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NONLINEAR OPTICAL PROPERTIES OF ZnO NANOWIRE



A GRADUATE PROJECT SUBMITTED TO THE DEPARTMENT OF PHYSICS
PRESENTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE IN PHYSICS (SOLID STATE PHYSICS)

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DEPARTMENT OF PHYSICS

As members of the board of examining of the final MSC Master Project open defense, we certify that we have read and evaluated the Master Project prepared by **Desta Negash** under the title “**Nonlinear optical properties of zinc oxide nanowire**” and recommended that the Master Project be accepted as fulfilling the Master Project requirement for the **Degree of Master of Physics (with specialization Solid State Physics)**.

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List of abbreviation

ZnO	Zinc oxide
CZnONW	Cylindrical Zinc Oxide Nanowire
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
PL	Photoluminescence
NW	Nanowire
NWl	Nanowell
ND	Nanodot
UV	Ultraviolet
LED	light Emitting Diode
SEM	Scanning Electron Microscopy
NL	Nonlinear

Abstract

The numerical values of linear and third order nonlinear optical absorption coefficients and refractive index changes are calculated for several configuration structural parameters and optical intensity. The result shows that in the absence of electric field when the optical incident intensity chosen to be $1\text{MW}/\text{cm}^2$ as asymmetry of the sample decreased the negative values of third order nonlinear absorption coefficient increased and at lower asymmetry the negative maximum value of nonlinear absorption coefficient is seen. Besides, the total absorption coefficient decreased from, because of negative contribution of nonlinear term. In addition, the linear coefficient of refractive index changes becomes decreased while the nonlinear refractive index changes slightly increased in magnitude but in opposite sign to the linear refractive index changes. Consequently, the total refractive index change is further decreased. This result clearly shows that the total refractive index coefficient strongly depends on the nanowire size change. Also, as the incident optical intensity increased from $0\text{ MW}/\text{cm}^2$ to $1.2\text{ MW}/\text{cm}^2$ the total absorption coefficient decreased and the total refractive index changes also decreased. From this result of study the optical absorption coefficient and refractive index changes for ZnO nanowire is strongly depends on both the size and optical intensity of the light. In general since, the size and optical intensity affects the nonlinear term, the material in our cases (ZnO cylindrical nanowire) exhibits nonlinear optical properties.

Keywords, Zinc oxide, Nano wire, optical property, potential model

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Desta Negash

Bahir Dar, Ethiopia

September, 2019

Chapter 1

Introduction

1.1 General Background

The notion of “nanotechnology” was introduced for the first time by Richard Feynman in 1959 in his famous Caltech lecture “There’s plenty of room at the bottom”, showing his vision towards small sized. Richard Feynman imagined the world of the Nano scale where the fundamental laws of quantum physics define the behavior of a single atom and control the formation of different structures from individual atoms [1]. Nanotechnology also defined as use of technology to create materials on an atomic scale. It is based on the ability to manipulate individual atoms and molecules in order to assemble them into bigger structures. Such artificial Nano scale structures, usually fabricated using self-assembly phenomena. Therefore, from the formal point of view nanostructures can be any objects with size (at least in one of the directions) of the order of 100 nm or less [2]. The transition of material structures from macro scale to Nano scale results in sharp changes of their properties. These changes are due to two reasons. The first reason is at Nano level the surface to volume ratio of any material increases. This brings most of the atom at the surface of Nano structure and hence surface becomes more reactive. So the performance of material increases as compared to its bulk form. The second reason is the surface atoms are under conditions, which are very different from the conditions for the bulk atoms, because they are bound to the neighboring atoms in a different way. Atoms in the surface layer have some of their chemical bonds broken and therefore they are free to make new bonds. Recent advances in semiconductor technology have made possible fabrication of low dimensional semiconductor hetero structures, because the main objectives of research in Nano electronics are quantum-dimensional structures [3].

1.2 Nanostructures

A low dimensional system is one in which microscopic degrees of freedom of carriers is restricted from moving in the full 3D space due to quantum confinement [4]. The dimensionality refers to the number of degrees of freedom in the electron momentum [5]. Structures designed, where the electrons motion is made to be restricted to move in less than three spatial dimensions are called nanostructures [3,6]. Low dimensional structures can be

classified according to the number of reduced dimensions. These are 2D (Nano well), 1D (Nano wire), and 0D (Nano dots).

a) Nanowell

In the case when electrons motion along only one direction is limited to Nano scale (for example, along the z-direction) i.e., when the condition, $L_z \leq \lambda$ is satisfied, where λ is the electron de Broglie wavelength, the electron energy states corresponding to this direction are quantized. At the same time, the electrons motion in the other two directions (x- and y-directions) stays free, with the continuous energy spectrum. Such a structure is called a Nanowell (NWL).

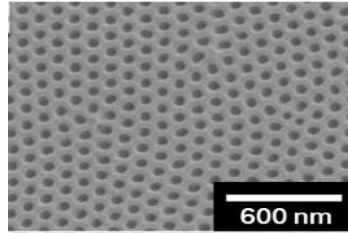


Figure 1.1 SEM image of the array of Nano wells in AAO template after pore-widening for 20 minutes [7].

b) Nanowire

In the case when the electrons motion is restricted along two directions (for example, along the y- and z-directions), i.e., when the conditions $L_y \leq \lambda$ and $L_z \leq \lambda$ are satisfied, the energy which corresponds to these two directions of motion is quantized. At the same time, the electrons motion in the other one direction (x-direction) stays free, with the continuous energy spectrum. Such a structure is called a Nano wire (NWR).

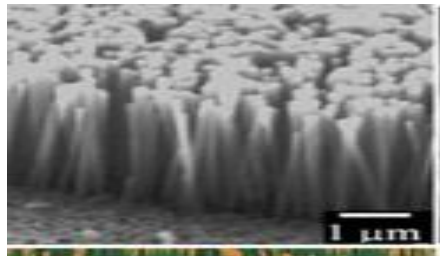


Figure 1.2 SEM images of ZnO NWs [8].

c) Nanodot

In the case when the electrons motion is restricted along all three directions, i.e., when the conditions $L_x \leq \lambda$, $L_y \leq \lambda$ and $L_z \leq \lambda$ are satisfied, the energy spectrum of such a structure, which is called a Nano dot(ND), is totally quantized. This means reducing the degrees of freedom to zero.

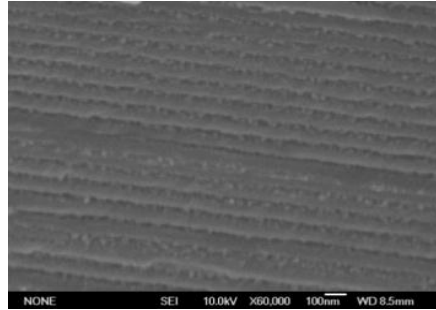


Figure 1.3 cross-section SEM image of ZnO Nanodots[9].

Nano dots can be regarded as artificial atoms to which the electrons are bound by a “manufactured” confining potential. They are a new class of artificially structured materials with atomic like discrete states which is ideal for use in laser structures [4,10]. Usually arrays of such dots are prepared on semiconductor hetero structures, such that all of them contain the same number of electrons. The spatial confinement of carriers enhances the coulomb interaction between the electron and hole, which leads to an increase in the exciton binding energy and oscillator strength [11,12]. As more number of the dimension is confined, more discrete energy levels can be found, that is carrier movement is strongly confined in a given dimension. The energy band structure of bulk semiconductor materials is almost continuous. In Nano size particles, the bands are split into sublevels because of the quantum confinement. The quantum confinement of carriers in the low-dimensional system leads to the formation of discrete energy levels and the drastic changes of physical and chemical properties such as the novel nonlinear optical effects [13].

During the last decade, the II–VI group zinc oxide (ZnO) thin films and nanowires (NWs) as well as the correlative quantum structures have attracted significant attention both in theories and experiments. This is mainly due to the following evident facts. ZnO semiconductor has a series of sole features and advantages [14–17]: wide direct band gap (~ 3.3 eV at 300 K) and a large exciton binding energy (~ 60 meV) which make the material quite attractive as a basis for the creation of short wavelength optoelectronic devices such as light-emitting and laser diodes operating in green-

ultraviolet range as well as high-power and high-temperature electronics; piezoelectric and pyroelectric properties which result in ZnO being an ideal candidate for fabricating electromechanical coupling devices; decomposable and possibly biocompatible characteristics that is suitable for medical and biological applications; easy fabrication of various nanostructures via a chemical approach or physical method, which leads to potentially lower costs for ZnO-based devices and equipment. Hence the investigation of physical properties in ZnO quantum structures has become a warm topic during the last decade. Among various investigations of ZnO-based nanostructures, the one dimensional (Q1D) ZnO NW structures have concerned special interest [18–28]. Due to the Q1D confined property of NWs almost being perfectly single crystalline at the Nano scale, they are ideal structures to study size dependent properties and quantum confinement phenomena. In addition, the NWs are also expected to be important useful units for optoelectronic Nano scale applications that can be easily combined in Nano-devices such as light emitting diodes [18], lasers [19], and photo detectors for the UV wavelength range [20, 21]. It is well-known that excitonic luminescence is one type of significant luminiferous mechanisms in semiconductor bulk materials and low-dimensional quantum systems [28]. Theories and experiments reveal that the quantum-confined structures can affect greatly the optical properties of excitonic states. Thus, the topic of excitonic states in low dimensional quantum structures has attracted considerable interest both in theoretical and experimental investigations. For the cubic GaAs-based quantum well (QW), quantum wire (QWR), and quantum dot (QD) systems, the properties of excitonic states have been widely studied and reported [29–34]. For the 1D wurtzite ZnO-based QWR and NW structures, the optical and optoelectronic features related to the excitonic states also have been reported [22–27]. Hwang et al. [22] investigated carrier depletion and transport in a single ZnO NW by using cathodoluminescence measurements, and an exciton diffusion length of 200 nm along the NW axis was determined. The groups of Chen et al. [24] and Liao et al. [25] studied the strain effect on the optical properties of excitonic states in ZnO NW structures, respectively. Their experiments show that the exciton emission peaks display a continuous blue-shift from tensile to compressive edges. Ahn et al. [26] observed the emission lines of free exciton 3.38 eV in 1D ZnO/MgZnO core/shell nanostructures. Recently, Wu's group [27] grew ZnO NWs with high crystallinity by metal-organic chemical vapor deposition. Dominant free exciton emission at a low temperature was observed by photoluminescence spectroscopy. It was attributed to both, the enhancement of the free exciton emission induced by the high crystalline quality of the NWs and the dominance of the donor-bound

exciton emission. On the other hand, it is well-known that the linear and nonlinear optical procedures, such as optical absorption and harmonic generation, are important and notable optical phenomena, especial in quantum-confined systems and in the case of strong incident light intensity [35–37]. Furthermore, the optical nonlinearities in ZnO low-dimensional quantum structures have been studied [38–47]. For example, very strong second-harmonic-generation ($\sim \text{pm/V}$) and third harmonic-generation ($\sim 10^{-18} \text{m}^2 \text{V}^{-2}$) susceptibilities have been observed in ZnO thin film structures [38–44]. These results reveal that the surface and excitonic effects enhance greatly the nonlinear susceptibilities. Al-Mossawi et al. [45] analyzed theoretically semiconductor optical amplifier in ZnO QD based on the non-Markovian gain model. Recently, the groups of Pedersen and Voss [46] investigated experimentally the second-harmonic-generation in Q1D ZnO NW systems, and they found that the features of second harmonic-generation in the ZnO NW structures are obviously different from the situations in ZnO thin film structures. However, to the best of our knowledge, there is rare theoretical work to investigate and analyze the excitonic states and their influence on nonlinear optical properties in Q1D ZnO based NW structures.

Exploring the influence of the spatial confinement on the electronic structure and corresponding intersubband optical transitions of the physical system plays an important role in optoelectronic device modeling. The effective confinement potential arises due to both dimensional quantization and field-induced quantization. Asymmetry of the confinement potential designates the nonlinear optical response of the low-dimensional systems. Asymmetry in a potential profile can be obtained through either the asymmetric compositional growth or by applying an electric field to a symmetric structure. S.Sakiroglu [47], studied the effect of spatial confinement under static external electric field and incident optical intensity on third order nonlinear absorption coefficient and refractive index changes of GaAS/AlGaAS core/shell nano well. He found that total optical absorption enhances and the resonant peaks move to the aspect of the higher energy with an increase in well parameter and electric field. Besides, the total refractive index changes decreased with the structural parameter and show strong confinement-induced blue-shift whereas the applied electric field makes significant change on the peak magnitude.

