Chapter 4

Quantum states and band offset for InP/GaAs type-II ultrathin QWs probed by capacitance-voltage measurements

4.1 Introduction and background

Carrier distribution characteristics play a very important role in determining the optimum performance of the optoelectronic devices. C-V measurements have been used to obtain the carrier distribution profiles in bulk [149] as well as quantum structures like QDs [52, 150], thick QWs [12, 151, 152] and even ultrathin QWs [13, 139]. Apart from this, temperature dependent C-V measurements have been used to distinguish whether the observed carrier distribution profile is due to the carriers confined in band offset systems or due to doping inhomogeneities [153]. There exist several reports dealing with the optical properties of InP/GaAs type-II QDs [11, 100, 103]. However, there is no report on the electrical properties of InP/GaAs ultrathin QWs. In addition to this, conduction band offset ($\Delta E_c$) for InP/GaAs hetero-junction has not been measured by the C-V method, which has been widely used to determine the band offset of hetero-junctions and QWs [140, 149, 151, 154]. We
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have performed room temperature C-V measurements on InP/GaAs type-II ultrathin QWs as discussed in the chapter 3 (Fig. 3.8(b)), where reduction in the carrier accumulation inside the QW region was noted with the decrease in QW thickness. This was attributed to the quantum size effect in the QW. As mentioned above, temperature dependent C-V measurements provide another way to confirm that the observed carrier accumulation is due to carriers occupying the quantum states formed in the QWs. Therefore, in this chapter we present detailed investigations on the temperature dependent C-V characteristics and also determine $\Delta E_c$ for MOVPE grown InP/GaAs ultrathin QWs.

4.2 Experimental procedure

InP/GaAs ultrathin QWs are grown in a horizontal MOVPE reactor (AIX-200) with a rotating substrate holder on nominally (0 0 1) oriented $n^+$-GaAs substrate at 50 mbar of reactor pressure. The growth process of the InP/GaAs ultrathin QW samples has been described in detail in chapter 3.

Current voltage (I-V) and C-V measurements on the ultrathin QWs are performed by making the Schottky contact on the top of n-GaAs cap layer and Ohmic contact on the back side of the $n^+$-GaAs wafer. Schematic of the sample used for the C-V measurements is shown in Fig. 4.1. Firstly, ultrathin QW samples are degreased by boiling in trichloroethele, acetone, and methanol for about a minute in each chemical sequentially and rinsed with de-ionized water. Then, samples are dipped in a dilute HCl solution (1HCl:10H$_2$O) to remove the native oxide on the sample’s surface, before loading them in the vacuum coating unit for making Schottky and Ohmic contacts. Ohmic contact is fabricated by thermal evaporation of Au-Ge/Ni/Au on the back
Figure 4.1: Schematic of the sample structure of ultrathin QWs used for C-V measurements. Au dots make Schottky contact on the top of the GaAs cap layer, while Au-Ge/Ni/Au material combination provides ohmic contact on the backside of the GaAs wafer.

Au dots make Schottaky contact on the top of the GaAs cap layer, while Au-Ge/Ni/Au material combination provides ohmic contact on the backside of the GaAs wafer. The ratio of Au and Ge is \( \sim 88\% \) and \( \sim 12\% \) respectively in the Au-Ge eutectic alloy. The typical thicknesses of Au-Ge, Ni and Au are 10 nm, 10 nm, and 100 nm, respectively. Subsequent to the evaporation of ohmic contact, rapid thermal annealing (RTA) of samples is performed in a home made RTA system at 450°C for about 50 sec in nitrogen (N\(_2\)) gas environment to reduce the contact resistance. Finally, Schottky contacts of about 100 nm thick are made by thermally evaporating the Au circular dots of about \( \sim 700 \mu\text{m} \) diameter on top of the n-GaAs cap layer.

