero delay position depends on the FWHM of the cross-correlation signal of the gate pulse and the signal pulse. This sets a limit on the depth resolution of the 3-D imaging technique using END-2PA. For a cross-correlation width of $\approx 350 \, fs$ the depth resolution was determined to be $8 \, \mu m$ which is limited by the signal to noise ratio. With this technique it is possible to obtain 3-D images of buried structures. As an example, post fabrication imaging of semiconductor structures is shown by scanning the structure from the substrate side.

The theory presented for ND-2PA in QW semiconductors in chapter 8 is the first work ever on 2PA in QWs for nondegenerate photon pairs. A theory for D-2PA in QW semiconductors is also presented and corrects several errors in previous publications [16]. The calculations carried out in chapter 8 are for a GaAs QW. 2PA in QWs depends on the polarization of the incident
photons. For TE-TE polarized photons the shape of the 2PA curve both for degenerate and nondegenerate cases does not predict a signature step-like density of states whereas the 2PA spectra for TM-TM polarized photons predicts step-like sharp features. The reason is for the TE-TE case the intraband matrix elements are \( k \) dependent hence no 2PA is observed for \( k = 0 \). The difference in shape of the 2PA spectra for TE-TE and TM-TM is already observed in D-2PA experiments in QWs [61], [64]. Since the selection rules for two-photon transitions are the same both for D-2PA and ND-2PA it is expected to show similar differences in 2PA shape for ND-2PA in QWs for TE-TE and TM-TM cases as predicted by theory. In the TM-TM case the ND-2PA coefficient of QW semiconductors shows orders of magnitude enhancement over the ND-2PA coefficient of bulk semiconductors. Another case for ND-2PA in QWs we investigated is the mixed case of TE and TM (TE-TM) where one of the photons is TE and the other photon is TM. The shape of the ND-2PA curve in the TE-TM case predicts a step-like density of states but does not predict much enhancement like the TM-TM case over the bulk ND-2PA coefficient.

9.2. Future Work

The work described in this dissertation was meant to demonstrate possible applications using END-2PA. It also indicated some interesting other avenues of investigation which may provide improvements to the present technique.

The p-i-n photodetector used in the experiment is not optimized for 2PA processes. Since in the 2PA based gated detection technique the quantum efficiency of the carrier generation process due to 2PA depends on the interaction length, it is expected that designing p-i-n photodiodes with thicker intrinsic elements may improve the quantum efficiency. Another possible solution is
to design a waveguide p-i-n photodetector where in this configuration both the gate and signal beam can be guided in the waveguide. In another possible configuration the gate beam can be guided in the waveguide and the signal beam can be grating coupled to the waveguide through the ridge.

In mid-IR imaging one possible future work is to find a solution for the long time taken for raster scanning. Designing an array of detectors with lock-in amplifiers for each pixel is one possible solution. Another possible solution is to design a computer-based lock-in amplifier which would be cost effective. More work can be carried out in the area of 3-D imaging of buried structures in bulk IR transmissive materials such as semiconductors and certain ceramics. Calibration of microchannels buried in ceramics is one such work described in reference [48] which can be performed using the END-2PA technique. As discussed in chapter 7 the mid-IR reflectance imaging of biological tissues is another important study that can be carried out with this technique. This system can provide similar information to that obtained with an OCT system.

The theory for ND-2PA for the TM-TM case in QWs predicts large enhancement in the ND-2PA coefficient over bulk semiconductors. The foremost future work that can be carried out for QWs is to measure these predicted large enhancements in ND-2PA for the TM-TM case. For this TM-TM case the electric vector polarization of light is oriented along the confinement direction of the QW. Thus the measurement of ND-2PA coefficient in the TM-TM case requires waveguiding both of the beams for ND-2PA.

Quantum well infrared photodetectors (QWIP) are the current technology for detection in the mid-IR region. The large enhancement predicted for ND-2PA in QWs for different cases can also be used for IR detection and IR experiments as described using a bulk semiconductor.
LIST OF REFERENCES