1.3 Significance of the study

The main significance of this project work is; i) The energy Eigen values of ground and first excited states are calculated using Schrodinger equation. ii) The dependence of linear and nonlinear

absorption coefficient and refractive index changes on the size and optical field intensity is analyzed and discussed in detail.

1.4 Objectives

1.4.1 General objective

- The general objective of this project to study the nonlinear optical properties of cylindrical ZnO nanowire.

1.4.2 Specific objectives

The specific objectives of this project are to:

- calculate the linear and third order nonlinear absorption coefficient and refractive index changes for ZnO nanowire at different structural parameter.
- calculate the linear and third order nonlinear absorption coefficient and refractive index changes for ZnO nanowire under the influence of electric field.
- determine third order nonlinear absorption coefficient and refractive index changes for ZnO nanowire for different optical field intensity.

Chapter 2

Literature Review

2.1 Semiconductors nanostructures

Nanometer range semiconducting materials have been a subject of intense study for last several years due to their size dependent physical and chemical properties [1-4], below a critical size characteristic of the material. Blue shift in the optical absorption spectrum, size dependent luminescence, enhanced oscillator strength optical effects are some examples of the interesting properties exhibited by these Nano crystals. All these properties are various manifestations of the so called size quantization effect which arises due to the increasing quantum confinement of the electrons and holes with diminishing size of crystallites and the consequent changes in the electronic structures. Their electronic structure is between that of a molecule and a bulk responsible to give rise to profound modification of the physical properties. Nanoparticles have been suggested for various potential applications in the electronic where quantum confinement effects may be of advantage. For example, quantum confinement affects in nanostructured semiconductors results in widening the band gap of semiconductor and act as an efficient light emitter. Recent reports suggest that nanoparticles can be used to produce light of various colors by band gap tuning using particle size effects [48]. As the life times of electronics in the excited state is large, efforts are being made to use in laser application. It has also got technological importance in the field of solar cells, catalysis, light emitting, resonant tunneling devices, laser, gas sensors and ultraviolet, etc. depending up on the dimensionality of low-dimensional homogenous semiconductors one can consider three categories of systems as 2D system which includes thin films, layer structures and quantum wells; 1D system such as semiconductor wires; 0D system such as clusters, quantum dots and colloids. Because of their many properties different from bulk system structures, the investigation on low-dimensional semiconductor has attracted much interest in recent years. There are two approaches to fabricate these low dimensional systems. One is the top-down approach where small structures are obtained from a large structure by using lithographic patterning, which is based on the sequential decrease of the object's size for the fabrication of objects of nano scale size and the other is the bottom-up approach where small structures are made by letting atoms or molecules self-assemble into the desired form [49]. That means the bottom-up technology is based on the self-assembly phenomenon. The main idea of technology is in the development of the

controlled self-assembly of the atoms, molecules, and molecular chains into nano scale objects. The bottom-up technology allows the fabrication of nano objects, such as nano dots, nano wires, and super lattices [50].

2.2 zinc oxide nanostructures

Zinc oxide is a transparent piezoelectric semiconductor which occurs naturally in the mineral called zincite [51]. Zinc oxide (ZnO) is one of II-IV semiconductor material and it is an important semiconductor material with a wide and direct band gap of 3.44 eV at low temperatures and 3.37 eV at room temperature, and it has relatively high Curie temperature, which has a large exciton binding energy of 60 meV at room temperature, even larger than the ionization energy at the same temperature [50–52]. This makes it especially appropriate for room temperature optoelectronics in the near UV spectral region. Having large exciton binding energy of ZnO, implies that it emits more excitons at room temperature when compared to others [53]. Note Materials with direct band gaps are better than those with indirect band gaps because their absorption is higher [54]. In a direct band gap semiconductor, large numbers of electrons are excited from the valence band to conduction band. ZnO is a key technological material [50,54], because ZnO has attracted more and more attention due to its interesting properties. The growth of nano sized ZnO, including the ZnO nano well, ZnO nano wire, and ZnO nano dots have been investigated widely and used as transparent conductors in solar cell, as a component in UV light emitters and high-power electronics. Recently, ZnO nano structures attracted attention for possible applications in optoelectronic and spintronic devices, such as light emitting and laser diodes, spin-based memory, and logic [55]. When the size of ZnO nano particles is smaller than the Bohr radius, the quantum confinement has a notable influence on the band gap and further causes a series of novel characteristics such as the blue-shift of luminescence in the cathode luminescence (CL) spectrum which implies that ZnO QDs would be applicable to optoelectronic and spintronic devices [56]. In general a partial lists of the properties of ZnO that distinguish it from other semiconductors or oxides: direct and wide band gap, large exciton binding energy, large piezoelectric constant, strong luminescence, the high electron mobility, high thermal conductivity, large non-linear optical coefficients, has high conductance, chemical and thermal stability, a good radiation resistance and is harmless to the environment, it has been also observed that ZnO exhibits exceptionally high radiation hardness, which is important for application at high altitude.

2.3 Nanowires

One of the most intensively explored classes of semiconductor structures is the class of Nanowire [57]. In a Nanowire the electrons motion is free along the length of the wire while its motion in the plane normal to the length is confined [58]. Quantum confinement of charge carriers in these structures leads to formation of discrete energy levels, the enhancement of the density of states at specific energies and the drastic change of optical absorption spectra [59]. In Nano wires, due to dimension decreasing in contrast to Nano well, the electron hole interaction is enhanced by two-dimensional confinement. As a result, the wave function overlap of the electron and the hole is enhanced, namely, the excitation effect becomes especially prominent. Many authors found that the binding energy and polaroid effect of an excitation are greatly larger in Nanowire than in Nano well and predicted application to electronic and optoelectronic devices. Among the low-dimensional structures, there has been a great deal of interest in the investigation of Nanowire. So far, many investigators studied the properties of Nanowire using several theoretical and experimental methods. The study of nano wires has been revolutionary in the fundamental sciences due to the potential applications of these structures in the technology of electronic and optoelectronics devices and fundamental physics investigations [60]. We know that Sakaki proposed the concept of nano wires for the first time in 1975. After this, with the advances in semiconductor growth techniques like chemical lithography, molecular beam epitaxy, and etching, researchers could fabricate Nanowire of nanometer size with various cross-sections such as circular, V-shape, triangular, parallelogram, T-shape, and hexagonal shape [61]. Recent advances in nanotechnology have made it possible to fabricate nanowires of different sizes and geometries [62]. Nanowires have a variety of novel properties, rendering them invaluable in diverse disciplines like medicine, optoelectronics and energy physics, among others. However, due to the small dimensions concerned, it is very difficult to fabricate nanostructures with controllable and uniform cross-sectional area, to which some effort has been directed. Apart from the difficulty in fabricating nanowires of uniform cross-sectional area, it may be beneficial to produce nanowires with non-uniform cross-sectional area. In nanostructures, cylindrical surfaces show physical interesting properties. These structures can be described using a parabolic potential model and it is one of the types confining potentials [63]. The parabolic confinement potential is also introduced for technological reasons. Electron confinement is selected in the form of transverse parabolic potential, since

there are no rigid interface boundaries. At the same time according to Kohn theorem, optical properties of the systems are independent of both electron-electron interaction and the number of electrons in the layer; i.e., it can be neglected. The parabolic potential is equivalent to the potential produced by a positive charge uniformly distributed over an infinite layer. However, we note that the Kohn theorem is not true for two basic cases: for multicomponent systems (such as double quantum wells and for a non-parabolic well). In such systems, electron-electron interaction can have a strong effect on the optical properties of electrons. At small values of the radius of the nano wire the parabolic confining potential can be regarded as a model for the real potential.

2.4 ZnO Nanowires

ZnO is easy to grow with rich morphologies and properties by a variety of economic processes. Among various nanostructures under study, ZnO nanowires (NWs) are of great interests due to their quasi one-dimensional (1-D) structures showing quantum confinement effects and high surface to volume ratios. A ZnO NW can be considered as a 1-D passage under absorption, emission, and transport of electrons, holes, and photons. The special geometry structures can lead to strong confinement effects on the carriers and photons, which could result in various novel optical and electrical properties for device applications such as short wavelength LEDs and lasers of nanometer size [64]. Scanning electron microscopy (SEM) images taken on an electrochemically grown ZnO NW array are shown in Fig. 2.1(b). The nanowires produced vertically on the substrate with an average diameter of about 100 nm and length up to a few micrometers. The upper part of the inset of Fig. 2.1(b) displays the top view of a ZnO NW array. Each NW has a flat hexagonal cross section. The lower part of the inset shows a transmission electron microscopy (TEM) image as well as an electron diffraction pattern of NW. These measurements suggest that the NWs have single crystalline structure with a preferred growth direction along $\langle 001 \rangle$. Fig.2.1(c) shows the X-ray diffraction (XRD) patterns taken on electrochemically grown ZnO NW arrays by an X-ray diffractometer. A strong (002) peak and a number of weaker peaks with indices of (101), (102), (110), (112), and (004) were observed, indicating that the sample consists of well-aligned ZnO NWs on the substrate. The XRD data also suggest that the applied negative electric field during growth does not noticeably affect the NW quality while it enhances the NW growth [65]. Electron diffraction measurements confirmed that the electrochemically grown NWs are single crystals.

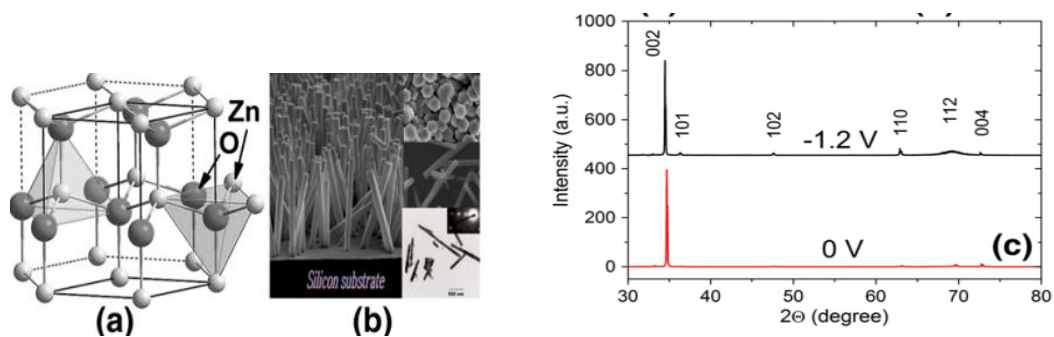


Figure 2. 1(a) ZnO wurtzite crystal structure; (b) SEM image of electrochemically grown ZnO NW arrays; top view and TEM images are included in the inset. (c) XRD of ZnO NW arrays grown under two different potentials of 0 and -1.2V [65].

2.5 Optical Properties

2.5.1 General optical Properties of semiconductor

A full understanding of the optical properties of semiconductors is thus deeply rooted in the foundations of modern solid-state physics. The optical properties of a semiconductor can be defined as any property that involves the interaction between electromagnetic radiation or light and the semiconductor, including absorption, diffraction, polarization, reflection, refraction, and scattering effects. From the macroscopic viewpoint, the interaction of matter with electromagnetic radiation is described by Maxwell's equations. The optical properties of matter are introduced into these equations as the constants characterizing the medium such as the dielectric constant, magnetic permeability, and electrical conductivity. From our optical viewpoint, we choose to describe the solid by the complex dielectric constant or complex dielectric function $\epsilon(\omega)$. The complex refractive index is the complex square root of the dielectric function. Its real and imaginary parts are the refractive index n and the extinction coefficient k . These optical constants describe an electromagnetic wave in the medium of propagation; the refractive index n gives the phase shift of the wave, and the extinction coefficient k gives the weakening of the wave. The field of optical spectroscopy is a very important area of science and technology since most of our knowledge about the structure of atoms, molecules, and solids is based upon spectroscopic investigations. Since the early 1950s, detailed knowledge about the various Eigen states present in semiconductors has arisen including energy bands, excitation levels, impurity and defect levels, densities of states,

energy-level widths (lifetimes), symmetries, and changes in these conditions with temperature, pressure, magnetic field, electric field, etc. Most optical properties of semiconductors are integrally related to the particular nature of their electronic and vibrational structures. These electronic and vibrational dispersion relations are in turn related to the type of crystallographic structure, the particular atoms, and their bonding. The optical properties of semiconductors are often subdivided into those that are electronic and those that are vibrational (lattice related) in nature. The electronic properties concern processes involving the electronic states of the semiconductor, while the lattice properties involve vibrations of the lattice (absorption and creation of phonons). Lattice properties are of considerable interest for heat dissipation, electronic transport, and lifetimes (broadenings) of electronic states, but it is the electronic properties which receive the most attention in semiconductors because of the technological importance of their practical applications. Modern day semiconductor optoelectronic technologies include lasers, light-emitting diodes, photo detectors, optical amplifiers, modulators, switches, etc., all of which exploit specific aspects of the electronic optical properties. The phenomena usually studied to obtain information on the optical properties of semiconductors are absorption, reflection or ellipsometry, photoconductivity, emission, light scattering, and modulation techniques [66].