I-V measurements are performed to check the rectifying nature of the contacts and to determine the range of reverse bias voltage for the C-V measurements. I-V measurements are carried out with the help of Keithley source measure units with a sensitivity of \( \sim 1 \) nV and \( \sim 1 \) pA. C-V measurements are performed using a Keithley...
capacitance meter at a frequency of 1 MHz. The ultrathin QW samples are placed into an indigenously developed close cycle refrigerator [155] for the temperature dependent C-V measurements from 50 to 300 K. We have studied the temperature dependent C-V characteristics for two ultrathin QW samples, sample A (∼2.14 MLs thick) and sample B (∼1.43 MLs thick). These two samples have been chosen because they show carrier accumulation at room temperature in the C-V plots as discussed in chapter 3.

4.3 Geometrical position of the ultrathin QWs

Geometrical position of the InP ultrathin QWs from the top surface is determined from the cross-sectional TEM measurements. Figure 4.2 shows the cross-sectional TEM micrograph for the two ultrathin QW samples. InP ultrathin QW corresponds to a thin dark line, which is observed at a depth of about 120 nm from the top surface that is in accordance with the planned position in MOVPE growth.

![Figure 4.2: Cross-sectional TEM micrograph of ultrathin QW (a) sample A and (b) sample B. InP ultrathin QWs are observed as thin dark lines.](image)
4.4 Probing the quantum states in InP/GaAs ultrathin QWs

Carrier distribution profile in quantum structures obtained from the C-V measurements does not follow the free carrier distribution (FCD) profile. Since FCD changes in a depth scale, which is smaller than the Debye length, this is represented as apparent carrier distribution (ACD) profile. However, useful information about the physical properties like band offset for the quantum structures can still be obtained by analyzing the ACD. ACD profile from the measured C-V characteristics has been derived by using the following relations [134]

\[ N_{C-V}(z) = \frac{-2}{\epsilon \epsilon_0 A^2 \partial (1/C^2)} \frac{\partial (1/C^2)}{\partial V} \]  
\[ z = \frac{\epsilon \epsilon_0 A}{C} \]

where, \( z \) represents the distance along the growth direction, \( V \) is the applied voltage, \( C \) is the measured capacitance, \( A \) is the Schottky diode area, \( \epsilon \) is the dielectric constant, and \( \epsilon_0 \) is the permittivity of the free space.

Figure 4.3 shows the I-V characteristics of both the ultrathin QW samples at room temperature. We clearly observe the rectifying nature of the contacts deposited for the C-V measurements. It is further noted that the reverse current shows a very little change in the 0 to 2.8 V of reverse bias voltage. Hence, this voltage range of the reverse bias is suitable for the C-V measurements. It is to be noted that current for the 2.14 MLs thick ultrathin QW is more as compared to 1.43 MLs thick ultrathin QW in the reverse bias voltage region, which can be due to the larger number of carriers present in the QW region for 2.14 MLs thick ultrathin QW. Figure 4.4(a) and Fig. 4.4(b) show the temperature dependent C-V characteristics for samples A
and B respectively. Corresponding ACD profiles as well as their peak values and widths at various temperatures for both the ultrathin QW samples are depicted in Fig. 4.5(a), Fig. 4.5(b), and Fig. 4.6, respectively.

We observe a well defined plateau region between 0.5 to 1.0 V of reverse bias voltage in the C-V profile (Fig. 4.4(a)) for 2.14 MLs thick ultrathin QW at 50 K, which corresponds to the carrier accumulation (a peak in the ACD profile, Fig. 4.5(a)) at around the geometrical position of the ultrathin QW. The carriers are electrons as confirmed from the sign of the slope of the C-V curve. Presence of the plateau region in C-V profiles is a typical characteristic of a QW structure \[140, 154\]. Capacitance decreases with increase in reverse bias voltage due to increase in the depletion width of the barrier region having a constant doping density. As the depletion width approaches the QW region with increase in the reverse bias voltage, capacitance varies very slowly because of a large number of carriers present in the QW, which screen the applied electric field effectively. These carriers are the two-dimensional (2D) carriers occupying the quantum states formed in the QW region. When the

