Chapter 2

Growth and Characterization techniques

2.1 Introduction

This chapter describes the MOVPE growth process and various characterization techniques that are used to grow and study the structural, optical, and electrical properties of InP/GaAs based type-II ultrathin QWs and superlattice structures. First, a brief discussion about various epitaxial growth techniques is presented, which is followed by a brief description of MOVPE growth technique along with its precursors and safety aspects. Thereafter, characterization techniques in which basic principal of the technique along with the details of the experimental setup and the properties of the quantum structures that can be measured by using the corresponding technique are described.

2.2 Epitaxial growth techniques

Epitaxial growth of a layer on a substrate corresponds to a well-defined relationship between the orientation of the crystal planes of the grown layer and the substrate. This is possible when there exists a matching of symmetry between the
crystal planes of the layer and the substrate. There are several techniques like liquid phase epitaxy (LPE) [110, 111], MBE [37–39], and MOVPE [40–43] that are commonly used for the growth of epitaxial layers on suitable substrates. Each technique has its own strength and weakness. Experimental setup of LPE, being the oldest among the epitaxial growth techniques, is very simple, where a III-V semiconducting epitaxial layer is grown on a substrate from a supersaturated solution of group-III rich element. High quality III-V epitaxial layers are grown using LPE [111]. However, this technique has some limitations when it comes to the growth of quantum structures like QWs having thicknesses lesser than 10 nm. MBE [40–43] is conceptually very simple technique, where elemental sources are evaporated at a controlled rate onto a heated substrate under ultra high vacuum (ultimate vacuum \( \sim 10^{-11} \text{ mbar} \)) conditions. In the ultra high vacuum environment, growth of an atomic layer can be very well controlled using in-situ monitoring technique like reflection high energy electron diffraction. It is to be noted that quantum size effect was demonstrated firstly by MBE grown QWs. Additionally, highly strained InAs/GaAs ultrathin QWs of very good quality have been reported by using this technique [112, 113]. This technique has produced high quality of arsenide based QWs [112,113], and QDs [114]. However, for phosphide based quantum structures, this technique has shown problems. On the other hand, MOVPE technique has been found successful in producing high quality epitaxial layers as well as quantum structures based on arsenides and phosphides. MOVPE has been very successful in producing device quality QW structures leading to the commercialization of number of devices like light emitting diodes [115], laser diodes [116], photodetectors [117], HEMT and solar cells [53]. InAs/GaAs ultrathin QWs have been grown by using this technique [8,118–121]. Hence, InP/GaAs based
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AsH$_3$

Figure 2.1: Schematic of the MOVPE growth system.

ultrathin QWs and superlattice structures studied in the present thesis are grown by using MOVPE technique. In view of this, a brief description of the technique alongwith its operational principle is given in the next section.

2.2.1 MOVPE growth process

MOVPE has been identified as an important epitaxial crystal growth technique to produce high quality opto-electronic devices based on the quantum structures of III-V semiconductors [40–43]. In addition, MOVPE is also found suitable for the large scale production of opto-electronic devices, thus making it highly suitable for the industrial use. MOVPE growth process of the epitaxial layers is quite complex [43]. In general, the epitaxial layer is formed from the precursor compounds that include
metal organics in the vapour phase and may also include hydrides in form of gases. The precursors are transported into the reactor, generally made of quartz, with the help of a carrier gas (generally hydrogen) as schematically shown in Fig. 2.1. The precursors arrive at the surface of a heated substrate inside a quartz reactor to provide the metal atoms through the pyrolysis that are subsequently adsorbed on the surface of the substrate/growing layer [43]. The adsorbed atoms are mobile and can migrate across the layer surface until they are incorporated into the growing layer. In reality, no macroscopic crystal surface is atomically flat over the entire area and have atomic terraces bounded by the step edges. Under typical MOVPE growth conditions, adsorbed atoms are preferentially incorporated at the step edges as schematically shown in Fig. 2.2. Epitaxial growth is driven by the thermodynamics at the vapour/solid interface. The system strives to reduce the difference in the chemical potentials [43, 122]