2.5.2 Optical Properties of Nanostructures

Optical and electronic properties of low-dimensional semiconductor structures are important part of the modern physics of semiconductors. The effect of confinement on the electronic and optical properties increases as one goes from nano wells to nano dots [62]. It is to be noted that the study of optical properties of low dimensional semiconductor structures is important, not only to know, but also in the fabrication and subsequent working of electronic and optical devices based on such systems. The decrease in dimensionality of system for semiconductors can lead to a dramatically enhancement of nonlinearities. So the nonlinear optical properties of semiconductor nano wells, nano wires, and nano dots have attracted much attention in the past few years in theoretical and applied physics sides [57]. The nonlinear optical properties in the low-dimensional materials have the potential for device applications in laser amplifiers, photo detectors, high-speed electro-optical modulators, and so on. The confinement of electrons in these systems changes the electron mobility remarkably. This results in a number of new phenomena, which concern a reduction of the sample dimensions. These effects,

for example, electron-phonon interaction and scattering rates, the linear and nonlinear optical properties, differ from those in bulk. When light beam incident on optical medium, it may be: reflected, propagated and transmitted. Absorption occurs during the propagation if the frequency of the light is resonant with the transition frequencies of the atoms in the medium. When light of sufficient energy shines on to a material, it induces transitions of electrons from occupied (lower level) states below the Fermi energy to unoccupied (higher level) states above the Fermi energy. Photon is absorbed by exciting an electron from a lower level to higher level. Therefore optical absorption can lift electrons from completely full valence band to empty conduction band. Exciting electrons in a solid in addition to by photon absorption is exciting electron by other electron. This done by shining a beam of mono energetic electron at a sample. The conduction band and valence band are separated by an energy called band gap $E_g = E_c - E_v$, where E_c and E_v are energy of conduction band and valence band respectively. Absorption can occur where $\hbar\omega > E_g$. Absorption cannot occur at $\hbar\omega = E_g$, where $\hbar\omega$ is the energy of the photon. The lowest energy at which absorption can occur is given by difference in energy, $E_{e1} - E_{h1}$, between the lowest state in the well on the conduction band and the lowest in the well in the valence band. Absorption can occur at higher energy. The strongest quantization occurs between corresponding states in two bands, so that $n_e = n_h = n$. The strong absorption occurs at the frequency given by, $\hbar\omega_n = E_{en} - E_{hn}$. The energy of the photons matches the difference in electric energy level. It is given by $\hbar\omega_n = E_{e2} - E_{h1}$. Atoms jump to an excited stated state by absorption of photon, and then relax to an intermediate state, before re-emitting a photon by spontaneous emission as it falls back to the ground state. In solids this re-emission process is called luminescence. In other words luminescence is the general name given to the process of spontaneous emission of light by excited atoms in a solid state material. The photon emitted has a smaller energy than the absorbed photon. This reduction in the photon energy is called Stroke's shift. Note Materials with direct band gaps are better than those with indirect band gaps because their absorption is higher [67]. In a direct band gap semiconductor, large numbers of electrons are excited from the valence band to conduction band. In semiconductor physics a direct band gap means that the minimum of the conduction band lies directly above the maximum of the valence band in the k space. In contrast, an indirect semiconductor refers to a semiconductor with a band gap in which the minimum energy in the conduction band is shifted by a k vector relative to the top of the valence band. Indirect

transitions(non-vertical transition) Semiconductors such as GaP, Ge, and Si have indirect gaps where the maximum valence band energy and minimum conduction band energy do not occur at the same k value. In this case, the electron cannot make a direct transition from the top of the valence band to the bottom of the conduction band because this would violate conservation of momentum. Such a transition can still take place but as a two-step process requiring the cooperation of another particle and which can then be described by second-order perturbation theory. Semiconductor nanowires (NWs) are usually characterized by anisotropic optical properties like optical absorption, photoluminescence, photoconductivity, as well as generation of higher harmonics, and strongly depend on the polarization of exciting light [68].

2.5.3 Optical Properties of ZnO nanowire

Optical methods provide an easy and sensitive tool for measuring the electronic structures of nanowires, since optical measurements require minimal sample preparation (for example, contacts are not required) and the measurements are sensitive to quantum effects. Optical spectra of 1-D systems, such as carbon nanotubes, often show intense features at specific energies near singularities in the combined density of states that are formed under strong quantum confinement conditions. A variety of optical techniques have shown that the properties of nanowires are different to those of their bulk counterparts, and this section of the review focuses on these differences in the optical properties of nanowires. Although optical properties have been shown to provide an extremely important tool for characterizing nanowires, the interpretation of these measurements is not always straightforward. The wavelength of light used to probe the sample is usually smaller than the wire length, but larger than the wire diameter. Hence, the probe light used in an optical measurement cannot be focused solely onto the wire, and the wire and the substrate on which the wire rests (or host material, if the wires are embedded in a template) are probed simultaneously. For measurements, such as photoluminescence (PL), if the substrate does not luminescence or absorb in the frequency range of the measurements, PL measures the luminescence of the nanowires directly and the substrate can be ignored. However, in reflection and transmission measurements, even a non-absorbing substrate can modify the measured spectra of nanowires. Effective medium theory used as a method to handle the optical properties of nanowires whose diameters are typically smaller than the wavelength of light, noting that observable optical properties of materials can be related to the complex dielectric function [69]. Effective medium theories [70] can be applied to model the nanowire and substrate as one continuous composite with a single complex dielectric

function ($\varepsilon_1 + i\varepsilon_2$), where the real and imaginary parts of the dielectric function ε_1 and ε_2 are related to the index of refraction (n) and the absorption coefficient (β) by the relation $\varepsilon_1 + i\varepsilon_2 = (n + i\beta)^2$. Since photons at visible or infrared wavelengths see a dielectric function for the composite nanowire array/substrate system that is different from that of the nanowire itself, the optical transmission and reflection are different from what they would be if the light were focused only on the nanowire. One commonly observed consequence of effective medium theory is the shift in the plasma frequency in accordance with the percentage of nanowire material that is contained in the composite [71]. The plasma resonance occurs when $\varepsilon_1(\omega)$ becomes zero, and the plasma frequency of the nanowire composite will shift to lower (higher) energies when the magnitude of the dielectric function of the host materials is larger (smaller) than that of the nanowire. Although reflection and transmission measurements probe both the nanowire and the substrate, the optical properties of the nanowires can be determined independently. One technique for separating out the dielectric function of the nanowires from the host is to use an effective medium theory in reverse. Since the dielectric function of the host material is often known, and the dielectric function of the composite material can be measured by the standard method of using reflection and transmission measurements in combination with either the Kramer–Kronig relations or Maxwell’s equations, the complex dielectric function of the nanowires can be deduced. An example where this approach has been used successfully is for the determination of the frequency dependence of the real and imaginary parts of the dielectric function $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ for a parallel array of bismuth nanowires filling the pores of an alumina template [72].

2.5.4 Linear and Nonlinear optics

Throughout the long history of optics, and in deed until relatively recently, it was thought that all optical media were linear. The consequences of this assumption are far-reaching:

- The optical properties of materials, such as refractive index and absorption coefficient, are independent of light intensity.
- The principle of superposition, a fundamental tenet of classical optics, is applicable.
- The frequency of light is never altered by its passage through a medium.
- Two beams of light in the same region of a medium have no effect on each other so that light cannot be used to control light.

The operation of the first laser in 1960 enabled us to examine the behavior of light in optical materials at higher intensities than previously possible. Experiments carried out

in the post-laser era clearly demonstrate that optical media do in fact exhibit nonlinear behavior, as exemplified by the following observations:

- The refractive index, and consequently the speed of light in a nonlinear optical medium, does depend on light intensity.
- The principle of superposition is violated in a nonlinear optical medium.
- The frequency of light is altered as it passes through a nonlinear optical medium; the light can change from red to blue, for example.
- Photons do interact within the confines of a nonlinear optical medium so that light can indeed be used to control light.

A linear dielectric medium is characterized by a linear relation between the polarization density and the electric field (F), $\vec{P} = \epsilon_0 \chi \vec{E}$, where ϵ_0 is the permittivity of free space and χ is the electric susceptibility of the medium. A nonlinear dielectric medium, on the other hand, is characterized by a nonlinear relation between P and $\vec{E}$. The nonlinearity may be of microscopic or macroscopic origin. The polarization density $\vec{P} = Np$ is a product of the individual dipole moment p induced by the applied electric field $\vec{E}$ and the number density of dipole moments N . The nonlinear behavior may reside either in p or in N . The relation between $\vec{P}$ and $\vec{E}$ is linear when $\vec{E}$ is small, but becomes nonlinear when $\vec{E}$ acquires values comparable to interatomic electric fields, which are typically $\sim 10^5 - 10^8$ V/m. Another possible origin of a nonlinear response of an optical material to light is the dependence of the number density N on the optical field. An example is provided by a laser medium in which the number of atoms occupying the energy levels involved in the absorption and emission of light are dependent on the intensity of the light itself. Since externally applied optical electric fields are typically small in comparison with characteristic interatomic or crystalline fields, even when focused laser light is used, the nonlinearity is usually weak. Therefore in nonlinear optics $\vec{P} = \epsilon_0 \chi \vec{E} + \vec{P}_{NL}$. The relation between $\vec{P}$ and $\vec{E}$ is approximately linear for small $\vec{E}$, deviating only slightly from linearity as $\vec{E}$ increases [72].

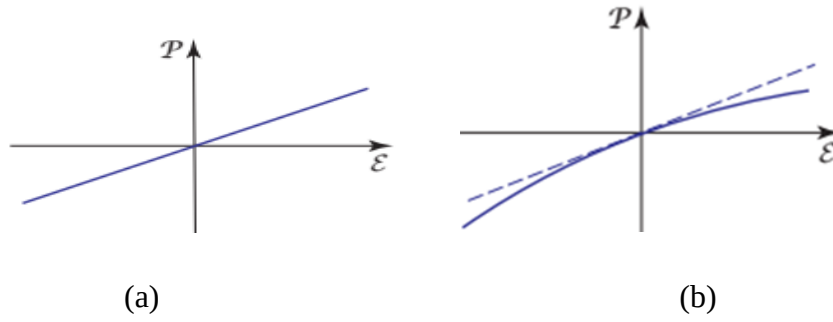


Figure 2. 2 The P–E relation for (a) a linear dielectric medium and (b) a nonlinear medium [72]

The nonlinear optical properties in the low-dimensional materials have the potential for device applications in laser amplifiers, infrared photo detectors, high-speed electro-optical modulators, light emitting diode, single electron transistors and so on [13].

The optical properties of semiconductors at low light levels are often referred to as linear properties in contrast to the nonlinear optical properties described later[68]. There are many physical processes that control the amount of absorption or other optical properties of a semiconductor. In turn, these processes depend upon the wavelength of radiation, the specific properties of the individual semiconductor being studied, and other external parameters such as pressure, temperature, etc. Just as the electrical properties of a semiconductor can be controlled by purposely introducing impurity dopants (both p and n type) or affected by unwanted impurities or defects, so too are the optical properties affected by them. With adding impurity dopants in nonlinear optics, the nonlinear properties of a material, including the variations of optical parameters such as nonlinear absorption coefficient, the nonlinear refractive index can be changed [74]. Optical absorption coefficient as a function of the photon energy in cylindrical ZnO NWR is determined, by considering the cases with the electric field applied parallel to the axis of the wire. Numerical results show that the optical absorption in cylindrical ZnO NWR decreases in the presence of the electric field. There is structure in the absorption above the effective band gap of ZnO NWR in addition to the structure in the absence of the electric field, which arises from the oscillations due to the Franz–Keldysh effect for the electric field parallel to the axis of the wire. In addition, the results and also the strength and the threshold energy of the absorption of ZnO QWR are decreased when quantum size increases [75].