**Figure 4.3:** Current-voltage characteristic of ultrathin QW samples at room temperature showing the rectifying nature of the contacts.
Figure 4.4: Temperature dependent capacitance-voltage curves for InP/GaAs ultrathin QWs: (a) sample A (b) sample B. Curves at different temperatures have been shifted vertically for clarity in viewing.

applied reverse bias voltage is large enough to sweep out all the carriers present in the QW, capacitance again decreases following increase in the depletion width of the barrier region having constant doping density. Thus a plateau region is observed in the C-V profile for a QW structure and its width is a measure of the number of the 2D carriers present in the QW. We also observe a plateau region in the C-V profile for 1.43 MLs thick ultrathin QW sample at 50 K as evident from the Fig. 4.4(b). We note that the plateau region is weaker for 1.43 MLs thick QW as compared to that of 2.14 MLs thick QW at the same temperature. This corresponds to lower peak value of ACD profile for 1.43 MLs thick QW as compared to that for 2.14 MLs thick QW (Fig. 4.5(a), Fig. 4.5(b), and Fig. 4.6).

Thus carrier accumulation in the thinner QW is less than that in thicker QW. Such behavior can be explained in terms of the quantum confinement effects in the QWs. We have noted earlier in chapter 3 that the transition energy in PL
measurements (Fig. 3.4) for thinner QW is higher than that for the thicker one. Hence, confined electronic level in the conduction band of InP QW comes closer to the conduction band of GaAs barrier, when well width is reduced because of the stronger quantum confinement effect in thin QW. Therefore, stronger confinement effect favors lower accumulation of carriers in the thin QW. We note that the plateau region gradually becomes weaker as the temperature is increased for both ultrathin QW as observed from Fig. 4.4(a) and Fig. 4.4(b). Such behavior in C-V profiles results in decrease in the peak value of ACD profile with increase in temperature as is evident from Fig. 4.5 and Fig. 4.6. This is due to the decrease in separation between Fermi level and quantum state (confined electronic level in the QW) as well as increased probability for thermal emission of electrons into the barrier region as a result of increased thermal energy with increasing temperature [152].

Another important observation made from the Fig. 4.5(a), Fig. 4.5(b), and Fig. 4.6
Figure 4.6: Apparent carrier distribution (ACD) peak value and its width as a function of temperature for both the InP/GaAs ultrathin QW samples.

is that the ACD profiles broaden with increase in the temperature for both the ultrathin QWs. Such observation has been noted earlier for the other quantum structures [12, 13]. It has been shown there that the ACD width at low temperatures is mainly decided by the change in position expectation value of 2D electrons, because of the negligible contribution from three dimensional (3D) electrons at low temperatures. Thus, a very small value of change in position expectation value of 2D electrons results in the small value of ACD width at low temperatures [12]. The contribution of 3D electrons increases with increase in temperature. Hence, Debye averaging effect between 2D and 3D electrons becomes very important in determining the width of ACD peak at higher temperatures, which results in the larger values of width of ACD peak at elevated temperatures [12, 13]. It has been reported in the literature that decrease in peak intensity and increase in width of ACD profile with increasing temperature are the typical characteristics of carriers occupying the
quantum states formed in the quantum structures [12, 13]. Therefore, temperature
dependent C-V measurements confirm that the peak observed in ACD profile in the
vicinity of the ultrathin QWs is due to 2D electrons occupying the quantum states
formed in the ultrathin QWs. This is in agreement with our earlier conclusion made
in chapter 3 that the carrier accumulation in InP/GaAs type-II ultrathin QWs is
due to the electrons confined in the conduction band of InP in these QWs, which
was drawn on the basis of the room temperature C-V measurements.

