Scanning Tunneling Spectroscopy of Molecular Thin Films and Semiconductor Nanostructures

Doctoral Thesis

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Sandeep Gaan

Advisor

Prof. R. M. Feenstra

Department of Physics Carnegie Mellon University, Pittsburgh, PA 15213

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THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY IN THE FIELD OF PHYSICS

TITLE: "Scanning Tunneling Spectroscopy of Molecular Thin Films and Semiconductor Nanostructures"

PRESENTED BY: Sandeep Gaan

ACCEPTED BY THE DEPARTMENT OF PHYSICS

RANDALL FEENSTRA, MAJOR PROFESSOR

FRED GILMAN, DEPT HEAD

DATE

DATE

APPBOVED, BY THE COLLEGE COUNCIL

DATF

Abstract

Work presented in this thesis mostly deals with nano-scale study of electronic properties of organic semiconducting molecules using pentacene (Pn) as a model system and compared with various SiC surfaces to gain more insight into physical processes at nanoscale. In addition, InAs quantum dots (QDs) in a GaAs matrix are studied to probe electronic states of individual QDs. Scanning tunneling microscopy (STM) and spectroscopy (STS) are the primary experimental techniques used to probe local electronic properties on the nano-scale.

Vacuum sublimated Pn thin films were deposited onto SiC substrates for STM/STS experiments. STM studies show high quality ordered Pn films. Atomic force microscopy (AFM) images reveal dendritic growth pattern of these films. Local density of states (LDOS) measurements using STS reveals a HOMO-LUMO bandgap. In order to study charge transport properties of Pn films, different amount of charge were injected into the sample by systematically changing the tip-sample separation. Saturation of the tunnel current was observed at positive sample voltages (LUMO states). This effect was attributed to a transport/space charge limitation in tunnel current by treating it as a situation analogous to charge injection into insulators which gives rise to space charge limited current (also previously observed in the case of organic semiconductors). Using a simple model we were able to derive a hopping rate that characterizes nano-scale transport in Pn films at least in the vicinity of the STM probe-tip.

We have studied effect of transport limitation in the tunnel current for various semiconductor surfaces. In order to probe surfaces of varying conductivities, we have used Si-rich SiC surfaces such as 3×3 and $\sqrt{3} \times \sqrt{3}$ -R30° (both Mott-Hubbard insulators) as well as a highly conducting C-rich graphene surface, and compared those results with the data obtained from Pn. We observe variation of the decay constant κ (which characterizes the tunneling process) on these surfaces of varying conductivities. The graphene surface shows no transport limitation in the tunnel current, as evidenced by only small changes in κ as a function of tunnel current for these surfaces. This result is in sharp contrast to the case of Pn where κ rapidly decays to zero with increasing tunnel

current due to transport/space charge limited effects in the semiconductor. Thus, the change is κ value in STM experiments is reflective of non-ideal behavior of the tunneling.

As a specific case of transport limitation on the nano-scale we have also studied InAs QDs grown in a GaAs matrix. We observe that the occupation of discrete quantized states in the dots with electrons has a significant effect on tunneling spectra. When the QD state is occupied by an electron the potential in the dot is modified such that this state does not contribute to the tunnel current. The state then remains "invisible" in the tunneling spectra. Only in presence of transport channels in the vicinity of the dots can the electron localized in the QD state leak out to the substrate, and only then does the state appears in the spectrum. In our experiments these transport channels arise from steps which form as a result of *in situ* cleaving process for cross-sectional STM (XSTM) measurements.

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Chapter 1

Molecular Thin Films and Semiconductor Nanostructures

1.1 Organic semiconductors

Interest in the field of organic semiconductors has grown sharply over last two to three decades. Extensive research efforts from both academic and research laboratories have made it possible for commercialization of devices made of organic semiconducting materials, and more advances are expected to follow in the near future. For electronic applications, some of the major advantages of using conducting molecules over inorganic are as follows: Because of the nanometer scale size of these materials there is an advantage in cost, efficiency, and power dissipation. A wide range of properties such as chemical solubility and the color of emitted light can easily be tuned via chemical synthesis. Low cost fabrication is possible with these materials since they can be coated or printed over large area. Also, these molecules are mechanically flexible making them ideal candidates for applications such as electronic paper and flexible displays.

Despite of all the advantages mentioned above, organic electronics is not meant to replace Si based devices. Rather, it can act as a powerful complement and it can augment the capabilities of conventional inorganic semiconductor based devices. The primary reason for this limitation is the low mobility values of charge carriers in these organic semiconducting materials as compared to the crystalline Si which forms the core of modern day semiconductor technology.

There are two major classes of organic semiconductors: low molecular weight materials and polymers. Polymers can be processed from solutions, whereas small molecules can be deposited from gas phase by sublimation or evaporation in a vacuum environment. Controlled growth of highly ordered thin films by vacuum evaporation or solution processing is still a subject of ongoing research, and is crucial for many applications.[1] In the following sections some basic properties of these materials will be discussed with more emphasis on electronic properties, in particular basic charge transport mechanisms will be introduced. Structural properties of Pentacene (Pn), a small semiconducting molecule which is used as a model system for studies for this thesis will be discussed along with a brief introduction to Pn thin film growth.