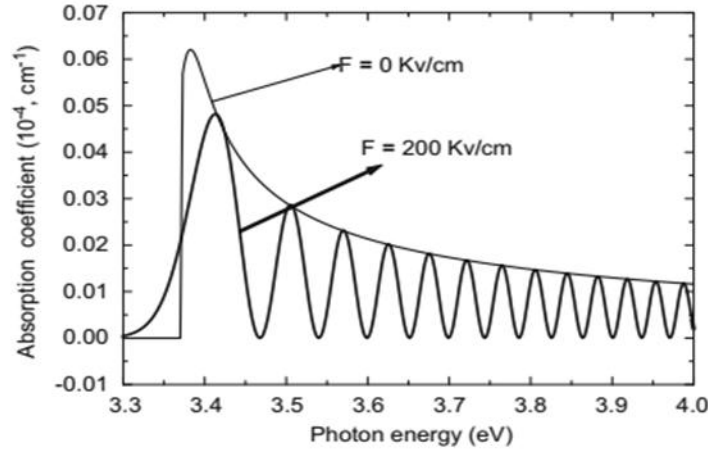


Figure 2. 3 The optical absorption coefficient is shown as a function of the photon energy for a cylindrical ZnO quantum wire with radius $R=50$ nm under zero field (thin line) and $F=200$ kV/cm (solid line) [75].

Figure 2.4 shows the nonlinear refractive index, n_2 , of the ZnO and ZnO:WO₃ is obtained. In this case, the coupling of ZnO and tungsten nanoparticles would be useful for the enhancement of the nonlinear refractive index [76].

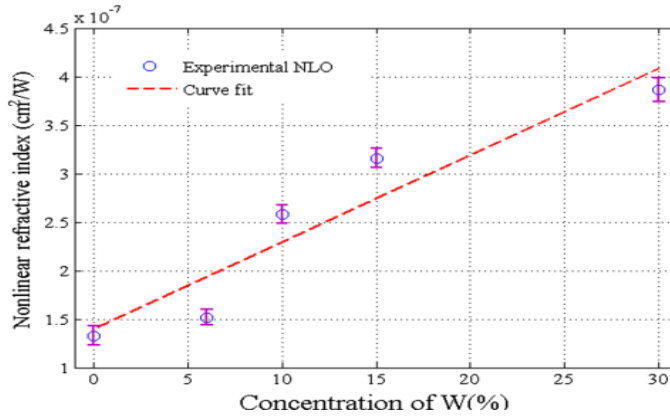


Figure 2. 4 The nonlinear refractive index of ZnO by Z-Scan [76].

2.6 Density matrix formalism of the third order susceptibility

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. In other words nonlinear optics is the study of the interaction of intense laser light with matter. Typically, only laser light is sufficiently intense to modify the optical properties of a material system [77]. The beginning

of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation. We are concerned with the effects that light itself induces as it propagates through the medium. Nonlinear optical phenomena are “nonlinear” in the sense that they occur when the response of a material system to an applied optical field depends in a nonlinear manner on the strength of the optical field. For example, second-harmonic generation occurs as a result of the part of the atomic response that scales quadratic ally with the strength of the applied optical field. Consequently, the intensity of the light generated at the second-harmonic frequency tends to increase as the square of the intensity of the applied laser light. The optical properties of materials are described through the real and imaginary parts of the dielectric constant ϵ_r . The dielectric constant is derived from the polarization $\vec{p}$ of the medium. In linear optics, we assume that $\vec{p}$ depends linearly on the electric field of the light wave, so that we can write:

$$\vec{P}(t) = \epsilon_0 \chi \vec{E}(t) \quad (2.1)$$

where χ is the electric susceptibility.

We derive the usual relationship between ϵ_r and χ namely:

$$\epsilon_r = 1 + \chi \quad (2.2)$$

In nonlinear optics we consider the possibility that relationship between $\vec{P}(t)$ and $\vec{E}(t)$ is more general than that given by equation 2.1

$$\vec{P}(t) = \vec{p}^1(t) + \vec{p}^2(t) + \vec{p}^3(t) + \dots \quad (2.3)$$

$$= \epsilon_0 [\chi^{(1)} \vec{E}(t) + \chi^{(2)} \vec{E}^2(t) + \chi^{(3)} \vec{E}^3(t) + \dots] \quad (2.4)$$

$$\vec{P}(t) = \epsilon_0 \chi \vec{E} + \vec{P}_{NL} \quad (2.5)$$

We now introduce nonlinear susceptibility as:

$$\vec{p}^{NL}(t) = \epsilon_0 \chi^{NL} \vec{E}(t) \quad (2.6)$$

$$\epsilon_r^{nonlinear} = 1 + \chi^{nonlinear} \quad (2.7)$$

We calculate the nonlinear optical susceptibility through use of the density matrix formulation of quantum mechanics [78]. We use this formalism because it is capable of treating effects, such as collisional broadening of the atomic resonances that cannot be treated by the simple

theoretical formalism based on the atomic wave function. Let us begin by reviewing how the density matrix formalism follows from the basic laws of quantum mechanics.

Third-order nonlinear optical interactions (i.e., those described by a $\chi^{(3)}$ susceptibility) can occur for both Centro symmetric and non-Centro symmetric media. In order to describe more precisely what we mean by an optical nonlinearity, let us consider how the dipole moment per unit volume or polarization $\vec{p}$ (t), of a material system depends on the strength $\vec{E}$ (t) of an applied optical field. In the case of conventional (i.e., linear) optics, the induced polarization depends linearly on the electric field strength in manner that often be described by the relationship

$$\vec{p}(t) = \epsilon_0 \chi^{(1)} \vec{E}(t) \quad (2.8)$$

Where the constant of proportionality $\chi^{(1)}$ is known as the linear susceptibility and ϵ_0 is the permittivity of free space. In nonlinear optics, the optical response can often be described by the polarization $\vec{p}(t)$ as a power series in the field strength $\vec{E}(t)$ as

$$\vec{p}^{(3)}(t) = \epsilon_0 \chi^{(3)} \vec{E}^3(t) \quad (2.9)$$

as the third-order nonlinear polarization. Where the electric field is given by;

$$\vec{E}(t) = \sum_r \vec{E}(\omega_r) e^{-i\omega_r t} \quad (2.10)$$

2.7 Energy eigenvalue and optical properties of ZnO cylindrical Nano wire

2.7.1 Mathematical formulation of energy Eigen value

One of the most intensively explored classes of low dimensional semiconductor structures is the Nano wire [62]. In recent years, Nano wires have attracted great attention due to their potential applications in optoelectronic devices and fundamental physics investigations. With the advances in semiconductor growth techniques it has been made possible to fabricate a wide variety of hetero-structures with well controlled dimension and composition. Among hetero-structures, Nano wires with rectangular T-shaped, V-groove, and other cross sections have received lots of attention by researchers during the last decade [59]. Optical and electronic properties of low-dimensional semiconductor structures are important part of the modern physics of semiconductors. The linear and nonlinear optical properties of low

dimensional semiconductor structures have been widely studied in the last few years, due to their potential applications in optoelectronic and photonic devices [1]. It is to be noted that the study of optical properties of low dimensional semiconductor structures is important, not only to know, but also in the fabrication and subsequent working of electronic and optical devices based on such systems. In this study, the selected hetero-structure of Nano wire is cylindrical with parabolic confining potential. The energy eigenvalues of ground and excited states of cylindrical quantum wire were calculated. Depending on these energy eigenvalues the refractive index and absorption coefficient are calculated for cylindrical Nano wire by using density matrix formalism [61].

If a quantum mechanical system (such as an atom) is known to be in a particular quantum-mechanical state that we designate S , we can describe all of the physical properties of the system in terms of the wave function $\psi_S(r, t)$ appropriate to this state. This wave function obeys the Schrodinger equation

$$\frac{i\hbar\psi_S(r,t)}{\partial t} = \hat{H}\psi_S(r, t) \quad (2.11)$$

where $\hat{H}$, denotes the Hamiltonian operator of the system. Under the cylindrical coordinates and within the framework of an effective-mass approximation, the Hamiltonian of an exciton in the ZnO NWs subjected to an external electric field (F), can be expressed as:

$$H = \frac{-\hbar^2}{2m^*} \frac{\partial^2}{\partial z^2} + V(z) + eEz \quad (2.12)$$

Here, m^* is the effective electron mass and e is the absolute value the electron charge. The functional form of the confinement potential is given by;

$$V(z) = V_0(1 - e^{-az})^2 \quad (2.13)$$

where the parameter $1/a$ describes the range of the confining potential and controls its asymmetry. We set depth of the potential to $V_0 = \lambda_2 E_{10}$, where the parameter λ controls the number of bound states [47]. In order to investigate the intersubband transitions in a two-level system (E_{10}), we take the parameter $\lambda = 2$.

Hamiltonian in a cylindrical co-ordinate system is used to calculate the ground and frist excited state energies and corresponding wave functions as:

$$\hat{H} = -\frac{1}{2} \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \theta^2} \right] + \frac{1}{2} \rho^2 \quad (2.14)$$

The Schrödinger equation for this Hamiltonian is given as:

$$\hat{H}_{nm}\psi_{nm} = \frac{-1}{2} \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \theta^2} - \frac{1}{2} \rho^2 \right] \psi_{nm} = \epsilon \psi_{nm} \quad \text{where, } \epsilon = \frac{E}{\hbar\omega} \quad (2.15)$$

The ground state wave function for parabolic confinement is given by

$$\psi_{00}(\rho) = \frac{1}{\sqrt{\pi}} e^{-\frac{\rho^2}{2}} \quad (2.16)$$

The first excited state wave function of cylindrical quantum wire in the parabolic potential energy operators of Hamiltonian respectively.

$$\psi_{01}(\rho) = \frac{1}{\sqrt{\pi}} \rho e^{-\frac{\rho^2}{2}} e^{i\theta} \quad (2.17)$$

2.7.2 Optical properties of ZnO cylindrical Nano wire using density matrix formalism

In this part the linear and third order nonlinear susceptibility, refractive index and absorption coefficient are calculated using density matrix formalism. Density matrix formalism is capable of treating effects such as collision broadening of atomic resonances that cannot be analyzed by simple theoretical formalism with respect to atomic wave functions. Considering that the charge carriers in a cylindrical ZnO quantum wire are excited by laser field,

$$\vec{E}(t) = \vec{E} e^{i\omega t} + \vec{E} e^{-i\omega t} \quad (2.18)$$

where ω is the frequency of the external field with a polarization vector normal to the nanowire. The electric polarization of the parabolic cylindrical quantum wire due to the time dependent electric field $\vec{E}(t)$ can be expanded. We consider only the first three lowest orders, and the second order is usually zero due to the symmetry condition.

$$P(t) = \epsilon_0 \chi^{(1)} \vec{E} e^{-i\omega t} + \epsilon_0 \chi_{2\omega}^{(2)} \vec{E} e^{-2i\omega t} + \epsilon_0 \chi_{3\omega}^{(3)} \vec{E}^3 e^{-3i\omega t} + cc \quad (2.19)$$

Where, $\chi^{(1)}$, $\chi_{2\omega}^{(2)}$ and $\chi_{3\omega}^{(3)}$ are the linear, third order & third order harmonic generation susceptibilities respectively, ϵ_0 is the permittivity of free space. In this study, the second order harmonic generation was not considered since it can occur only in non-Centro symmetric structures, that is, in structures that do not display inversion symmetry [35].

The electronic polarization of the n^{th} order is given by

$$P^{(n)}(t) = \frac{1}{V} T_r(\rho^{(n)} \mu) \quad (2.20)$$

where μ is the transition dipole moment which is given by

$$\hat{\mu} = \langle \varphi_{nm} | er | \varphi_{nm} \rangle \quad (2.21)$$

V is the volume of the interaction and T_r denotes the summation over the diagonal element of the matrix $\rho^{(n)} \hat{\mu}$.

The analytical expression for $\chi^{(1)}$ and $\chi^{(3)}$ are described by [36].

$$\chi^{(1)} = \frac{1}{\epsilon_0} \frac{N |\mu_{nm}|^2}{E_{nm} - \hbar\omega - i\hbar\Gamma_{nm}} \quad (2.22)$$

$$\chi^{(3)} = \frac{1}{\epsilon_0} \frac{N |\mu_{nm}|^2 E^2}{E_{nm} - \hbar\omega - i\hbar\Gamma_{nm}} \left[\frac{4 |\mu_{nm}|^2}{(E_{nm} - \hbar\omega)^2 + (\hbar\Gamma_{nm})^2} \right] - \frac{(\mu_{nn} - \mu_{mm})^2}{(E_{nm} - i\hbar\Gamma_{nm}) (E_{nm} - \hbar\omega - i\hbar\Gamma_{nm})} \quad (2.23)$$

The susceptibility $\chi(\omega)$ is related to the absorption coefficient $\beta(\omega)$ by

$$\beta(\omega) = \omega \sqrt{\frac{\mu}{\epsilon_r}} \text{Im}[\epsilon_0 \chi(\omega)] \quad (2.24)$$

where μ is the permeability of the system. $\epsilon_r = n_r^2$ ϵ_0 is the real part of the permittivity and n_r is the medium refractive index.