Furthermore, it is to be noted from Fig. 4.5(a) and Fig. 4.5(b) that there is no
appreciable peak shift within the error of ±2 nm in the ACD profiles with temper-
ature for both the ultrathin QWs. This is in contrast to the reported results in the
literature, where large peak shifts in the ACD profiles with temperature have been
observed. For example, ACD peak shift of 8 nm in the temperature range of 75-300
K for InGaAs/GaAs QW [152] and about 55 nm in 10-300 K temperature range for
InAs/GaAs QDs [150] have been reported. ACD peak shifts with temperature in
C-V measurements have been attributed to the change in Debye length with tem-
perature [150]. Qualitative behavior of ACD peak shift as a function of temperature
in C-V measurements can be understood from the temperature dependence of the
Debye length ($L_D$), which is given by the following relation [134]

$$L_D = \sqrt{\frac{\epsilon \epsilon_0 k_B T}{e^2 N_d}}$$

(4.3)

where, $N_d$ is the doping density in the barrier region, $k_B$ is the Boltzmann constant,
$T$ is the temperature, $\epsilon$ is the dielectric constant, and $\epsilon_0$ is the permittivity of free
space. To provide a simple and qualitative picture, ionization probability of dop-
ing density with temperature has not been considered. Fig. 4.7 shows the variation
of Debye length with temperature as a function of doping density using equation 4.3. We note that the Debye length decreases when temperature is lowered and it is the reason for the ACD peak shift. It is to be noted from Fig. 4.7 that the change in Debye length with temperature is less as doping density in the barrier region is increased. Therefore, ACD peak will show smaller shift with temperature for the higher doping density. We note that the doping density used in the barrier region for InGaAs/GaAs QW [152] and InAs/GaAs QDs [150] is $5 \times 10^{16}$ cm$^{-3}$ and $2 \times 10^{16}$ cm$^{-3}$ respectively. Thus higher doping density used in the barrier region of InGaAs/GaAs QW is responsible for smaller peak shift of ACD profile with temperature as compared to InAs/GaAs QDs systems. We have even larger doping density of $3-4 \times 10^{17}$ cm$^{-3}$ in the barrier region of our ultrathin QWs. This explains why we do not observe any appreciable ACD peak shift with temperature. Petrovskaya et
al. [152] have reported similar observation that the shift in ACD peak increases with the decrease in doping density by treating the quantum states of the QW as deep centers in the bulk semiconductors.

4.5 Determination of the conduction band offset for InP/GaAs ultrathin QWs

It has been shown in the literature that the band offset values for the QW structures can be determined by simulating the C-V curves [140,151,154]. Simulation of the C-V curves has been performed by solving Schrodinger and Poisson equations self-consistently under envelop function approximation (EFA) by taking the band discontinuities ($\Delta E_c$ and $\Delta E_v$) as fitting parameters. We have simulated the C-V curve following the procedure as described in the literature [140, 154] and briefly described later in the appendix-A of this thesis. Fig. 4.8 shows the simulated as well as experimental C-V profile for the 2.14 MLs thick ultrathin QW sample. We

![Figure 4.8: Experimental as well as simulated C-V profile at 50 K for 2.14 MLs thick ultrathin QW sample.](image)
observe a reasonable fit for the conduction band discontinuity ($\Delta E_c$) value of 180 meV. We associate an error bar of 30 meV in the value of $\Delta E_c$, which can arise due to the QW thickness uncertainty, doping density in the barrier region as well as other source of errors that are inherently present in the C-V measurements as discussed in the literature [140, 149]. Now, we compare the value of $\Delta E_c$ determined in this work with the values reported in the literature. A value of 197±50 meV for the valence band discontinuity ($\Delta E_v$) has been measured by using x-ray photoelectron spectroscopy for the InP/GaAs hetero-junction, which is also in corroboration with the value reported in the literature for the unstrained case [100, 156]. The estimated unstrained value of $\Delta E_c$ is 297±50 meV for InP/GaAs type-II system [100] as shown in Fig. 4.9, where a band diagram for unstrained and fully strained (3.8%) cases of the InP/GaAs type-II QW system has been drawn. The effect of strain in shifting the conduction and valence bands of InP has been considered by the following equations reported in the literature [157].

