Chapter 5

Electronic Properties of CdTe Nanowires and Molecular Control over the Band Gap of Nanowires

“We are shaped by our thoughts; we become what we think. When the mind is pure, joy follows like a shadow that never leaves.”

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Lord Buddha
5.1 Introduction

The emergence of molecular nanotechnology has introduced a wide range of potential applications of nanostructured materials for a variety of purposes. One-dimensional (1-D) nanostructures such as nanowires and nanotubes have been proposed as important components, playing an integral party in the design and construction of both electronic and optoelectronic nanodevices [21, 352–356]. While a great deal of work has been centered on carbon nanotubes [353], nanotubes and nanowires made of inorganic semiconductors have become the subject of extensive studies in recent time. The reason for the interest in this particular class of materials stems from the fact that in addition to the quantum size effect, properties of these materials may also be tuned by varying their structure and morphologies. The particular physical and chemical properties of 1D nanostructures promise new inventions, new materials with interesting properties. Chemically derived, synthetic nanomaterials with low dimensionality and well defined atomic composition present a unique route toward miniaturization of electronic and sensor components with enhanced performance and functionality [3, 357–359]. It has already been demonstrated that nanostructures with well-defined tailored properties can be served as the building blocks of various high-performance device elements, such as transistors [360–363], optical devices [25, 364], sensors [247, 365], energy scavenging devices [366], and simple circuit structures [361, 363, 367]. These synthetic materials present a number of key advantages over their bulk counterparts. For instance, down-scaling of the active sensing material to the nanoscale regime has been shown to enhance the sensitivity of chemical, biological, and optical sensors by orders of magnitude [247, 365]. There are both extensive theoretical [341, 368, 369] and experimental [78, 149, 370–373] research efforts to elucidate how the geometric dimensionality of confinement influences the electronic structures of quantum-confined systems.

The increasing availability of semiconductor quantum wires has allowed us to draw experimental comparisons between wires and corresponding sets of quantum dots [370, 372], rods [371, 373],
and wells [374].

Among practical alternatives to crystalline Si, CdTe is an attractive material for potential low cost photovoltaics [375]. Its near-infrared band gap \( E_g \approx 1.5 \) eV, 827 nm, 300 K [376] and large bulk absorption coefficient (>10^4 cm\(^{-1}\) in the red, approaching 10^5 cm\(^{-1}\) in the blue) [377] make it an ideal material for matching photovoltaic responses to the visible part of the solar spectrum. Resulting thin film CdTe solar cells have demonstrated external efficiencies meeting or exceeding 16% [378]. Compared with its thin film and bulk counterparts, one dimensional CdTe nanowires (NWs) or nanorods have received a great deal of attentions over the past few years due to their improved light absorption efficiency and carrier transport. Therefore, controlling the size and shape of CdTe nanostructure has been the most significant issue [379,380]. Several techniques have been developed to control the size and shape of one-dimensional CdTe nanomaterial such as template directed electrodeposition [381, 382], solvothermal route [383, 384] etc. Xu et al. [382] prepared CdTe nanowires by AAO template directed electrodeposition in a non-aqueous electrolyte bath. Li et al. [385] successfully prepared CdTe nanorods by using solvothermal reaction of tellurium with cadmium metal powder in different organic solvents in the temperature range 120-200 °C.

Although, there are large number of experimental studies reporting the synthesis, characterization and optical properties of CdTe NWs [379–382, 386–389] theoretical studies addressing the electronic structure are scarce [165, 390]. However, extensive theoretical studies, in particular the evolution of electronic structure as a function of the size and morphologies are of crucial importance because it allows one to investigate both fundamental physics and to optimize nanostructure devices. The theoretical simulation sometimes offering new results to be verified experimentally. But theoretical studies of nanostructures composing large number of atoms is prohibitive because of their high computational demands. Therefore, self-consistent charge density-functional tight-binding (SCC-DFTB) method [224–229], which has been successfully applied to large-scale quantum-mechanical simulations, is suitable candidate for the task. In this chapter, we have investigated the relative stability and electronic structure of wurtzite [0001] CdTe nanowires
by employing the self-consistent charge density functional tight binding method (SCC-DFTB). Our results demonstrate that the surface and size effects play an important role in determining the structural and electronic properties of CdTe nanowires. The dependence of the formation energy, electronic band gap, and tendency for surface atoms to reorient are assessed as a function of the cross-sectional topology and diameter for a series of unpassivated, infinitely long, [0001] CdTe nanowires. Furthermore, the effect of hydrogen passivation of the dangling bonds on the geometric and electronic properties are also considered in this context. The possibility of utilizing CdTe nanowires as adsorbents or as sensors upon adsorption of dicarboxylic acid derivatives with different substituted phenyl rings which can tune the electronic band gap of the nanowires are also explored.