The linear and third-order nonlinear optical absorption coefficients are given as

$$\beta^1(\omega) = \omega \sqrt{\frac{\mu}{\epsilon_r}} \frac{|\mu_{10}|^2 N \hbar \Gamma_0}{(E_{10} - \hbar\omega)^2 + (\hbar\Gamma_0)^2} \quad (2.25)$$

$$\beta^3(\omega) = -\omega \sqrt{\frac{\mu}{\epsilon_r}} \left(\frac{I}{2\epsilon_0 n_r c} \right) \frac{|\mu_{10}|^2 N \hbar \Gamma_0}{[(E_{10} - \hbar\omega)^2 + (\hbar\Gamma_0)^2]^2} \times \left\{ \begin{aligned} &4 |\mu_{10}|^2 - \frac{(\mu_{11} - \mu_{00})^2}{E_{10}^2 + (\hbar\Gamma_0)^2} \times \\ &\left[(3E_{10} - 4E_{10} \hbar\omega) + \hbar^2 (\omega^2 - \Gamma_0^2) \right] \end{aligned} \right\} \quad (2.26)$$

where, I is the intensity of the incident field and N is the density of electrons. $E_{10} = E_1 - E_0$ is energy difference between two electronic states

Therefore, one can express the total absorption coefficient as

$$\beta^3(\omega) = \beta^1(\omega) + \beta^3(\omega). \quad (2.27)$$

In addition, the susceptibility $\chi(\omega)$ is related to the change in the refractive index as follows:

$$\frac{\Delta n(\omega)}{n_r} = \frac{\text{Re } \chi(\omega)}{2n_r^2} \quad (2.28)$$

Therefore, the linear and third-order nonlinear refractive index changes are given as follows:

$$\frac{\Delta n^{(1)}(\omega)}{n_r} = \frac{1}{2n_r^2} |\mu_{10}|^2 N \left[\frac{E_{10} - \hbar\omega}{(E_{10} - \hbar\omega)^2 - (\hbar\Gamma_0)^2} \right] \quad (2.29)$$

$$\begin{aligned} \frac{\Delta n^{(3)}(\omega)}{n_r} = & \frac{-\mu c}{4n_r^2 \epsilon_0} |\mu_{10}|^2 \frac{NI}{[(E_{10} - \hbar\omega)^2 + (\hbar\Gamma_0)^2]^2} \times \left[4(E_{10} - \hbar\omega) |\mu_{10}|^2 - \frac{(\mu_{11} - \mu_{00})^2}{(4E_{10})^2 + (\hbar\Gamma_0)^2} \right] \\ & \times \{ (E_{10} - \hbar\omega) E_{10} [E_{10} - \hbar\omega - (\hbar\Gamma_0)^2] - 2E_{10} - \hbar\omega \}^2 \end{aligned} \quad (2.30)$$

The total magnitude of the relative change in the refractive index

$$\frac{\Delta n^{(T)}(\omega)}{n_r} = \frac{\Delta n^{(1)}(\omega)}{n_r} + \frac{\Delta n^{(3)}(\omega)}{n_r} \quad (2.31)$$

L. Zhang,* et al [79] determined the absorption coefficients of the linear and the third-order nonlinear optical absorption in the in ZnO cylindrical Nano wires using the f parameters; electron effective masses (in unit of m_0 , m_0 is the free electron mass), the static and the high frequency dielectric constants, the refractive index, the refractive index, the density of carriers (in 10^{22} cm^{-3}), the magnetic permeability (in 10^{-7} H m^{-1}), and relaxation time (in fs) of ZnO material, and the optical beam intensity (in 10^{10} W m^{-2}).

Table 2.1: Different parameters of ZnO nanowire

m^*	ϵ_0	ϵ_∞	n_r	N	μ	T	I
0.28	4	8.1	2.33	5	4π	120	10

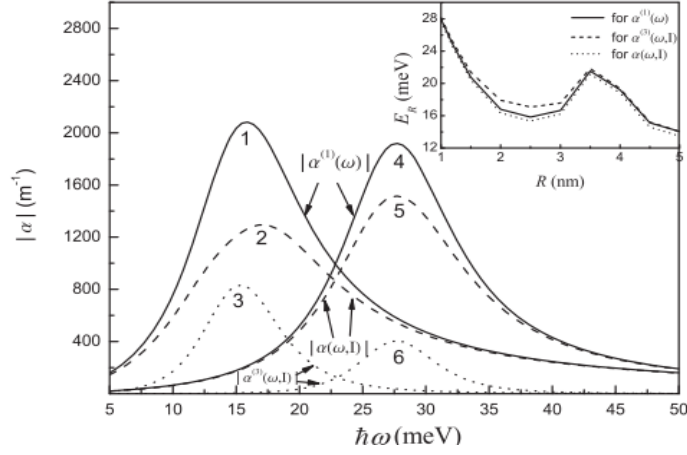


Figure 2. 5 Linear absorption coefficients $|\alpha^{(1)}(\omega)|$ (solid lines), then third-order nonlinear absorption coefficients $|\alpha^{(3)}(\omega, I)|$ (dotted lines) and the total absorption coefficients $|\alpha(\omega, I)|$ (dashed lines) as functions of photon energy ω [82].

Figure (2.5) depicts the linear absorption coefficients $|\alpha^{(1)}(\omega)|$ (solid lines), the third order nonlinear absorption coefficients $|\alpha^{(3)}(\omega, I)|$ (dotted lines) and the total absorption coefficients $|\alpha(\omega, I)|$ (dashed lines) as a function of photon energy ω . In fact, the lines 1–3 correspond to the ZnO NW with radius being 2.5 nm, and the lines 4–6 correspond to the ZnO NW with radius being 1 nm. The dependence of the resonant photon energy E_R of the linear (solid line), the third-order nonlinear (dotted line), and the total absorption coefficient peaks (dashed line) with NW radius R is plotted in the inset panel. As it can be seen from the graph the total absorption coefficients $|\alpha(\omega, I)|$ (dashed lines) increases with decreasing radius of ZnO cylindrical quantum wire and the change is very large and nonlinear.

Also S. Sakiroglu [47] studied the linear and third-order nonlinear optical absorption coefficients and the refractive index changes are investigated as a function of the incident photon energy for several configurations of the structural parameter and the applied electric field using the compact density-matrix approach for a typical GaAs/AlGaAs quantum well. From his studies he concluded that the electric field has a significant effect on the optical characteristics of these structures and intersubband transitions can be modified by tuning the structural range parameter of the potential.

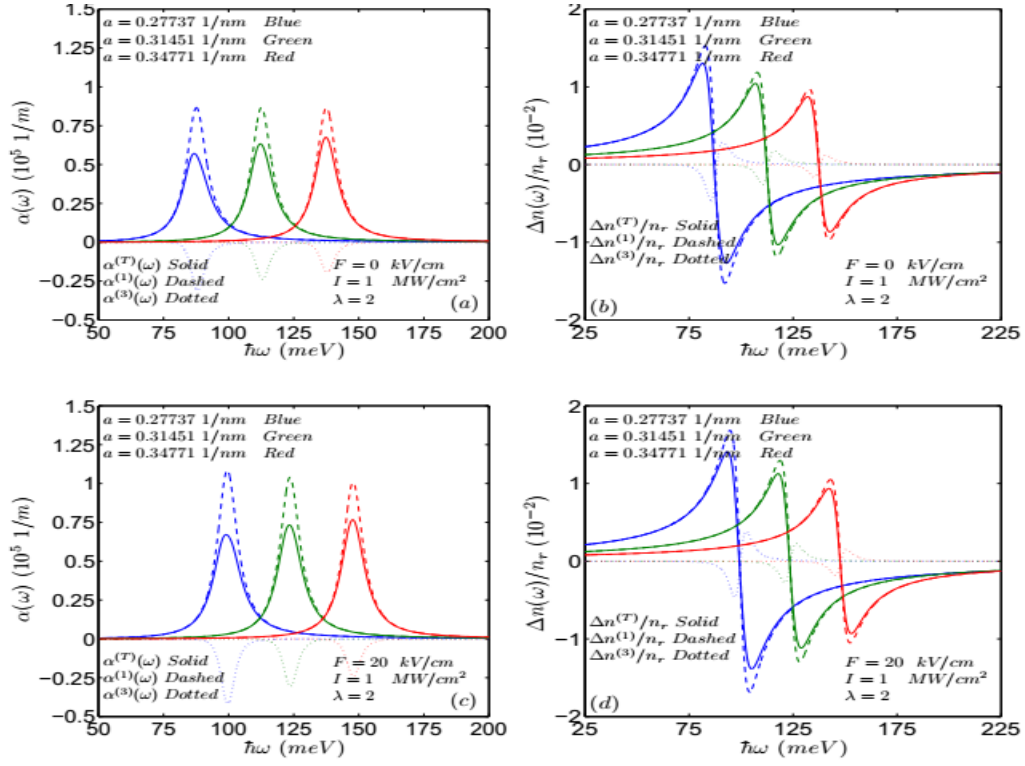


Figure 2. 6 Linear, third-order nonlinear and total absorption coefficient and linear third-order nonlinear and total refractive index changes as a function of the incident photon energy for three values of the well parameter $a = 0.27737, 0.31451, 0.34771 \text{ nm}^{-1}$, with $I = 1.0 \text{ MW/cm}^2$ in the case of absence of electric field (a) and (b) and for field of $F = 20 \text{ kV/cm}$ (c) and (d) [47].

Figure (2.6) shown below is the comparison of the linear and third-order nonlinear optical absorption coefficients and the refractive index changes where electric field $F=0$ and $F=20\text{kv/cm}$. In these figures; linear (dashed line), third-order nonlinear (dotted line) and total (solid line) optical absorption coefficients and changes in the index of refraction are plotted as a function of incident photon energy for three different values of the parameter a where blue, green and red lines stand for $a = 0.27737, 0.31451, 0.34771 \text{ nm}^{-1}$, respectively.

Figure 2.6 (a) and (b), when zero-electric field case the larger the asymmetry of the well, the sharper third-order nonlinear optical absorption coefficients. Positive contribution due to linear term is significantly reduced by the third order nonlinear term and as a consequence, small diminishment in the peak of total changes of absorption coefficient and refractive index coefficients. Besides, clear blue-shift in the resonance energy with increasing well parameter is visible and we should note that, large changes in refractive index can be obtained when the optical absorption is small. Turning

on the external static electric field ($F = 20$ kV/cm) causes a blue-shift in the resonant peaks of both the absorption coefficients and refractive indexes figure 2.6(c) and (d). These findings exhibit the striking influence of the geometrical confinement and electric field on the optical properties.

Figure 2.7 (a) and (b) shows the total absorption coefficient and the total change in the index of refraction as a function of different optical intensities in the presence of external electric field, respectively.

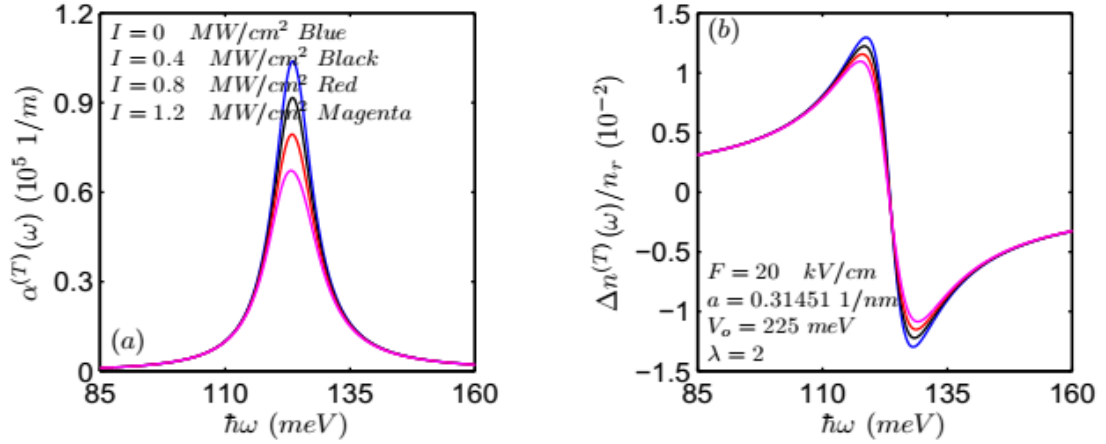


Figure 2. 7 Variation of the (a) total optical absorption and (b) changes in the refractive index as a function of different optical intensities in a Morse QW with range parameter $a = 0.31451/\text{nm}$ and electric field of 20 kV/cm [47].