FIGURE 1.1: Left: Molecular orbitals of C_2H_4 , an example of a simple conjugated π electron system. The figure on the right shows the energy levels of a π -conjugated molecule. The lowest electronic excitation is between the bonding π -orbital and antibonding π^* -orbital. Adapted from [2].

1.1.1 Basic properties

Semiconducting polymers and small molecules share a common structural feature. Both have in common a conjugated π -electron system being formed by the p_z-orbitals of sp²-hybridized C-atoms in the molecules. This bonding arrangement is illustrated in Fig. 1.1. Compared to the σ -bonds which form the backbone of the molecules, the π -bonding is significantly weaker. Therefore the lowest electronic excitations of conjugated molecules are these π - π * transitions which span the visible spectrum between 1.5 to 3 eV.

The nature of bonding in organic semiconductors is fundamentally different in than the inorganic semiconductors. The former crystals are van der Waals bonded solids, implying a weaker intermolecular bonding as compared to covalent bonding in materials such as Si or GaAs. The wavefunctions of organic semiconductors therefore have much less delocalization among neighboring molecules, a fact which has direct implication for optical properties as well as charge carrier transport. Figure 1.2 shows the energy levels of isolated molecules as compared to molecular crystals. We will focus mainly on charge



FIGURE 1.2: Energy levels of a molecular crystal (right) as compared to that of molecule (left). I_g and A_g denote the ionization potential and electron affinity in the gas phase, I_c and A_c are the respective quantities in the crystal. Due to the polarization energies P_h and P_e charged states are stabilized in the crystal. E_g is the single particle gap being relevant for charge carrier generation, whereas E_{opt} denotes the optical gap. Exciton levels are also indicated in the diagram. Adapted from [3].

carrier transport in the following sections. Readers are referred to the following books for further study on organic semiconductors.[2,3,4,5,6]

1.1.2 Charge carrier transport in organic semiconductors

Despite impressive progress in organic thin-film transistors during the past two to three decades, charge transport in organic materials is still not well understood. We briefly describe below different charge transfer mechanisms in organic molecules. The basic processes involved are the following. (1) Conduction along the polymer backbone, (2) hopping across chains due to inter-chain interactions and (3) tunneling between conducting segments of a polymer separated by non-conducting portions. There are two families of charge transport mechanisms. The first one is more suitable to describe

polymer systems and is based on hopping transport.[7] The second is used to describe molecular crystals. In those systems charge transport occurs via charge-carriers in delocalized states, as in conventional semiconductors, the so-called band-like transport. However one drawback of this model is that it is only valid at low temperatures (i.e. when hopping rates become very small, so that only band-like effects remain).[8] At higher temperatures, charge transport by polaron hopping has been proposed to describe transport in molecular crystals.[9,10] Another frequently used model to describe gate voltage-dependent mobility is based on multiple trapping and release of charge carriers, as originally proposed for a-Si:H.[11] In this model, transport limited by a distribution of traps near the band edge is proposed.[12] Some aspects of these models are explained in more detail below.



FIGURE 1.3: Energy levels of an isolated molecule (left), a molecular crystal (middle), and an amorphous solid (right). The width of the Gaussian density-of-states is of the same order as the band widths in molecular crystals ($\sim 0.1 \text{ eV}$). Adapted from [3].

As mentioned briefly above, there are three primary models to describe charge carrier transport in organic molecules. (1) Hopping in Gaussian disorder model (GDM). (2) Polaron transport. (3) Multiple trapping and release (MTR).

Hopping in GDM

This model pioneered by Bässler is used to describe transport in disordered semiconducting polymers.[13] Localized states in the polymers which arise because of their spatial disorder (fluctuations in inter-site distance) and energetic disorder (fluctuations in site-energy) configurations are assumed to have a Gaussian energy distribution. This is schematically shown in Fig. 1.3. In this model, electron-phonon coupling is assumed to be sufficiently weak so that polaronic effects are neglected. Thereby the charge carriers hop in a regular array of hopping sites. Further improvements in this model have been proposed where a spatially correlated site-energy distribution was considered. This is known as the correlated disordered model (CDM).[14]

Polaron transport

In case of strong electron-phonon interaction, charge transport in molecular crystals and polymers can be understood in terms of polarons. A polaron is basically a quasiparticle which results from the combination of a charge carrier with a lattice deformation induced by its charge. Charge transport occurs via hopping of polarons instead of the charge carriers itself.[15] The transition rates have been modeled by Marcus,[16] and the field and temperature dependence of the mobility has been obtained.[16,17]



FIGURE 1.4: Energy level diagram illustrating the trapping and release transport mechanisms. Adapted from [18].