5.2 Computational Simulation and Modeling

In this work, properties of crystalline hexagonal and triangular CdTe nanowires of various sizes have compared. In this context we would like to mention that Sadowski et al. [165] have recently studied small CdTe nanowires by using the first principle as implemented in SIESTA [283]. Similar to DFTB method, this method described the core electrons by norm-conserving pseudo potentials and constructed according to the Troullier-Martins scheme [284]. The valence electrons wave functions in SIESTA are expanded using a double -ζ plus polarization (DZP) basis set while in DFTB method the valence electrons wave functions are constructed as a linear combination of Slater type atomic orbitals. Sadowski et al. [165] in their calculation used local density approximation for exchange correlation functional we however used PBE (Perdew, Burke and Ernzerhof) exchange-correlation functional [214]. Being an ab initio nature the method as implemented in SIESTA is very computationally demanding and treating large systems with reasonable computer resource are prohibitive. The DFTB method is a parametrized density-functional method and being semi-empirical in nature can treat relatively large systems. We therefore have applied the SCC-
DFTB method in our study. CdTe usually exhibits a typical wurtzite structure with two cadmium and two tellurium atoms in a tetrahedral coordination per unit cell. CdTe nanowires are generated from the optimized wurtzite crystal structure and oriented along the [0001] direction (c axis) and are enclosed by (1\(\bar{0}10\)) surfaces. These surfaces are non polar and contain Cd and Te atoms with one dangling bond. Based on the experimental and theoretical studies, all of the nanowires under consideration have approximately a cylindrical shape. We consider hexagonal nanowires \(W_{H1}, W_{H2}, W_{H3}, W_{H4}\) and \(W_{H5}\) with 48, 108, 192, 300 and 432 atoms per unit cell respectively and the triangular nanowires \(W_{T1}, W_{T2}, W_{T3}, W_{T4}\) and \(W_{T5}\) with 26, 44, 66, 92 and 122 atoms per unit cell respectively. All the above structures were simulated as infinite structures by using periodic boundary conditions and suitably oriented supercells. The calculations have been performed with a suitable vacuum region of 100 Å surrounding the structures - along the x and y directions - to avoid spurious interactions among consecutive periodic replicas. Geometry optimizations have been performed with the conjugated gradient algorithm, until all forces became smaller than 0.001 eV/Å. Convergence tests on the k-points sampling showed that a \((1 \times 1 \times 8)\) Monkhorst-Pack grid [216] is appropriate for our calculations. All calculations have been performed with the DFTB+ package [229], using our recently derived set of parameters for CdTe [325]. The transferability of these parameters have been tested by calculating the structural, electronic and energetic properties for the relevant bulk phases, surfaces, nanowires and small molecular systems. The calculated values agree well with those obtained either from experiment or \textit{ab initio} results. For example, the lattice parameters, \(a = b = 4.56\) Å, \(c = 7.44\) Å we calculated with SCC-DFTB method are in good agreement with the experimental lattice parameters \((a = b = 4.55\) Å and \(c = 7.45\) Å). The band gap \((E_g)\) of bulk wurtzite CdTe as calculated by SCC-DFTB method is 1.89 eV and the value is slightly greater than the experimental band gap \(\approx 1.50\) eV. This is because of the use of minimal basis set in SCC-DFTB method which always causes the overestimation of the band gap values. The details of the parametrization can be found in Chapter 3 or in ref. [325].
5.3 Results and Discussion

In this section, we discuss about the structural relaxation, stability and electronic properties of (10\(\overline{1}0\)) faceted CdTe nanowires. We also discuss the adsorption of dicarboxylic acid (DCA) derivatives on the surface of CdTe nanowire and investigate the electronic structure of CdTe NW-dye hybrid systems.