$$\Delta \mu = \mu_v - \mu_s$$  \hspace{1cm} (2.1)
where, $\mu_s$, and $\mu_v$ are the chemical potentials of the solid and vapour respectively. However, other factors are also involved, which are related to the kinetics of surface diffusion, surface reactions and hydrodynamics of mass transport to the growing surface. Three growth regimes [43] have been classified on the basis of the growth temperature ($T$) as schematically drawn in Fig. 2.3. At low temperatures ($T < 550^0C$), the growth rate increases with temperature and is controlled by the kinetics. Decomposition of the group-III precursors is believed to be the growth limiting factor at low temperature. In the temperature range of 550-750$^0C$, mass transport which is the diffusion of the reactants through the boundary layer is the limiting factor. In this growth regime, the growth rate is very weakly dependent on the temperature and only depends on the group-III flow rate. This is the reason why mass transport region is generally used for the epitaxial growth. The growth rate again decreases with temperature in high temperature region ($T > 750^0C$), which happens either due to the thermal decomposition of the group-III element from the surface (desorption process) or due to the depletion of reactants from the gas stream. MOVPE growth is performed by keeping the over pressure of group-V element because they are highly volatile [43]. Thus, the growth rate in MOVPE is determined by the supply of group-III elements under normal operating conditions.

The typical precursors for the group-III elements are trimethyl gallium (TMGa), trimethyl aluminum (TMAI), and trimethyl indium (TMIn), while arsine (AsH$_3$), and phosphine (PH$_3$) are used for the group-V elements. Following are the requirements for the precursors for MOVPE growth technique [43].

1) Precursors should be sufficiently volatile at room temperature so that it can allow the acceptable growth rates.
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Figure 2.3: Graph between MOVPE growth rate and inverse of growth temperature indicating the three growth regions.

2) They should pyrolyze at low temperature.

3) Precursor molecule should not take part in the parasitic gas reaction that may deplete the nutrients from the vapour.

4) Precursor should be available in very high purity to produce high quality epitaxial layers.

5) Precursor should be less hazardous.

It is known that the precursors (AsH$_3$ and PH$_3$) used in the MOVPE growth are highly toxic materials and thus, this technique requires safety precautions in the laboratory. This is the reason why TBAs [123, 124] and TBP [125, 126] are used as an alternative precursor materials in place of AsH$_3$ and PH$_3$. The advantage with TBAs and TBP are that they are not only less toxic but also they pyrolyze at lower temperatures as compared to the conventionally used hydride (AsH$_3$ and PH$_3$) materials.
2.3 High Resolution X-Ray Diffraction

X-ray diffraction is a powerful characterization tool to determine crystal structure and crystalline quality of the materials [127]. However, resolution of X-ray system is an important issue in characterization of several systems such as 1) in case of single crystals, where full width at half maximum (FWHM) of X-ray rocking curves are of the order of $\sim 5$-10 arcsecs; 2) in case of nearly lattice matched systems such as GaAs/Al$_x$Ga$_{1-x}$As, where the separation of the diffraction angles for (0 0 4) reflection are in the range of $\sim 370 \times x$ arc sec ($x$ is the Al composition in Al$_x$Ga$_{1-x}$As material), and 3) in case of QWs and superlattice structures, where the period of interference fringes are of the order of several tens of arcsecs. Hence, very high resolution ($\sim 5$-10 arc secs) is required in this technique, which is provided by a high resolution X-ray diffraction (HRXRD) system: we have used PANalytical X’PERT diffractometer with CuK$_{\alpha_1}$ X-rays ($\lambda = 1.54056$ Å). In this system, a fixed X-ray

![Figure 2.4:](image)