When the incident optical intensity I , is strong enough third-order nonlinear contribution needs to be taken into account. In this case a considerable decrease in the total optical absorption coefficient and comparatively lesser reduction in the total refractive index changes with an increased optical intensity I is evident. The third-order nonlinear absorption coefficient and refractive index changes terms are affected by the incident optical field which implies the fact that when the optical intensity is relatively strong, third-order nonlinearities resulting of the modulation of phase coherence need to be taken into account.

Chapter 3

Results and discussion

The numerical results are presented for a typical ZnO/ZnMgO. The parameters I used in this calculations are taken from different literatures $N = \rho V = 5 \times 10^{28} \text{ m}^{-3}$, $\Gamma_{01} = 8.3 \times 10^{12} \text{ s}^{-1}$ and $n_r = \sqrt{\epsilon_r} = 2.33$. The electron effective mass $m_e^* = 0.28m_0$, for ZnO NWs, where m_0 is the free electron mass), the dipole moment (transition) is $\mu_{01} = 0.672 \times 10^{-28} \text{ m}$ [79]. The radiation intensity $I = 1 \text{ MW/cm}^2$, three different values of the confinement parameter $a = 0.27737, 0.31451, 0.34771 / \text{ nm}$ are taken [47]. The effect of the radiation intensity on the optical properties of ZnO cylindrical nanowire checked by varying the values of light intensities at fixed confinement parameter. For systems with inversion symmetry, e.g., impurity free cylindrical ZnO nanowires system or this system doped by a core center impurity, the diagonal matrix elements μ_{11} and μ_{00} vanish, leading to a zero contribution from the last term of Eq. (2.26) & (2.30) to $\Delta\beta^{(3)}(\omega)$ and $\Delta n^{(3)}(\omega)$ respectively.

The functional form of the confinement potential is given by:

$$V(z) = V_0(1 - e^{-az})^2 + eEz, \quad \text{where } E \text{ is electric field.}$$

where the parameter $1/a$ describes the range of the confining potential and controls its asymmetry. We set depth of the potential to $V_0 = \lambda_2 E_{10}$, where $E_{10} = \hbar^2 / m^* a^2$ which is obtained using Schrodinger equation and the parameter λ controls the number of bound states. The potential representing of zinc oxide nanowire in the case of absence and presence electric field for different values of parameters is shown in figure 3.1(a-c). As it can be seen from the graphs, as the structural parameter a increases, the asymmetry of the nanowire decreases. Also as the static electric field increases from 0 kv/cm to 20 km/cm as shown from figure 3.1 (a-c), the asymmetry of the sample decreases. This means that large electric field is evident for small asymmetry.

Table 3. 1 Values of the nanowire potential profile with respect to the range parameter (a) for different value of electric field (E).

z (nm)	V(z) in (meV)								
	$a=0.27737/\text{nm}$			$a=0.31451/\text{nm}$			$a=0.34771/\text{nm}$		
	E=0kV/ cm ²	E=20kV /cm ²	E=50k V/cm ²	E=0kV /cm ²	E=20k V/cm ²	E=50k V/cm ²	E=0kV/ cm ²	E=20k V/cm ²	E=50k V/cm ²
-5	55.3	39.28	15.25	69.71	53.69	29.66	84.29	68.27	44.24
5	30	46.02	70.05	38.71	54.73	78.76	47.73	63.75	87.78
15	37.59	85.65	157.74	48.04	96.10	168.19	58.77	106.83	178.92
25	39.21	119.31	239.46	50.02	130.12	250.27	61.11	141.21	261.36
35	39.91	152.05	320.26	50.89	163.03	331.24	62.13	174.27	342.48

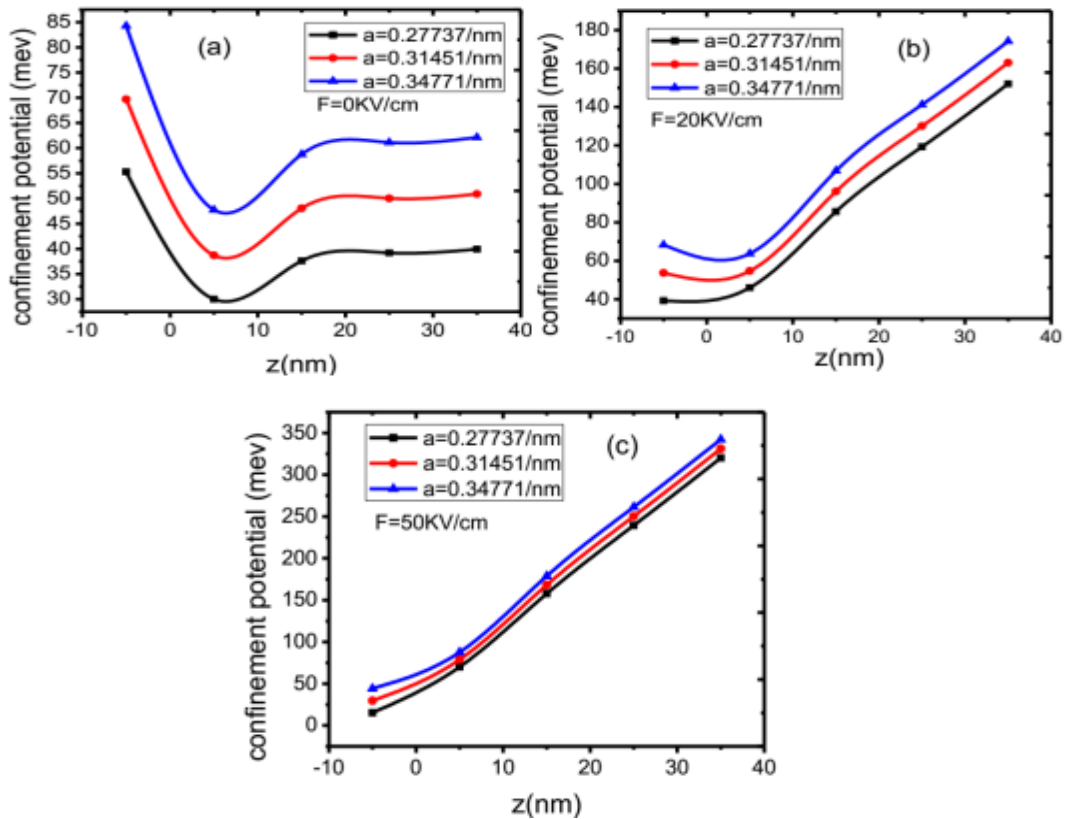


Figure 3.1 (a-c) Variation of the nanowire potential profile with respect to the range parameter (a) for different value of electric field (E).

The dependence of ground and first excited state energy level on the applied electric field is shown in figure 3.2 below. As shown in the figure the increase in static electric field leads to the increase in the difference of the two lowest-lying energy states with increasing confined parameter from 0.27737/nm to 0.34771/nm.

Table 3. 2 Values of the two lowest-lying energies (E_{10}) at different values of electric field (E).

E(kV/cm)	E_{10} (meV)		
	$a=0.27737/\text{nm}$	$a=0.31451/\text{nm}$	$a=0.34771/\text{nm}$
0	20.83	47.75	57.34
20	20.88	38.75	46.31
50	20.86	26.60	32.33

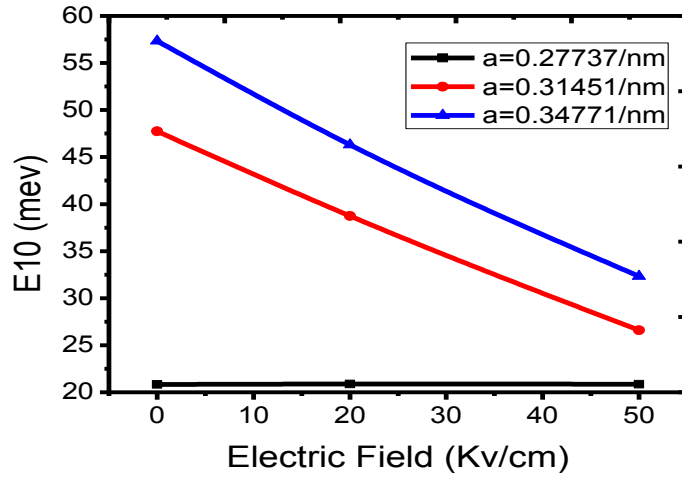


Figure 3. 2 Energies of the first two-lowest lying states (E_{10}) versus electric field (E).

Using the following equations and parameters obtained from a literature, the linear ($\beta^1(\omega)$), third order nonlinear ($\beta^3(\omega)$) and total ($\beta^T(\omega)$) in absorption coefficient and the linear ($\frac{\Delta n^{(1)}(\omega)}{n_r}$), third order nonlinear ($\frac{\Delta n^{(3)}(\omega)}{n_r}$) and total ($\frac{\Delta n^{(T)}(\omega)}{n_r}$) refractive index changes at $E=0$ and $E=20\text{kv/cm}$ are calculated by varying the size and the radiation intensities respectively.

The absorption coefficients are given by;

$$\beta^1(\omega) = \omega \sqrt{\frac{\mu}{\epsilon_r}} \frac{|\mu_{10}|^2 N \hbar \Gamma_0}{(E_{10} - \hbar \omega)^2 + (\hbar \Gamma_0)^2}$$

$$\beta^3(\omega) = -\omega \sqrt{\frac{\mu}{\epsilon_r}} \left(\frac{I}{\epsilon_0 n_r c} \right) \frac{2 |\mu_{10}|^4 N \hbar \Gamma_0}{[(E_{10} - \hbar \omega)^2 + (\hbar \Gamma_0)^2]^2}$$

$$\beta^T(\omega) = \beta^1(\omega) + \beta^3(\omega)$$

Similarly, the refractive index changes are given by;

$$\frac{\Delta n^{(1)}(\omega)}{n_r} = \frac{1}{2n_r^2} |\mu_{10}|^2 N \left[\frac{E_{10} - \hbar \omega}{(E_{10} - \hbar \omega)^2 - (\hbar \Gamma_0)^2} \right]$$

$$\frac{\Delta n^{(3)}(\omega)}{n_r} = \left(\frac{-\mu c}{n_r^2 \epsilon_0} |\mu_{10}|^4 \right) \frac{NI}{[(E_{10} - \hbar \omega)^2 + (\hbar \Gamma_0)^2]^2} \times [(E_{10} - \hbar \omega)]$$

$$\frac{\Delta n^{(T)}(\omega)}{n_r} = \frac{\Delta n^{(1)}(\omega)}{n_r} + \frac{\Delta n^{(3)}(\omega)}{n_r}$$

In Figure 3.3 linear (black line), third order nonlinear (red) and total absorption coefficient and change of refractive index are plotted as a function of photon energy for different value of parameter a . with the assumption of low temperature the absorption coefficient and refractive index changes for the intersubband transition between the two lowest-lying energy has been performed. The calculated result obtained for linear, third order nonlinear and total absorption coefficient and refractive index changes is shown in figure 3.3 (a–c) and 3.4 (a–c) below.

Table 3.3 Values of linear, nonlinear and total change in absorption and photon energy of cylindrical zno nanowire at different values of parameter a , when $E=0\text{kv/cm}^2$.