5.3.1 Geometric Structures of CdTe Nanowires

We have first optimized the atomic positions and lattice parameters along the axial direction of all CdTe nanowires by allowing all atoms to move without any symmetry constraints. The interatomic topology and the wurtzite structure are retained in the CdTe nanowires, although the bond lengths and angles change in the lateral surface. In Figure 5.1 we have shown the optimized structures of CdTe (10\(\overline{1}0\)) \(W_H\) (a) nanowire (top view) and (b) surface (side view). The results of the surface relaxation obtained from SCC-DFTB and PP-PBE method (as implemented in SIESTA)

![Figure 5.1 Optimised structure of (a) CdTe (10\(\overline{1}0\)) faceted nanowire (top view) and (b) CdTe (10\(\overline{1}0\)) surface (side view). Cd and Te atoms are represented by grey (dark) and yellow (light), respectively.](image)
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[283, 284]) of (10\overline{1}0) CdTe surface and (10\overline{1}0) CdTe nanowire are shown in Table 5.1. From the table, it is seen that the results of surface relaxation obtained through SCC-DFTB and PP-PBE results are very close to each other. The surface relaxation normally causes the Te atoms to move outward while Cd atoms move inward, and this behaviour is in accord with other studies [304–307].

For (10\overline{1}0) surface of CdTe, the bond lengths $d_{Cd-Te}$ are largely shortened compared with the bulk values (2.80 Å and 2.89 Å in SCC-DFTB and PP-PBE method respectively), while the bond lengths between the second and third layers are little larger compared to the bulk values. The Te-Cd-Te angle ($\alpha$) changes from bulk value 109$^\circ$ to around 120$^\circ$ at the top surface layer, while the same angle in the inner layers ($\beta$) show very little change. The prediction of the surface relaxation of CdTe is similar to the results of a low energy electron diffraction (LEED) study of related semiconductor ZnO [308].

Table 5.1 Structural relaxation of (10\overline{1}0) CdTe surface and (10\overline{1}0) CdTe nanowire (bond lengths are in Å and bond angles are in degrees.)

<table>
<thead>
<tr>
<th>parameter</th>
<th>10\overline{1}0 CdTe surface</th>
<th>10\overline{1}0 CdTe nanowire</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>SCC-DFTB</td>
<td>PP-PBE</td>
</tr>
<tr>
<td>$d_{Cd-Te}$</td>
<td>2.55</td>
<td>2.77</td>
</tr>
<tr>
<td>$d'_{Cd-Te}$</td>
<td>2.94</td>
<td>2.90</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>121</td>
<td>125</td>
</tr>
<tr>
<td>$\beta$</td>
<td>102</td>
<td>103</td>
</tr>
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</table>

The Cd-Te bond lengths ($d_{Cd-Te}$) and ($d'_{Cd-Te}$) of (10\overline{1}0) faceted nanowires are shortened as compared to their bulk values. This shortening of bond lengths occurs because surface atoms of the nanowire with one dangling bonds rehybridize from $sp^3$ to $sp^2$. This is in contrast to the behavior of the corresponding surfaces where the $d'_{Cd-Te}$ bond lengths were expanded compared to the bulk values. The Te-Cd-Te bond angles $\alpha$ and $\beta$ of (10\overline{1}0) faceted CdTe nanowires are equivalent and
both are belonging to the top surface layer of the nanowires. As it is evident from the Table 5.1, the relaxation causes large deviation of these bond angles from the bulk value (109°). This large change in the bond angle values are due to the inward movement of Cd atoms and the outward movement of Te atoms. The surface Cd and Te atoms in the nanowire are all 3-fold coordinated, and the large surface strain induces structural distortions. Similar structural distortions also occur in CdTe nanowires with triangular cross sections (W_{T1}, W_{T2} etc.). We have considered the W_{H1} CdTe nanowire as a model system to investigate the effect of hydrogen passivation. The surface Cd and Te atoms of the nanowire with one dangling bonds are all saturated with H atoms, and the H-passivated nanowire is fully relaxed. In the relaxed W_{H1} nanowire, the surface atoms show almost the same structural features as atoms in the core region of CdTe nanowires; for example, the CdTe bond lengths of the surface layers are about 2.77 Å close to the bulk value.