**Figure 2.4:** (a) Schematic of the rocking curve geometry and (b) triple axis scan geometry alongwith the monochromator details. (c) Schematic of the geometry of the sample mounting illustrating possible angles of rotation for the sample.
tube with a Cu anode is used to generate the X-rays. The beam passes through a
four bounce monochromator as schematically shown in Fig. 2.4(a). The resulting
beam becomes monochromatic, containing only CuKα X-rays, and is collimated to
\( \sim 12/\sim 5 \) arcsec if we use Ge(2 2 0) or Ge(4 4 0) reflections for monochromatization.
The beam falls on the sample and gets diffracted to be detected by the detector. This
is the geometry of the rocking curve measurements as shown in Fig. 2.4(a). If there
is a three bounce channel cut analyzer in between sample and detector, then the
geometry is referred to triple axis geometry as shown in Fig. 2.4(b). This geometry
is primarily used for an accurate determination of \( 2\theta \) values and reciprocal space map
(RSM), which is defined later. The sample is mounted vertically on a cradle, known
as goniometer, which provides x, y and z linear motions as well as various angles (\( \omega \),
\( \chi \), \( \phi \), and \( \theta \)) to the sample as shown in Fig. 2.4(c). Figure 2.5(a) shows the reciprocal
lattice space diagram around the reciprocal lattice point (RLP) of (0 0 4) reflection
of the substrate, which is oriented along (0 0 1) direction. The directions of \( \omega \) and
\( \omega /2\theta \) scans in the reciprocal space are also shown and it is noted that direction of
both scans is perpendicular to each other. Thus, a series of \( \omega \) and \( \omega /2\theta \) scans are
required to map the reciprocal space. Figure 2.5(a) shows the RLP of the substrate
and epitaxial layer for (0 0 4) and (2 2 4) reflections. (0 0 1) and (1 1 0) directions
are also indicated, which are perpendicular and parallel to surface of the substrate,
respectively. \( Q_\perp \) represents the component of the reciprocal lattice vector along (0
0 1) direction and \( Q_{\parallel} \) are the in plane component (along (1 1 0) direction) of the
reciprocal lattice vector. The components of the reciprocal lattice vector of a RLP
are calculated by using the following relations

\[
Q_\perp = \frac{2}{\lambda} \sin \theta \cos (\omega - \theta) \tag{2.2}
\]
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Figure 2.5: (a) Reciprocal lattice space diagram for (0 0 4) reflection along with the directions of $\omega$ and $\omega/2\theta$ scans. (b) Reciprocal lattice space diagram for (0 0 4) and (2 2 4) reflections of substrate and epitaxial layer. Perpendicular ($Q_\perp$) and parallel ($Q_\parallel$) component of the reciprocal lattice vector are also indicated. Strained and relaxed position of the reciprocal lattice point for the epitaxial layer is marked.

and

$$Q_\parallel = \frac{2}{\lambda} \sin \theta \sin (\omega - \theta),$$  \hspace{1cm} (2.3)

where, $\lambda$ is the wavelength of X-rays. The angles $\omega$ and $\theta$ are defined in Fig. 2.5(a). Thus, RLP for (0 0 4) reflection will have the contribution from perpendicular component of the lattice constant of the epitaxial layer. On the other hand, RLP for (2 2 4) reflection will have contribution from both perpendicular and parallel components of the lattice constant of the epitaxial layer. Hence, information about the strain status of the epitaxial layer is determined from the RLP of the (2 2 4) reflection.

If the RLP of substrate and epitaxial layer both falls on a straight line parallel to the $Q_\perp$ axis, then the epitaxial layer is fully strained. If the layer RLP is shifted from this straight line, then it is relaxed as shown in Fig. 2.5. This procedure has been used to determine the strain status of the superlattice structures studied in this
thesis.

2.4 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a powerful tool for material characterization at the scale of lattice spacing owing to very small de-Broglie wavelength of electrons. In this technique, very high energy electrons (about hundreds of kV) are transmitted through a very thin sample (tens of nanometer). In their way through the sample, they get scattered by the sample in several ways. The spatial (imaging) and angular (diffraction) distribution of electron intensity is then displayed on the

![Figure 2.6: Schematic of the ray diagram for a transmission electron microscope in image mode.](image)
screen to get the results.

Block diagram of the TEM microscope is schematically shown in Fig. 2.6. A stream of mono energetic electrons are produced by electron gun, which is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first lens largely determines the spot size and the general size range of the final spot that strikes the sample. The second lens actually changes the size of the spot on the sample, thus changing it from a wide dispersed spot to a pinpoint beam. The beam is then restricted by the condenser aperture to knock out high angle electrons. The beam strikes the sample and parts of it is transmitted. This transmitted portion is focused by the objective lens into an image. Optional Objective and Selected Area metal apertures can restrict the beam and the Objective aperture enhances the contrast by blocking out high-angle diffracted electrons, while Selected Area aperture enables to examine the periodic diffraction of electrons by the ordered arrangements of atoms in portion of the sample selected in the aperture. The image is passed down the column through the intermediate and projector lenses, being enlarged all the way. The electrons strike the phosphor screen to produce the visible image. The darker areas of the image represent those areas of the sample that fewer electrons are transmitted through (they are thicker or denser). The lighter areas of the image represent those areas of the sample that more electrons are transmitted through (they are thinner or less dense). The information about the sample is obtained by analyzing and inspecting the image produced in different modes. Sample preparation for TEM imaging is a tedious job, because sample thickness should be around tens of nanometer so that electrons can transmit through the sample. Cross-sectional sample preparation scheme is illustrated sequentially in Fig. 2.7. First, samples are
cut in a $3\text{mm} \times 700 \ \mu\text{m}$ size. Then, they are mechanically ground and polished so that thickness of the sample is $\sim 100 \ \mu\text{m}$. Thereafter, sample is placed in the dimpling machine to dimple it upto $\sim 20 \ \mu\text{m}$ and polished with diamond paste. Finally, the sample is placed in the ion milling system to reduce the sample thickness in the nanometer range. TEM instrument used in this thesis work is a Philips CM200 TEM system, which is operated at 200 keV energy.