$$\delta E_C = 2a_c \frac{(a_0 - a)}{a} \left[ \frac{C_{11}}{C_{11}} - \frac{C_{12}}{C_{11}} \right]$$ \hspace{1cm} (4.4)

$$\delta E_{VHH} = 2a_v \frac{(a_0 - a)}{a} \left[ \frac{C_{11} - C_{12}}{C_{11}} \right] - b \frac{(a_0 - a)}{a} \left[ \frac{C_{11} + 2C_{12}}{C_{11}} \right]$$ \hspace{1cm} (4.5)

where, $\delta E_C$ and $\delta E_{VHH}$ are the shifts in the conduction band edge and the heavy hole band edge of InP QW respectively. $a_c$ and $a_v$ are the hydrostatic deformation potential for the conduction and valence band respectively, while $b$ is the shear deformation potential for InP material. $a_0$ and $a$ are the lattice constants of GaAs barrier layer and InP QW respectively. $C_{11}$ and $C_{12}$ are elastic stiffness constants of InP material.

The values of these parameters have been taken from the reference [157]. Wang et. al. [100] have also calculated a value of 130±50 meV for $\Delta E_c$ of fully strained (3.8%)
Figure 4.9: Band diagram for InP/GaAs type-II QW. Dashed and solid lines are for the unstrained and fully strained cases of InP QW. All values are given for temperature of 10 K.

InP/GaAs hetero-junction. It is to be noted that the InP/GaAs ultrathin QWs studied in the present work are also fully strained as discussed in chapter 3. Therefore, the value of $\Delta E_c$ determined by using the C-V method for the InP/GaAs ultrathin QWs is in agreement with the strained value of $\Delta E_c$ reported in the literature within the associated error bar. However, it is to be noted that calculations based on EFA have been found limitation in case of ultrathin QWs [8,142]. In spite of this, such a simple approach is found extremely helpful in explaining the experimental results [8,142]. Therefore, precise calculations using empirical tight binding [158] or self-consistent pseudo potential [159] method are desirable to obtain very accurate value of band offset for such ultrathin QWs. However, these calculations are beyond the scope of the present thesis.

4.6 Summary

We have carried out temperature dependent C-V measurements on MOVPE grown InP/GaAs ultrathin QWs. Cross-sectional TEM and HRXRD measurements
confirm good crystalline and interfacial quality of the grown ultrathin QWs. We observe a plateau region in the C-V characteristics of the ultrathin QWs, which corresponds to a peak in the ACD profile at around the geometrical position of the ultrathin QWs. ACD peak value decreases with the reduction in the QW thickness. This has been attributed to the stronger quantum confinement effect in the thinner QW, which favors less accumulation of 2D electron in thin QW as compared to thicker one. Plateau region becomes weaker as the temperature is increased resulting in a decrease in the ACD peak value. This is due to the decrease in the separation between the confined electronic state and Fermi level as well as increased probability of the thermal emission of electrons in to the barrier regions. ACD width is found to increase with increase in temperature. Debye averaging process between 2D and 3D carriers is responsible for the ACD width at high temperature, while at low temperature ACD width is mainly due to the small value of change in position expectation value of 2D electrons, because of the negligible contribution from 3D electrons at low temperature. Therefore, temperature dependent C-V results confirm that the observed ACD profile is due to the 2D electrons occupying the quantum states formed in the ultrathin QWs. ACD peak does not show appreciable shift with temperature for both the ultrathin QWs. This has been understood in a simple and qualitative way by considering the temperature dependence of Debye length, where we have noted that Debye length is less susceptible to the temperature variation as doping density in the barrier is increased. A value of 180±30 meV of the conduction band discontinuity for the fully strained InP/GaAs hetero-junction has been obtained by simulating the C-V curve for the InP/GaAs ultrathin QW.