5.3.2 Stability of CdTe Nanowires

We have calculated the formation energy to assess the structural stability of the CdTe nanowires. The formation energy (E_f/CdTe) of a given nanowire is defined by the Eq. 3.3 (in Chapter 3). The formation energy of bulk CdTe corresponds to the energy zero. In Figure 5.2a we have shown the formation energy, E_f of CdTe nanowires (both hexagonal and triangular) as a function of the diameter of the nanowire. The figure suggests that the formation energies of the nanowires decreases with increasing wire diameter (d). As it is found for InAs nanowires studied by Shu et al. [391] we also see that the formation energies follow an inverse relationship with diameter, namely, E_f = k/d. The decreasing formation energies with the wire diameter indicate the higher stability of CdTe nanowires at relatively large size. By fitting the data points, the value of k (in eV.nm) we obtained are 0.325 and 0.397 for (10\bar{1}0) hexagonal and (10\bar{1}0) triangular CdTe NWs. From these relationship it is understood that the CdTe (10\bar{1}0) hexagonal NWs have greater stability than the CdTe (10\bar{1}0) triangular NWs.

The surface atom ratio is an another important factor for determining the stability of the
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![Graphs](image)

**Figure 5.2** Evolution of formation energies as a function of (a) diameter and (b) surface atom ratio of the CdTe (10\(\bar{1}0\)) faceted nanowires. Blue solid line represents the NWs of hexagonal cross sections and the red solid line represents the NWs of triangular cross sections.

The evolution of \(E_f\) of CdTe nanowire as a function of surface atom ratio \((R_s)\) is plotted in Figure 5.2b \((R_s\) is defined as the number of unsaturated Cd and Te atoms in the surface divided by the total number of Cd and Te atoms in the system). The formation energy, \(E_f\) satisfied a linear relationship with the surface atom ratio and can be expressed as \(E_f = \lambda R_s\). By fitting the data, we obtain the formation energy for (10\(\bar{1}0\)) hexagonal CdTe NWs, \(E_f \approx 0.398R_s\) and for (10\(\bar{1}0\)) triangular CdTe NWs, \(E_f \approx 0.463R_s\), where \(\lambda\) in eV. For bulk CdTe, the surface atom ratio is zero and so also the formation energy. In the case of nanowire of the largest diameter, the formation energy and surface atom ratio are closest to the bulk. As surface atom ratio increases, the strain in the system increases dramatically and surface restructuring alone is not enough to eliminate the large strain and therefore formation energy increases.
5.3.3 Electronic Structures of CdTe Nanowires

Let us now consider the electronic structure of CdTe nanowires. It is useful to promote the applications of these materials in developing the nanoscale electronic and optoelectronic devices. Figure 5.3 shows the electronic band structures of both triangular and hexagonal bare CdTe (10\(\overline{1}0\)) nanowires along the growth direction. The band gaps \(E_g\) of all nanowires are direct at the \(\Gamma\) point and showing a semiconducting character. The band gap \((E_g)\) of the nanowire is greater compared to bulk wurtzite CdTe (1.89 eV). The electronic band structures of the unpassivated CdTe nanowires are free of gap states due to rehybridization (from \(sp^3\) to \(sp^2\)) of the dangling bonds upon relaxation. A comparison of the band structure with the passivated nanowire (not shown here) finds the two to be nearly identical. Moreover the passivation with hydrogen atoms causes the increase in band gap value by only 0.06 eV as compared to the unpassivated nanowire [165]. This result of 1-d nanowire is in sharp contrast to quasi-0d systems where the surface has strong influence on the band gap values. The reason for this difference in behaviour is the presence of relatively large number of dangling bonds. The presence of large number of dangling bonds results in surface states in the band gap region. The surface passivation essentially removes these surface states thereby resulting an increase in band gap values of these systems. Here we wish to mention that as density-functional theory is an one electron theory, the band gap calculated from this has to be handled with great care. However, the qualitative trend obtained from one electron theory is often very useful in predicting and explaining material properties.

Figure 5.4a summarizes the result of our calculation for the band gaps of CdTe nanowires (both hexagonal and triangular) as a function of the diameter \(d\). The band gap values of all the CdTe nanowires are larger than that of the bulk CdTe. As the size of the nanowire decreases, \(E_g\) increases, reflecting the impact of the quantum confinement. This clear blue shift in band gap values is in good qualitative agreement with the recent experimental observation of Kuno et al. [387] and Rakovich et al. [386]. Sun et al. also in their experimental study on absorption
Figure 5.3 Electronic band structures of bare triangular [top (a, b, c, d, e)] and hexagonal [bottom (f, g, h, i, j)] (10T0) faceted CdTe nanowires of five different sizes. a, b, c, d, e represents the band structure of W_{T1}, W_{T2}, W_{T3}, W_{T4} and W_{T5} triangular nanowires, respectively. f, g, h, i, j represents the same for W_{H1}, W_{H2}, W_{H3}, W_{H4} and W_{H5} hexagonal nanowires, respectively. The zero of energy is set at the fermi energy for each case.
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Figure 5.4 Variation of band gaps with the wire (a) diameter and (b) surface atom ratio of the CdTe (10\(\overline{1}0\)) faceted nanowires. Blue solid line represents the unpassivated hexagonal NWs, blue dotted line represents the H-passivated hexagonal NWs, the red solid line represents the unpassivated triangular NWs and the red dotted line represents the H-passivated triangular NWs.