### 2.5 Atomic Force Microscopy

Atomic force microscopy (AFM) is a useful scanning probe microscopy technique, which is used to determine the surface morphology of the samples [128]. AFM instrument used in this thesis is a multimode scanning probe microscope (NT-MDT, SOLVER-PRO). The schematic diagram of AFM instrument is depicted in Fig. 2.8.
Cantilever is thin enough so that there should be a measurable deflection of the cantilever caused by the interatomic forces between the tip and the sample surface. The deflection is measured by a laser light, which is reflected from the top side of the cantilever and the reflected laser light is detected by the position sensitive detector. The AFM is operated in the feedback mode, where the sample is moved in the vertical direction to keep the deflection of the cantilever constant. The movement of the sample, both in vertical and horizontal directions, is provided by the piezo-electric scanners, which is mounted on the sample stage. Figure 2.9 shows the variation of the interatomic forces with the distance between sample surface and the tip. Attractive Van der waal’s forces dominate in the larger distance, while repulsive electrostatic forces dominate in the smaller distances. Operation with net repulsive force is known as contact mode, while operation with an attractive force is known as the non-contact mode in AFM measurements. Silicon cantilever tips having a radius of curvature of 10-40 nm, resonant frequency \(\sim 170-210 \text{ kHz}\) and spring constant \(\sim 5.5 \text{ N/m}\) are used.
Figure 2.9: Schematic variation of interatomic forces with the distance between tip and sample surface. Region of contact and non-contact mode of operation of AFM is also indicated.

in non-contact mode for the AFM measurement used for the surface topography of the superlattice structures studied in the thesis.

2.6 Photoluminescence spectroscopy

Photoluminescence (PL) is an important but simple technique for the optical characterization of bulk semiconductors and their quantum structures [129]. In this technique, optical response from the semiconductor sample is analyzed by measuring the energy distribution of emitted photon after excitation of the sample by optical means. Experimentally, optical excitation of the semiconductor sample is done by using a pump beam (generally a laser light), which has the photon energy greater than the band gap of the semiconductor sample. Electrons (holes) are created in the conduction (valence) bands of the semiconductor through optical excitation. These excited electrons (holes) then quickly relax to the bottom (top) of the conduction
Figure 2.10: Schematic of photoluminescence process (a) bulk semiconductor (b) type-I QW and (c) type-II QW.

(valence) bands as schematically shown in Fig. 2.10(a). Thereafter, various transitions are possible and can be observed in the PL measurements such as; 1) band to band, 2) donor level to valence band, 3) conduction band to acceptor level, and 4) donor to acceptor level. The situation for the quantum structure like type-I and type-II QWs are schematically shown in Fig. 2.10(b) and Fig. 2.10(c), respectively. In type-I QW, electrons (holes) can move to the respective potential well after their relaxation to the conduction (valence) bands. Electrons and holes occupy different confined energy levels in the respective potential wells and in addition to the transitions mentioned for bulk structure, different transitions between confined levels of electrons and holes can be observed in PL experiments of a type-I QW structure.
Figure 2.11: Schematic of the photoluminescence experimental setup. L₁, L₂, and L₃ are the focusing lenses and D is the photodetector.