$\hbar \omega$ (meV)	Absorption coefficient $\beta(\omega) \times 10^2 \text{ 1/m}$								
	$a=0.27737/\text{nm}$			$a=0.31451/\text{nm}$			$a=0.34771/\text{nm}$		
	$\beta^1(\omega)$	$\beta^3(\omega)$	$\beta^T(\omega)$	$\beta^1(\omega)$	$\beta^3(\omega)$	$\beta^T(\omega)$	$\beta^1(\omega)$	$\beta^3(\omega)$	$\beta^T(\omega)$
10	16.9	-1.88	15.02	14.84	-1.67	13.17	11.62	-1.39	10.23
15	10.92	-1.80	9.12	9.16	-1.746	7.414	7.31	-1.56	5.75
20	6.56	-1.16	5.40	5.42	-1.131	4.11	3.79	-0.92	2.87

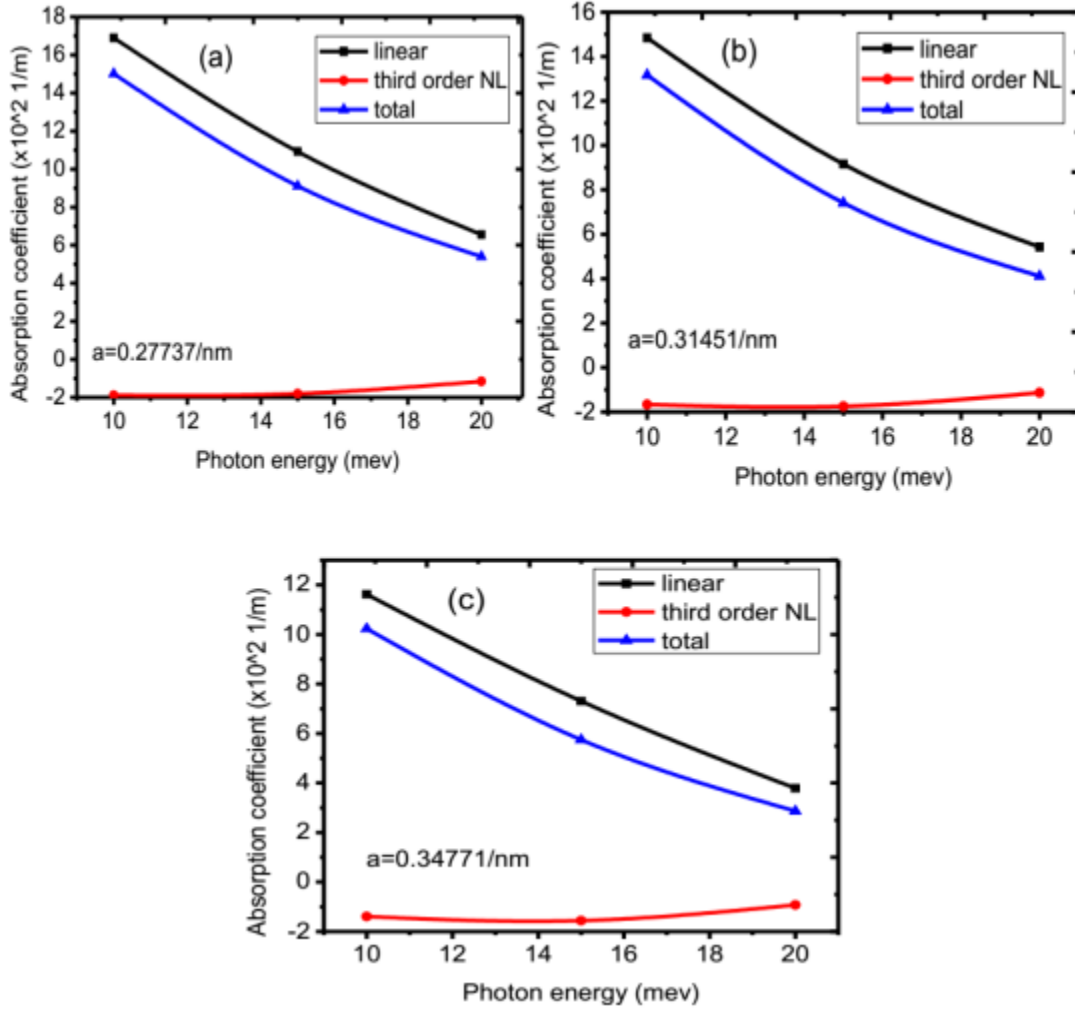


Figure 3. 3 Shows the calculated linear, third order nonlinear and total absorption coefficients for different nanowire parameters ($a = 0.27737$ (a), 0.31451 (b) and 0.34771 /nm (c) as a function of the photon energy for an incident light intensity of $1\text{MW}/\text{cm}^2$, $E=0$ KV/cm.

Figure 3.3(a-c) shows the linear, third order nonlinear and total absorption coefficient as a function of the photon energy for different values of confined parameter a for ZnO nanowire. In the absence of electric field when the optical incident intensity chosen to be $1\text{MW}/\text{cm}^2$. And from the graph as the asymmetry of the sample decreases the negative values of third order nonlinear absorption coefficient increases and at lower asymmetry the negative maximum value of nonlinear absorption coefficient is seen. Besides, the linear absorption coefficient is becomes reduced from $16.69 \times 10^2 \text{ m}^{-1}$ to $11.62 \times 10^2 \text{ m}^{-1}$ and $6.56 \times 10^2 \text{ m}^{-1}$ to $3.79 \times 10^2 \text{ m}^{-1}$ at lower and higher photon energy respectively, because of negative contribution of nonlinear term. As a result, the total absorption

coefficient decreases from $15.02 \times 10^2 \text{ m}^{-1}$ to $10.23 \times 10^2 \text{ m}^{-1}$ and $5.40 \times 10^2 \text{ m}^{-1}$ to $2.87 \times 10^2 \text{ m}^{-1}$ at lower and higher photon energy respectively is strongly influenced by the increase in the nanowire structural parameter.

In addition in zero electric field cause, as the asymmetry of wire decreases, the linear coefficient of refractive index changes becomes decreases from 1.73×10^{-8} to 0.93×10^{-8} and 1.41×10^{-8} to 0.63×10^{-8} at lower and higher photon energy respectively, while the nonlinear refractive index coefficient slightly increases in magnitude but in opposite sign to the linear refractive index changes. Consequently, the total refractive index change is further decreased from 1.12×10^{-8} to 0.73×10^{-8} and 0.92×10^{-8} to 0.498×10^{-8} at lower and higher photon energy respectively, as the nanowire asymmetry decreases when compared to its linear part. This result clearly shows that the total refractive index coefficient strongly depends on the nanowire size change. For this reason, for accurate evaluation of the refraction index change, it is recommended to take into account the third order nonlinear term for larger nanowire size.

Table 3.4 Values of linear, nonlinear and total change refractive index coefficients and photon energy of cylindrical ZnO nanowire at different values of parameter a , when $E=0\text{kv/cm}$.

$\hbar \omega$ (meV)	Change in refractive index ($\Delta n(\omega)$) $\times 10^{-8}$								
	$a=0.27737/\text{nm}$			$a=0.31451/\text{nm}$			$a=0.34771/\text{nm}$		
	$\frac{\Delta n^1(\omega)}{n_r}$	$\frac{\Delta n^3(\omega)}{n_r}$	$\frac{\Delta n^T(\omega)}{n_r}$	$\frac{\Delta n^1(\omega)}{n_r}$	$\frac{\Delta n^3(\omega)}{n_r}$	$\frac{\Delta n^T(\omega)}{n_r}$	$\frac{\Delta n^1(\omega)}{n_r}$	$\frac{\Delta n^3(\omega)}{n_r}$	$\frac{\Delta n^T(\omega)}{n_r}$
10	1.73	-0.61	1.12	1.15	-0.475	0.675	0.93	-0.20	0.73
15	-1.46	0.56	-0.90	1.13	-0.42	0.71	0.87	-0.17	0.70
20	-1.41	0.49	-0.92	-1.10	0.401	-0.699	0.63	-0.132	0.498

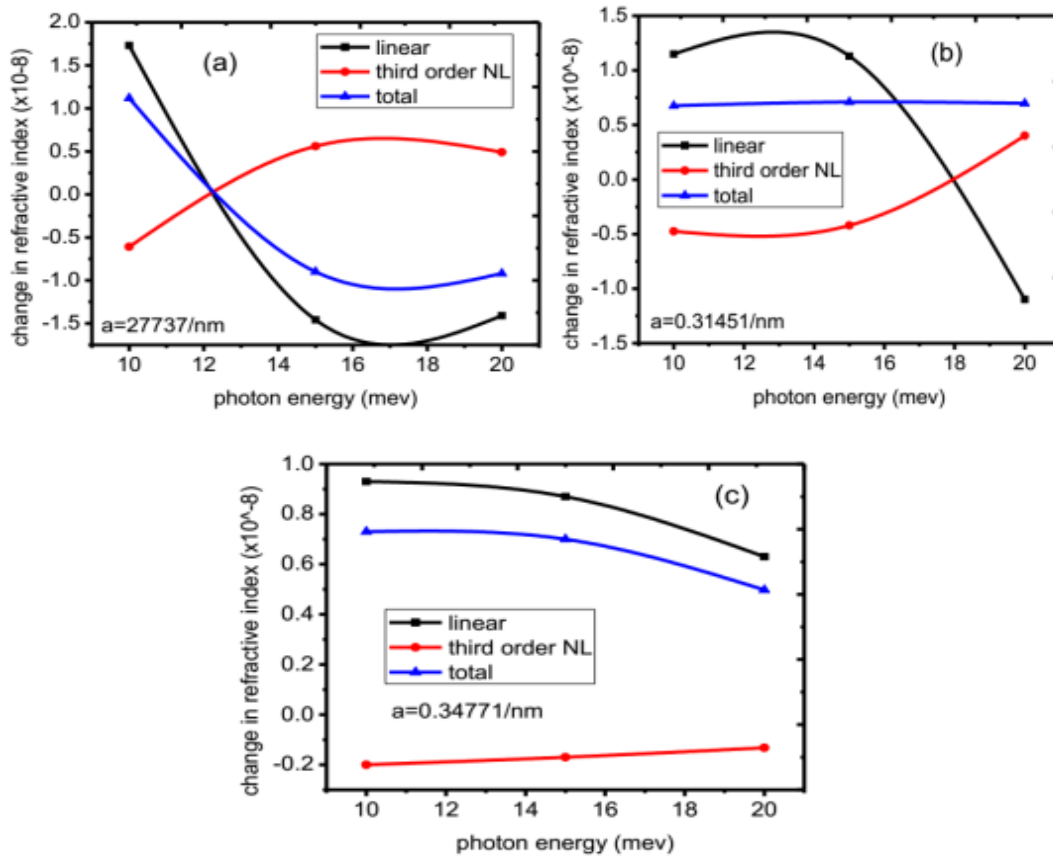


Figure 3.4 Shows the calculated linear, third order nonlinear and total refractive index changes for different nanowire parameters ($a = 0.27737$ (d), 0.31451 (e) and 0.34771 /nm (f) as a function of the photon energy for an incident light intensity of $1\text{MW}/\text{cm}^2$, $E=0$ KV/cm.

Turning on an external electric field ($E=20\text{KV}/\text{cm}$) Figure 3.5 (a–c) and Figure 3.6 (a–c) causes the increment in energy differences between the two lowest-lying electronic states. Increasing values of structural parameters from $0.27737/\text{nm}$ to $0.34771/\text{nm}$ leads to decreasing third order nonlinear contributions which results in increment of total absorption coefficient from $2.33 \times 10^2 \text{ m}^{-1}$ to $19.92 \times 10^2 \text{ m}^{-1}$ and $0.30 \times 10^2 \text{ m}^{-1}$ to $1.23 \times 10^2 \text{ m}^{-1}$ and decrement in the total change in refractive index from 7.2×10^{-8} to 2.47×10^{-8} and 3.77×10^{-8} to 2.37×10^{-8} at smaller and larger structural parameters respectively.

Table 3. 5 Values of linear, nonlinear and total change in absorption and photon energy of cylindrical ZnO nanowire at different values of parameter a, when E=20kv/cm.