of CdTe nanowires of different diameters found similar behaviour [389]. From the figure it is also clear that passivation has only little influence on the band gap values. A close inspection of the band structures (Figure 5.3) reveal that for both triangular and hexagonal CdTe nanowires the conduction band minimum shifted downward as the diameter of the nanowire increases. But the valence band top almost remain unshifted. Because of the downward shift of the conduction band minimum, the band gap value decreases as the size of the nanowire increases. The band gaps exhibit a good linear relationship with surface atom ratios as shown in Figure 5.4b. From the figure it is clear that the intercept of both the linear curve is \(\approx 1.86\) eV which is very close to the band gap of the bulk CdTe as obtained in SCC-DFTB method.

In recent times, the research on solar cells including organic, hybrid organic-inorganic and dye-sensitized cells (DSCs) have received serious attention [392, 393]. The main component of this DSCs is a thick nanoparticle film that provides a large surface area for adsorption of light-harvesting molecules. However, the efficiency of the nanoparticle DSCs is limited because of the
Figure 5.5 The charge densities at (a) CBM (blue) and (c) VBT (red) for the unpassivated nanowire \( W_{H1} \) and (b) CBM (blue) and (d) VBT (red) for the H-passivated nanowire \( W_{H1} \). The isosurface value 0.0004 e Å\(^{-3}\) was used.
slow diffusion of the carrier. Very recently, Law et al. [394] and Tetreault et al. [395] have shown that single-crystalline nanowire based DSCs present a significantly higher conductivity over a wide range of applied potential as well as faster electron transport than comparable nanoparticle DSCs. One can adjust both light absorption and the energetics at the interfaces of the nanowire with the surrounding media by controlling the diameter of the nanowires. As the light absorption and the energetics at the interfaces depend very much on the charge densities at valence band top (VBT) and conduction band minimum (CBM), a clear understanding of the spatial distribution of the charge densities at VBT and CBM is very important in the fabrication of nanowire-dye sensitized solar cells [396, 397]. In what follows, we present in Figure 5.5 the charge densities at VBT and CBM of both bare and H passivated CdTe nanowires. For bare nanowire, the charge densities both at CBM and VBT are delocalized and are largely dispersed along the growth direction. However the extent of delocalization is larger at VBT as compared to CBM. The charge density at CBM of the passivated NW is less delocalized compared to the charge density at CBM of the bare NW. The charge density at VBT of the passivated NW is also delocalized throughout the whole NW and it spreads from the center to the surface of the NW. Our results are very much similar on recently studied ZnS NWs [398]. A detailed analysis (shown later) of the VBT, CBM suggest that VBT has major contributions from Te $p$ orbitals and also contributions from Cd $p$ orbitals while the major contribution to CBM comes from Te $d$ orbitals and little contribution from Cd $p$ orbitals. So, our results show that although the passivation does not affect the band gap too much but it greatly influences the spatial distribution of charge densities at VBT and CBM. The knowledge of the spatial distribution of the nanowire helps to identify the surface atoms to which the densities of these reactive orbitals are high and accordingly the adsorption of organic molecules will takes place through these atoms.
5.3.4 Adsorption of Dicarboxylic Acids (DCA) on CdTe Nanowires

The performance of the semiconductor containing electronic and optoelectronic devices depends very much on the surface properties of the corresponding semiconductor nanostructures. The modification of the surface structure allows one to tune the properties of the semiconductor devices and enhance their performances. So, the development of chemical methods to modify the surface structure is very much essential.