On the other hand, electrons can move to the quantized levels in the potential well formed in the conduction band of a type-II QW as shown in Fig. 2.10(c), while holes are in the barrier region because of the formation of potential barrier for them. Hence, an indirect transition between the electron confined in the QW and the hole in the barrier region along with a direct transition between the electron confined in the QW and the free hole in the valence band of QW can be observed. The experimental setup for the PL spectroscopy is schematically shown in Fig. 2.11. PL is excited with a laser light, dispersed by a 1/4 m Sciencetech monochromator and detected by a Si photodiode. PL spectroscopy enables to determine the optical quality along with the band gap (quantized energy levels) of the bulk semiconductor (quantum structures). Usually, this technique provides the information about the lowest energy transition for the quantum structures.
2.7 Photoreflectance spectroscopy

Reflectivity spectra of bulk semiconductors (quantum structures) show broad features corresponding to their band gaps (quantized levels). Therefore, modulation spectroscopy (PR and ER) is generally used to study the band structures, which yields relatively sharp spectral features in their spectrum [130]. This helps in the accurate determination of the band structure of semiconductors (quantum structures).

In PR measurements, change in reflectivity along with the reflectivity from the bulk semiconductors (quantum structures) is measured. Reflectivity is measured by using a light of variable wavelength known as the probe beam, while change in reflectivity is done by using a laser light having photon energy greater than the band gap of the semiconductor (quantum structure) known as the pump beam. The basic principle behind the PR experiment is schematically shown in Fig. 2.12.

![Figure 2.12: Schematic of the basic principle of the photoreflectance technique.](image)

Built-in field direction

**Figure 2.12**: Schematic of the basic principle of the photoreflectance technique.
There exist surface states on the surface of the semiconductors created by the dangling bonds. These surface states capture the free carriers near the surface of the semiconductors, that leads to the pinning of the Fermi level at some position. This causes the band bending at near the surface and creating a depletion region having a built-in surface electric field. When a pump beam falls on the sample surface, electron and hole pairs are generated in the conduction and valence bands by absorbing the laser light. These electrons and holes then get separated by the built-in surface electric field. As a result, one of the carriers move upto the surface and modulates the built-in surface electric field. Hence, periodic generation of electron and hole pairs by the pump beam provides the required periodic modulation of the built-in surface electric field, which changes the reflectivity of the sample that is measured in the PR measurements. The experimental setup for the PR measurements is schematically drawn in Fig. 2.13. Light from a 100 W quartz tungsten halogen (QTH) lamp
dispersed by a 1/4 m Sciencetech monochromator is used as the probe beam. The chopped laser beam of a He-Ne laser (pump beam) is used to modulate the built-in surface electric field of the sample. Change in the reflectivity ($\Delta R$) due to the modulation as a function of wavelength of probe beam is measured by using a lock-in amplifier at the chopping frequency of the pump beam (330 Hz). The dc part of the signal from Si photodiode, which is proportional to the reflectivity (R), is also extracted, and the final spectrum $\Delta R/R$ is obtained by dividing the ac signal by the dc signal.

PR measurements, being equivalent to absorption spectroscopic measurements, provide the information about the band gap and higher order band gaps of the bulk semiconductors. For the quantum structures, it not only determines the energy of ground state transition but also maps the higher energy transitions.

### 2.8 Electroreflectance spectroscopy

The basic principle for electroreflectance (ER) technique (being another form of modulation spectroscopy) is similar to the PR technique, where the change in reflectivity along with the reflectivity is measured. The only difference between the two measurements is the way by which the built-in surface electric field is modulated. In PR measurements, it is done by using pump beam of a laser light, which is an indirect way. On the other hand in ER measurements [130], it is done in a direct manner by applying an external AC bias to the sample, which modulates the surface electric field. The experimental setup is similar to PR setup except no laser light (pump beam) is used. The built-in surface electric field is modulated in a capacitive geometry under soft contact mode by placing the sample in a specially designed
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Figure 2.14: Schematic of the generation of photovoltage through various processes.

2.9 Surface photovoltage spectroscopy

Surface photovoltage spectroscopy (SPS) [131, 132] is another form of absorption spectroscopy like PR and ER. The basic principle behind SPS technique is schematically shown in Fig. 2.14. It has been mentioned in the section describing PR technique that the surface of semiconductors has band bending leading to the depletion region and a built-in surface electric field associated with it due to the presence of surface states. When a light of photon energy greater than the band gap of the semiconductor falls on it, electron and hole pairs are created in a region depending upon the penetration depth of the light in the semiconductor. Generated electron and hole pairs then get separated by the built-in surface electric field and change the surface potential. This change in surface potential is picked up in SPS technique. There several processes occur in the semiconductor after absorption of the light, which contribute in the SPS magnitude. 2) Electrons and holes generated
within the diffusion length of the carriers from the edge of the depletion region may diffuse to the depletion region and are separated by the built-in electric field, 3) The electron and hole pairs generated in the zero electric field region (flat band condition) can also be separated due to the difference in their mobility and contribute in the SPS magnitude. This contribution is known as the Dember voltage. The experimental setup for SPS is schematically shown in Fig. 2.15, where the measurements are performed in the chopped light geometry under soft contact mode [132]. Periodic excess carrier generation and subsequent redistribution changes the surface potential, which is picked up by a transparent conducting glass (TCG) electrode. The TCG plate coated with indium-tin-oxide on the surface facing the sample is used as the second electrode as well as the window for the light. A 100 W quartz-tungsten-halogen lamp along with a 1/4 m SCIENCETECH monochromator is used as the