$\hbar \omega$ (meV)	Absorption coefficient ($\beta(\omega)$) $\times 10^2$ 1/m								
	$a = 0.27737/\text{nm}$			$a = 0.31451/\text{nm}$			$a = 0.34771/\text{nm}$		
	$\beta^1(\omega)$	$\beta^3(\omega)$	$\beta^T(\omega)$	$\beta^1(\omega)$	$\beta^3(\omega)$	$\beta^T(\omega)$	$\beta^1(\omega)$	$\beta^3(\omega)$	$\beta^T(\omega)$
10	3.78	-1.45	2.33	0.65	-0.14	0.51	0.42	-0.127	0.3
15	13.08	-7.58	5.50	1.42	-0.25	1.17	0.83	-0.14	0.69
20	36.84	-16.92	19.92	2.93	-0.44	2.49	1.55	-0.32	1.23

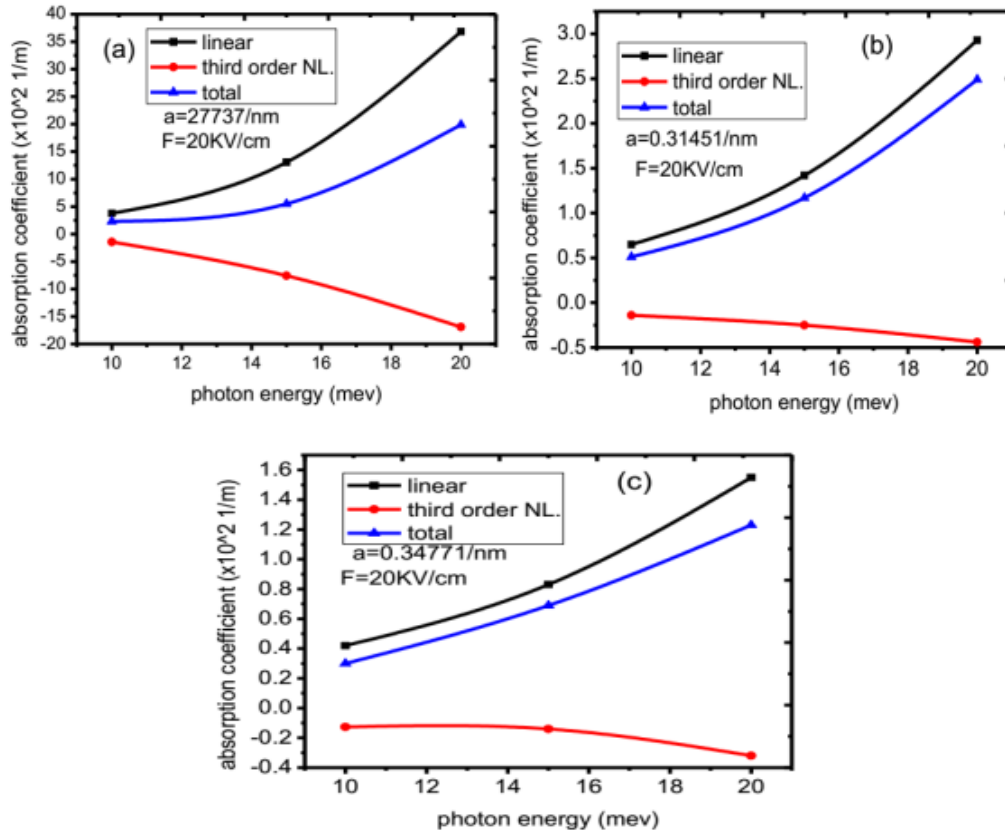


Figure 3.5 Shows the calculated linear, third order nonlinear and total absorption coefficient changes for different nanowire parameters ($a = 0.27737$ (a), 0.31451 (b) and 0.34771 /nm (c) as a function of the photon energy for an incident light intensity of $1\text{MW}/\text{cm}^2$, $E=20 \text{ KV/cm}$.

Table 3.6 Values of linear, nonlinear and total change refractive index coefficients and photon energy of cylindrical ZnO nanowire at different values of parameter a , when $E=20\text{kv/cm}$.

$\hbar \omega$ (meV)	Change in refractive index $(\Delta n) \times 10^{-8}$								
	$a=0.27737/\text{nm}$			$a=0.31451/\text{nm}$			$a=0.34771/\text{nm}$		
	$\frac{\Delta n^1(\omega)}{n_r}$	$\frac{\Delta n^3(\omega)}{n_r}$	$\frac{\Delta n^T(\omega)}{n_r}$	$\frac{\Delta n^1(\omega)}{n_r}$	$\frac{\Delta n^3(\omega)}{n_r}$	$\frac{\Delta n^T(\omega)}{n_r}$	$\frac{\Delta n^1(\omega)}{n_r}$	$\frac{\Delta n^3(\omega)}{n_r}$	$\frac{\Delta n^T(\omega)}{n_r}$
10	9.5	-2.3	7.2	4.3	-1.91	5.37	3.5	-1.13	3.77
15	6.8	-1.8	5.0	5.2	-1.68	3.52	4.0	-1.10	2.90
20	3.7	-1.23	2.47	6.4	-1.03	2.39	4.7	-0.93	2.37

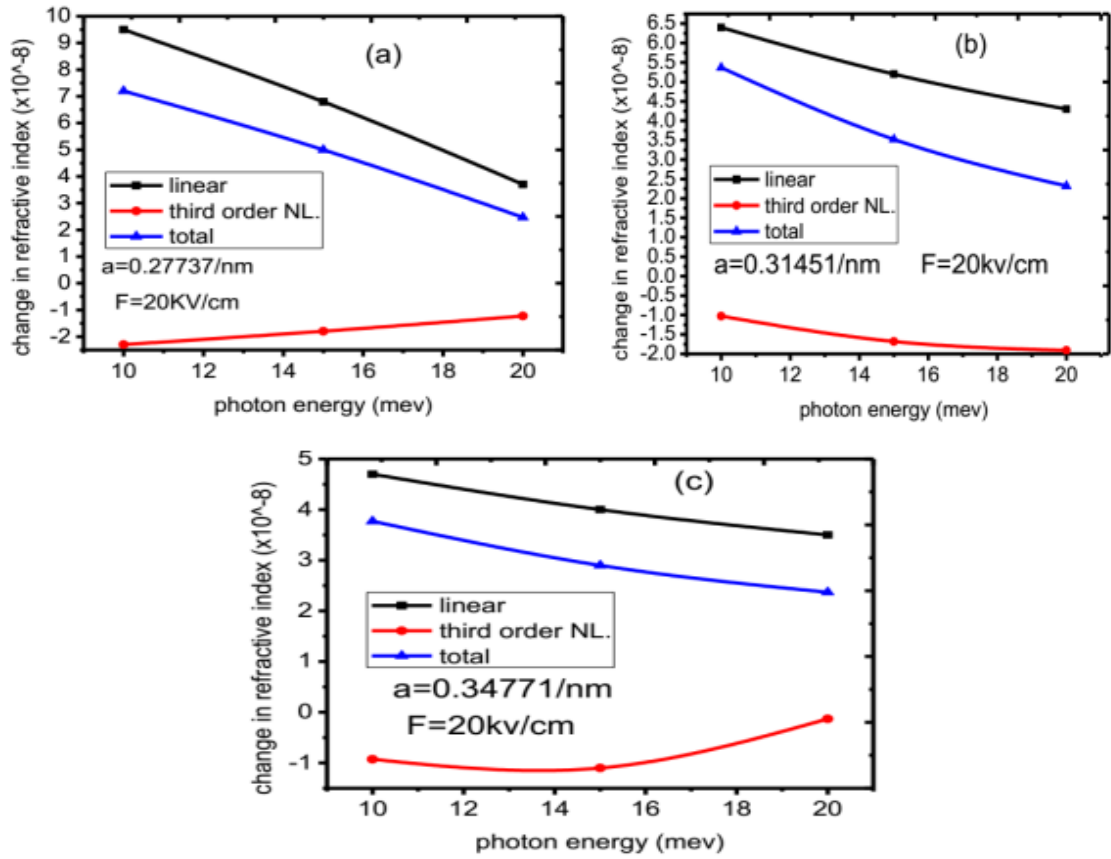


Figure 3.6 Shows the calculated linear, third order nonlinear and total refractive index changes for different nanowire parameters $a = 0.27737$ (a), 0.31451 (b) and $0.34771/\text{nm}$ (c) as a function of the photon energy for an incident light intensity of 1MW/cm^2 , $E=20\text{KV/cm}$.

Figure 3.7(a) shown below shows the effect of optical light intensity on the total absorption coefficient and refractive index changes at the wire parameter ($a=0.31451/\text{nm}$). In fact, the total terms strongly dependent on the incident light intensity. Since the linear and third order nonlinear terms are of opposite sign, the total absorption coefficient and refractive index coefficient will consequently affected, by incident light intensity ranging from 0 to $1.2 \text{ MW}\cdot\text{cm}^{-2}$.

Table 3.7 total absorption and change in refractive index as a function of photon energy at different values of optical light intensity I (MW/cm^2).

$\hbar \omega(\text{meV})$	Total absorption coefficient($\times 10^2 \text{ 1/m}$)				Total change in refractive index($\times 10^{-8}$)			
	I=0	I=0.4	I=0.8	I=1.2	I=0	I=0.4	I=0.8	I=1.2
10	2.33	0.59	0.54	0.45	4.3	3.5	2.77	2.008
15	5.50	1.37	1.32	1.26	5.2	4.53	3.86	3.18
20	6.92	2.75	2.58	2.40	6.4	5.99	5.58	5.16

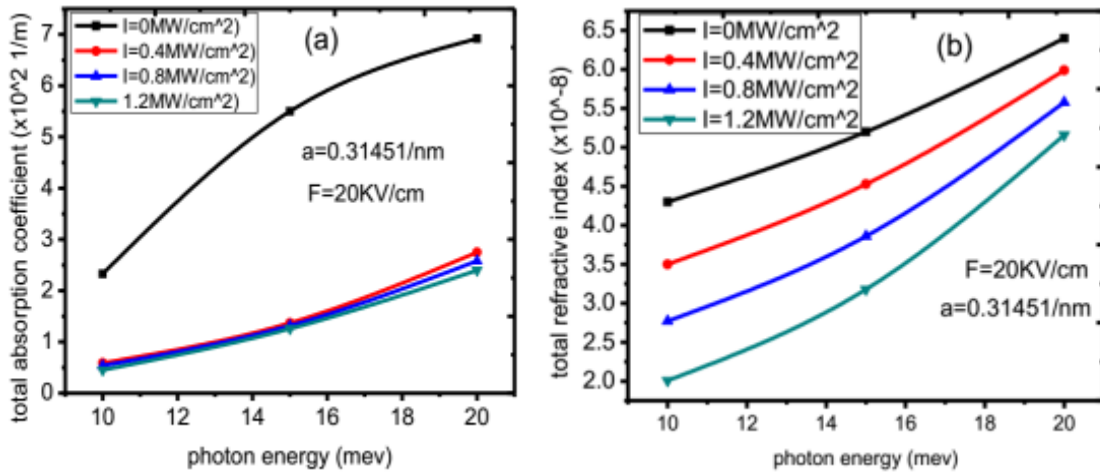


Figure 3. 7 The calculated total absorption coefficients (a) and refractive index coefficients (b) for nanowire parameter ($a = 0.31451/\text{nm}$) as a function of an incident light intensity.

The calculation results show that the magnitude of the total absorption coefficient decreased from $2.33 \times 10^2 \text{ m}^{-1}$ to $0.45 \times 10^2 \text{ m}^{-1}$ at lowest photon energy and at highest photon energy it decreased from $6.92 \times 10^2 \text{ m}^{-1}$ to $2.40 \times 10^2 \text{ m}^{-1}$ with increased the incident light intensity from 0 to $1.2 \text{ MW}/\text{cm}^2$

(figure 3.7a). Similarly, increased the incident optical intensity leads to an overall reduction in the total refractive index coefficient from 4.3×10^{-8} to 2.01×10^{-8} and from 6.4×10^{-8} to 5.16×10^{-8} at lower and higher photon energy (figure 3.7b) which is the same result as for GaAs Nano well of the same structural parameter [47] qualitatively. Generally from the result of the study the optical absorption coefficient and refractive index coefficient for ZnO Nanowire appear to be strongly dependent on both size and incident light intensity. Accordingly, for larger nanowire sizes the nonlinear effects are dominant factors, especially for relatively high intensity incident.

Chapter 4

Conclusion

In this study, the nonlinear optical properties of ZnO cylindrical Nano wire in parabolic confining potential is calculated with help of density matrix formalism. Such nonlinear optical properties are susceptibility, index of refraction and absorption coefficient. These optical properties were calculated using its discrete energy eigenvalues. In this study the dependence of the linear and nonlinear optical properties of ZnO nanowire on the size and optical field intensity is identified. In the absence of electric field as the asymmetry of the sample decreased, the linear absorption coefficient is becomes reduced, because of negative contribution of nonlinear term and the total absorption coefficient decreased. Also in zero electric field case, as the asymmetry of wire decreased, the linear coefficient of refractive index changes decreased and the total refractive index change is further decreased. In the presence of static electric field, increased values of structural parameters lead to decreased third order nonlinear contributions which results in increment of total absorption coefficient and decrement in the total change in refractive. At fixed structural parameter and electric field, the magnitude of the total absorption coefficient decreased and an overall reduction in the total refractive index changes occurred with increased the incident optical intensity from 0 to $1.2\text{MW}/\text{cm}^2$. In general our result shows that the structural parameter (size) of ZnO nanowire and the optical intensity may affects the nonlinear optical properties of ZnO nanowire which is qualitatively the same result as that of literature [47] for GaAS studied at same structural parameters.

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