5.3.4.1 Designing the Hybrid Nanostructures

During the last couple of decades, there have been extensive investigation on chemical treatments based on inorganic or organic compounds that interact with the nanowire surface and stabilize it [399–403]. Because of the structural versatility and flexibility, organic molecules are better linker than inorganic counterparts. They may be designed to incorporate several properties simultaneously and allow systematic modifications of one specific property independently of others. The ability to include several functional groups in single organic molecule, each performing a specific role, offer great potential for electronic band gap modification [402]. In view of this we here performed a study on the adsorption of a series of dicarboxylic acid derivatives on CdTe nanowires. Our objective is to see how the adsorption of dicarboxylic acid with different functional groups modifies the electronic properties of CdTe nanowires. The adsorption of dicarboxylic acids on etched $n$-CdTe surfaces was experimentally investigated earlier [402–404]. These authors have considered a series of dicarboxylic acid (DCA) derivatives possessing two functional groups; a di-carboxylic acid binding group identical for all derivatives, and a polar group consisting of para-substituted phenyl rings. In this way, by simple chemical modification of the phenyl ring substituent, one can vary the molecule’s energy levels. To the best of our knowledge there are no studies on the adsorption behaviour of carboxylic acids on the surface of CdTe nanowires and we hope that our study will throw some light on the electronic structure of these hybrid nanosystems.
Figure 5.6 Optimized structure of the dihydrogen dicarboxylic acid (DHDC) derivative adsorbed on CdTe nanowire ($W_{H_1}$).

We show that chemisorption of these molecules on the surface of CdTe nanowires can systematically modify the electronic band gap.

Figure 5.6 present the optimized structure of dihydrogen dicarboxylic acid (DHDC) adsorbed on CdTe nanowire. To optimized the structure we used 3 units of the nanowire which contain 144 CdTe atoms per unit cell. We have considered only one organic molecule per three units the molecules with their periodic replicas. We have used $(1 \times 1 \times 4)$ Monkhorst-Pack grid and a periodic box of length 100 Å in our calculation. In the optimized structure of the hybrid systems (nanowire-molecule), the molecule bind to Cd sites on the surface because the binding groups are carboxylate and in all cases molecule exhibits bridging co-ordination [403,405]. The H atom of the carboxylic
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The surface of the nanowire does not exhibit structural distortions, except for the adsorption sites, where the substrate derelaxes, removing only the buckling of the dimers (Cd-Te) involved in the bonding process. The adsorption energy \( E_{ads} \), of the molecule is defined as:

\[
E_{ads} = (E_{tot} - E_{wire} - E_{mol})
\]

where \( E_{tot} \), \( E_{wire} \), and \( E_{mol} \) stand for the total energy of the CdTe nanowire-molecule, the clean CdTe nanowire, and the pristine (fully protonated) molecule, respectively. The adsorption energies of the dimethoxy dicarboxylic acid (DMDC), dihydrogen dicarboxylic acid (DHDC), dicyano dicarboxylic acid (DCDC) and dinitro dicarboxylic acid (DNDC) derivatives are 0.65, 0.61, 0.57 and 0.54 eV respectively. The resulting exothermic energy balance confirms that dicarboxylic acid derivatives are very good linker for molecular anchorage on the \((10\overline{1}0)\) surface of CdTe nanowires.

5.3.4.2 Controlling the Band Gap of CdTe Nanowires by DCA

Adsorption of dicarboxylic acid derivatives strongly affects the electronic properties of CdTe nanowires. As for instance, the band gap of the \( W_{H1} \) CdTe hexagonal wire changes from 2.46 eV to 1.86 eV and 1.26 eV upon adsorption of DCDC and DNDC respectively but it is more or less unchanged upon adsorption of DHDC and DMDC \( (E_g \) is 2.43 eV for CdTe nanowire-DHDC and 2.44 eV for CdTe nanowire-DMDC). The adsorption of DCDC and DNDC molecules on the surface of CdTe nanowire considerably modified the DOS as compared to the clean nanowire. The most pronounced feature is that a new peak appears at 1.86 eV and 1.26 eV (above the valence band) for the DCDC and DNDC respectively (Figure 5.7). These peaks are attributed to the LUMO of the DCDC and DNDC respectively. To have a detailed understanding of different orbital contributions of Cd, Te and atoms of adsorbed molecules we have shown the projected density of states (PDOS) of one representative system (NW-DNDC) in Figure 5.8. From the figure it is clear that the major contribution of the VBT in nanowire-molecule system comes from Te atoms of the
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Figure 5.7 Total density of states (shaded area) for (a) clean CdTe nanowire, (b) NW-DHDC interface, (c) NW-DMDC interface, (d) NW-DCDC interface and (e) NW-DNDC interface. The zero of energy is set at the Fermi energy.
nanowire while C and O atoms of the molecule have major contribution to the CBM of the hybrid system. Figure 5.9 shows the position of the VBT (HOMO) and CBM (LUMO) level of the clean

![Projected local Density of States](image)

**Figure 5.8** The Projected local Density of States of NW-DNDC hybrid system showing the contribution from different orbitals. The zero energy is set at Fermi energy.