**Figure 2.15:** Schematic of the surface photovoltage experimental setup. L₁ and L₂ are focusing lenses.
light source. The AC photo voltage signal is measured with a lock-in amplifier.

SPS technique is used to determine the band gap of the bulk semiconductors. In addition, it has been used to determine the ground as well as excited states of the quantum structures like thick QWs, QDs and even ultrathin QWs. Apart from this, SPS technique has been applied to determine the absorption co-efficient ($\alpha$) of GaAs thick wafers [132, 133].

2.10 Capacitance-Voltage profiling

2.10.1 Theory

Studies on the capacitance associated with the depletion region of a Schottky barrier or an $p-n$ junction provide information of the concentrations and characteristics of electrically active centers in the near surface region of bulk semiconductors and their quantum structures [134]. Measurement of the depletion capacitance with applied voltage gives information about the fixed impurity and defect centers in semiconductors, in contrast to the carrier transport measurements (Hall measurements), which provide the information related to the density of free carriers and their mobility. Thus, capacitance-voltage and transport measurements give complementary information about the semiconductors. However, under some appropriate conditions as described in literature [134], the density obtained from the depletion capacitance measurements is equal to the free carrier density measured from the Hall measurements. In particular, depletion capacitance measurements provide information of the depth distribution of both shallow and deep impurity levels. On the other hand, transport measurements are unique in providing the mobility values [134]. Determination of the net dopant density from the measurement of the
capacitance associated with the depletion region of a metal semiconductor contact is described as follows. Real metal semiconductor contacts are generally described by Schottky model [134], which are characterized by a barrier height ($\phi_b$) and have diode like characteristics. According to the Schottky model, the energy band diagram is constructed by reference to vacuum level, which is defined as the energy of an electron at rest outside the material. The material properties like work function of metal ($\phi_m$) and electron affinity ($\chi_s$) of semiconductor are defined as the energies required to remove one electron from the Fermi level of metal and conduction band of semiconductor, respectively, to the vacuum level. These are supposed to be the material properties, which are assumed to be constant in a given material right up to the interface and it is further assumed that the vacuum level is continuous across the interface. Hence, there must be a step between the Fermi level of metal and
conduction band of semiconductor because of the difference in the values of $\phi_m$ and $\chi_s$ as schematically shown in Fig. 2.16. This difference is known as the barrier height ($\phi_b$) and is given by

$$\phi_b = \phi_m - \chi_s - eV_m \approx \phi_m - \chi_s,$$

(2.4)

because the band bending ($eV_m$) in the metal is very small due to the large electron density and can be neglected.

As we move away from the interface region (Fig. 2.16), the conduction band energy of the semiconductor changes such that it matches the bulk value $E_C$ with respect to the Fermi level at large distances from the interface. The band bending results from the movement of free electrons, which leave behind a distribution of fixed ionized donor atoms with positive charge. The band bending region is called the depletion region (W), which is depleted from the free charge carriers and has only the density of non mobile ionized atoms. The region at which the band becomes flat and the associated electric field is zero is called the depletion edge. In metals, a neutralizing negative charge in the form of free electrons is accumulated at the contact region over a distance ($x_m$) known as the free carrier screening length. Since, electron density in the metals are quite large as compared to that in semiconductor, hence, $x_m << W$ and can be assumed that the potential drop across the metal contact ($V_m$) is small as compared to that in semiconductor ($V_s$). Thus, built-in voltage (zero bias band bending) can be written as

$$eV_b = eV_m + eV_s \approx eV_s = \phi_m - \chi_s - (E_C - E_F)$$

(2.5)

$$eV_b \approx \phi_b - (E_C - E_F),$$

(2.6)

where $e$ is the electronic charge.
The total band bending across the depletion region with the applied external reverse bias \( V_a \) is, therefore, equal to

\[
V = V_b + V_a
\]  
(2.7)