CdTe NW, molecules and NW-molecule hybrid systems. The idea of the position of VBT and CBM of the hybrid systems have great impact on the characteristic properties of the final device such as the polarization offset of photodiodes or the open-circuit voltage in excitonic solar cells. The figure reveals very interesting feature. For all hybrid nanowire-molecule systems, the position of the VBT remain close to the VBT of the NW. But depending on the nature of the molecule the position of the CBM is either close to the CBM of NW or LUMO of the molecule. Thus, for all NW-molecule hybrid systems VBT is primarily on the NW while the CBM of NW-DHDC and NW-DMDC are on the NW but it is on the molecule for NW-DCDC and NW-DNDC. The figure also show that the band gap of NW-DHDC and NW-DMDC hybrid systems remain almost same as that of clean NW while there are substantial decrease in band gap in NW-DCDC and NW-
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DNDC hybrid systems. So, depending on the nature of the molecule in the NW-Molecule system,
electronic structures are quite different. Because of the electron withdrawing nature of -NO$_2$ and
-CN, the CBM of NW-DNDC and NW-DCDC shifts to lower energy and accordingly there is a
substantial reduction in the band gap values. As the electron withdrawing ability of -NO$_2$ is larger
than -CN, the lowering of CBM energy of NW-DNDC is more compared to NW-DCDC system.
In contrast, the electron donating effect of -H and -OCH$_3$ elevates both the VBT and CBM levels.
From the position of the VBT and CBM we can conclude that the hybrid systems NW-DCDC and
NW-DNDC represent type II surface characterized by the presence of molecular states in the gap
which reduce the optical gap. The conductance and luminescence of CdTe nanowires should also
change upon DCA derivatives adsorption, which can then be used for chemical sensor.

**Figure 5.9** VBT/HOMO (red) and CBM/LUMO (blue) energy alignment for the considered NW-molecule hybrid systems (bold) and molecules in the gas phase. The region inside the dotted lines identifies the band gap of clean CdTe nanowire ($W_H^{1}$). The zero energy is set at the VBT of the clean nanowire.
5.4 Conclusion

In this chapter we have investigated the structural and optoelectronic properties of (10\overline{1}0) faceted CdTe nanowires. The formation energy of the nanowires is studied as a function of both the nanowire diameter and surface atom ratio to understand the possibility of its formation. The steady decrease of the formation energy with the wire diameter strongly suggest its formation at large size. The possibility of band gap engineering is explored either by varying the size or shape of the nanowire. We have also shown the tuning of the band gap by organic functionalization. The passivation of the nanowire has only little influence on the band gap values but strongly affects the spatial distribution of the charge densities. Thus, the charge densities at CBM of the passivated nanowires is comparatively less delocalized than that of bare nanowire and both are dispersed along the growth direction. However, although the charge densities at VBT of the bare nanowire is dispersed along the growth direction the corresponding densities of the passivated nanowires spreads from the center to the surface of the nanowire. The study of PDOS reveal that HOMO density has the major contributions from Te \( p \) orbitals and also contributions from Cd \( p \) orbitals while the major contribution to CBM comes from Te \( d \) orbitals and little contribution from Cd \( p \) orbitals. The functionalization of CdTe nanowire with carboxylic acid derivatives (DHDC, DMDC, DCDC and DNDC) offers further possibility of tuning the optoelectronic properties. Our study reveals that the functionalization of the nanowire with DHDC and DMDC molecules have little impact on the band gap of the nanowire however DCDC and DNDC molecules have substantially reduce the band gap [406]. We suggest that the DCDC and DNDC functionalized CdTe nanowires may be a suitable candidate for use in nanowire-dye sensitized solar cells. We hope that our theoretical prediction will stimulate experimentalists to design CdTe nanowire based dye sensitized solar cells.