The depletion width \( W \) can be calculated by knowing charge density \( \rho_x \) and solving Poisson’s equation. For simplicity, it is assumed that the semiconductor has a constant doping density \( N_d \), which leads to the constant charge density in the depletion region

\[
\rho (x) = eN_d^+ \]  
(2.8)

where, \( N_d^+ \) is the density of ionized donor in the depletion region. The electrostatic potential, \( \phi \), is given by the Poisson’s equation [134]

\[
-\nabla^2 \phi (x) = \nabla E (x) = \rho (x) \frac{\varepsilon}{\varepsilon_0} = \frac{eN_d^+}{\varepsilon_0}, \quad 0 \leq x \leq W; 
\]  
(2.9)

where, \( E (x) \) is the electric field inside the depletion region. \( \varepsilon \) and \( \varepsilon_0 \) are the dielectric constant of the semiconductor and the permittivity of free space. Integration of above equation gives the electric field as

\[
E (x) = E (0) + \frac{eN_d^+ x}{\varepsilon \varepsilon_0}, \quad 0 \leq x \leq W; 
\]  
(2.10)

and \( E (x) = 0 \), for \( x < 0 \) or \( x > W \). Boundary condition of the zero electric field value at the depletion edge, \( W \), leads to the determination of constant \( E (0) \) and is found to be

\[
E (0) = -\frac{eN_d^+ W}{\varepsilon \varepsilon_0}, 
\]  
(2.11)

hence,

\[
E (x) = \frac{eN_d^+}{\varepsilon \varepsilon_0} (x - W) 
\]  
(2.12)
The above equation in terms of electrostatic potential can be written as

$$-\nabla \phi (x) = \frac{eN_d^+}{\epsilon \epsilon_0} (x - W). \quad (2.13)$$

Integration of above equation with the boundary condition, $\phi (0) = -V$, yields the following form of the electrostatic potential in the depletion region

$$\phi (x) = \frac{eN_d^+ W}{\epsilon \epsilon_0} \left( x - \frac{x^2}{2W} \right) + V, \quad 0 \leq x \leq W. \quad (2.14)$$

Since, the potential is zero at the depletion edge, $\phi (W) = 0$ at $x = W$ leads to the determination of the expression for the depletion width

$$W = \sqrt{\frac{2\epsilon \epsilon_0 V}{eN_d^+}}. \quad (2.15)$$

The assumption of sharp depletion edge in the depletion approximation is not generally true. For a non-degenerate n-type semiconductor in the thermal equilibrium, the free carrier density $n$ is given by the Boltzmann relation [134]

$$n = N_C \exp \left( -\frac{E_C - E_F}{k_B T} \right), \quad (2.16)$$

where, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $N_C$ is the effective density of states in the conduction band. Hence, the charge density, earlier given by equation 2.8, can be written as

$$\rho (x) = e \left[ N_d^+ - n (x) \right]. \quad (2.17)$$

Using the first order approximation for $n(x)$ from equation 2.17, the charge density can be written as [134]

$$\rho (x) = eN_d^+ \left[ 1 - \exp \left\{ -\frac{1}{2} \left( \frac{W - x}{L_D} \right)^2 \right\} \right], \quad (2.18)$$
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where, \( L_D \) is the Debye length and is given by

\[
L_D = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{e^2 N_d^+}}.
\] (2.19)

It is noted from equation 2.17 that the free carrier density decreases approximately exponentially with the square root of the distance from \( W \) at a rate characterized by Debye length within the depletion region. Hence, Debye length is indicative of the abruptness of depletion edge and it represents the distance over which the free carriers redistribute themselves in the vicinity of a fixed charge. Thus, the free carrier density at a distance \( L_D \) and \( 3.03L_D \) from \( W \) is \( n(x) = 0.61N_d^+ \) and \( n(x) = 0.01N_d^+ \) respectively. This result indicates that the depletion region is depleted from the free carriers throughout its width except near the depletion edge. So, the requirement of the abruptness of depletion edge in depletion approximation is satisfied when the depletion width is much greater than the Debye length \( L_D \).

The capacitance associated with the depletion region is known as the depletion capacitance as mentioned above. The depletion region of a Schottky barrier on a n-type semiconductor contains a distributed fixed charge density of ionized donor atoms. When the reverse bias is increased by a small amount \( \Delta V \), the depletion width increases causing an increase in the fixed charge per unit area \( \Delta Q \) so that one can define a small signal capacitance associated with the depletion region as

\[
C = A \lim_{\Delta V \to 0} \left( \frac{\Delta Q}{\Delta V} \right) = A \frac{dQ}{dV},
\] (2.20)

where, \( A \) is the diode area. The incremental charge, \( dQ \), stored in the increased depletion width, \( dW \), is given by [135]

\[
dQ = AeN_d^+ dW.
\] (2.21)
The change in voltage is determined from equation 2.15 as

\[ dV = \frac{eN_d^+}{\epsilon\epsilon_0} W dW. \] (2.22)

Thus, the capacitance is given by

\[ C = \frac{dQ}{dV} = A\frac{\epsilon\epsilon_0}{W} = A\sqrt{\frac{\epsilon\epsilon_0 eN_d^+}{2V}}. \] (2.23)

The depletion capacitance given by the above equation is similar to the expression for the capacitance of a parallel plate capacitor with the distance W and dielectric constant \( \epsilon \), although the charge is stored in the volume rather than on the edges of the depletion region. The expression for the depletion capacitance can be rewritten as

\[ \frac{1}{(C/A)^2} = \frac{2V}{\epsilon\epsilon_0 eN_d^+}. \] (2.24)

Thus, if we plot \( 1/(C/A)^2 \) versus \( V \), then it will yield a straight line for the constant doping density. The slope of the linear line will give the doping density by the following relation

\[ N_d^+ = \frac{2}{\epsilon\epsilon_0 e} \left[ \frac{d}{dV} \left(\frac{1}{(C/A)^2}\right)\right]^{-1}, \] (2.25)

and the intercept at the bias axis provides the information about the built-in voltage. The equation 2.25 remains valid for a non-uniform doping density, because in the depletion approximation the charge fluctuations occur at the depletion edge. Hence, the doping profile can be obtained by measuring the capacitance as a function of reverse bias voltage and by using equation 2.25 along with

\[ W = \frac{\epsilon\epsilon_0 A}{C}. \] (2.26)

It is to be noted from the above discussion of the depletion approximation that the depth resolution of the capacitance-voltage profiling technique has a fundamental
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limit of about $\pm L_D$. The detailed discussion about this technique, limitations and interpretations of the capacitance-voltage profiles can be found in the literature [134].

2.10.2 Experiment

In experiment, when a small ac voltage $V_{ac} = V_0 e^{i\omega t}$ is applied to a the depletion region, which is equivalent to a capacitor with capacitance $C$, then the current flow is given by

$$I_C = \frac{dQ}{dt} = C \frac{d}{dt}(V_{ac}) = i\omega CV_{ac}, \quad (2.27)$$

which can be written as

$$I_C = I_0 e^{i(\omega t + \pi/2)}, \quad (2.28)$$

where, $i = e^{i\pi/2}$ and $I_0 = CV_0 \omega$. This tells that current is 90° out of phase with voltage. But in reality, there exists some leakage through the capacitor, which gives rise to the leakage current of the form

$$I_L = V_{ac}/R = V_{ac}G, \quad (2.29)$$

where, $R$ is the resistance and $G$ is the conductance. Hence, the total current is given by

$$I = I_C + I_L = (i\omega C + G) V_{ac} = YV_{ac}, \quad (2.30)$$

where, $Y = (i\omega C + G)$ is called admittance. Thus, measurement of current and voltage with their respective phases determines the capacitance (imaginary part) and conductance (real part). So, every diode is represented by a junction capacitance $(C)$, junction conductance $(G)$ and a series resistance $(R_s)$, which can be represented by the equivalent circuits as shown in Fig. 2.17. $C_s$ and $G_s$ are the capacitance and conductance when they are in series equivalent circuit, while $C_p$ and $G_p$ are
the capacitance and conductance when they are in parallel equivalent circuit. The capacitance meter assumes the device to be represented either in parallel or series equivalent circuit. Generally, series equivalent circuit is chosen if the device has larger impedance and if the device has low impedance, then parallel equivalent circuit is chosen. In our experiments, we have chosen parallel equivalent circuit because of the low impedance due to larger doping density in the barrier regions of ultrathin QWs. The details of the C-V experiments can be found in reference [136].

Figure 2.17: (a) Equivalent circuit of the actual device, (b) series equivalent circuit and (c) parallel equivalent circuit.