Multiple trap and release model

In the multiple trap and release model a narrow band of highly concentrated trap states are assumed. The traps are levels localized at lattice defects or impurities in which charge carriers are immobilized. These traps can be either deep traps near mid-gap or shallow traps located near the conduction and valence band edges. This was developed by Le Comber and Spear[11] and applied to organic field effect transistors (OFETs) by Horowitz *et al.*[12] This model assumes an exponential distribution of gap states. The charges injected or the charges which are already present in the organic semiconductor are trapped in the localized states and subsequently released in a thermally activated process. A schematic diagram showing the MTR processes is shown in Fig. 1.4. Different charge transport mechanisms are reviewed in Refs. [18,19,20].

1.2 Pentacene (Pn)

Among organic semiconductors, the small molecule Pn (see Ref. [21]) has attracted much attention because of its high charge carrier mobility values exceeding that of amorphous Si. High structural order has made it possible to built Pn based devices in technologically relevant areas such as large area[22,23] and mechanically flexible organic electronics.[24,25,26] Pentacene routinely yields organic field effect transistor (OFET) devices with reliable hole mobility values greater than 1 cm² V⁻¹ s⁻¹, with mobility > 3 cm² V⁻¹ s⁻¹ for thin film based devices and even close to 60 cm² V⁻¹ s⁻¹ for transistors made of single crystals of Pn.

The structure of Pn ($C_{22}H_{14}$) is planar, composed of five benzene rings linked as shown in Fig. 1.5(a). Pn is known to exist in two phases depending on the preparation technique. In the bulk phase it has triclinic structure with density of 1.365 g/cm³. The "thin film" phase is obtained by vacuum evaporated thin films.[27] The bulk phase however is found to coexist with the thin film phase beyond a certain critical thickness.[28] Since charge transport properties depend on an efficient π -orbital overlap between the molecules, structural arrangement plays an important role in defining electronic properties.



FIGURE 1.5: (a) Pentacene molecule. (b) Sketch along the c axis of the herringbone crystalline structure of the "thin film" phase of Pn. Labels 1 and 2 refer to the two inequivalent molecules rotated by $\theta \sim 53^{\circ}$. Adapted from Ref. [74].

1.2.1 Structure and mobility

The bulk crystal structure of Pn consists of molecules arranged in a herringbone packing motif with an interlayer spacing of 1.41 nm.[29,30] Using wide angle X-ray diffraction four thin film multilayer phases have been identified with interlayer spacing d_{001} values of 1.41, 1.44, 1.50, and 1.54 nm respectively.[31,32,33] Figure 1.6[34] shows a triclinic unit cell of bulk Pn with the following crystal constants:

a = 0.63 nm, b = 0.77 nm, c = 1.44 nm, $\alpha = 76.75^{\circ}$, $\beta = 88.01^{\circ}$, and $\gamma = 84.52^{\circ}$.[29] The unit cell contains two inequivalent molecules marked by (1) and (2) in Fig. 1.5(b). The molecules are not perpendicular to the molecular planes, but are at finite angles. The angle between the inequivalent molecules is about 53°.[35]





There are only a few organic semiconductors who have field effect mobility values greater than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. One interesting property shared by all such materials is that they all pack in a herringbone or herringbone-like structure in which molecules have a large overlap of their conjugated portions.[9] The molecules are typically tilted with respect to alternating rows of molecules resulting in a zigzag of the molecular axis as shown in Fig 1.5(b). Although the effect this structure on mobility is still not properly understood it can be tentatively argued that due to this interlocking nature of the

molecular layers there is an effective increase in bond strength. It is generally expected that stronger bonds (as in the case of covalent solids) give better mobility than that of solids with weaker van der Waals bonds. With the herringbone-like motifs these organic solids will have higher crystal cohesion (higher effective bond strength) compared that with just simple van der Waals bonds, and hence possibly higher mobility. However this does not necessarily imply that every van der Waals crystal with herringbone motif will have mobility higher than 1 cm² V⁻¹ s⁻¹, as other effects such as film morphology, interface effects, and crystal structure will play a big role. The transport properties of crystalline organic films depend strongly on the intermolecular overlap of electronic wave functions within the semiconducting layer, which is very sensitive to molecular packing in crystals[35,36] as well as in ultrathin films.[37]

1.2.2 Thin film growth

As Pn belongs to the class of small molecules, it can be prepared under ultra high vacuum (UHV) conditions by sublimation. High quality thin films of Pn can be routinely obtained by this method. Other possible deposition methods for small semiconducting molecules include organic molecular beam deposition[27], common high vacuum bell-jar deposition, and organic sublimation systems that employ a carrier gas to transport the organic molecules from the source to the substrate.[38,39]

Growth modes for depositing Pn depend on the interactions between the molecules, their neighbors, and also the substrate.[40] This is because of the weak van der Waals interaction between the molecules and the long planar shape and hence relative orientation of the ad-molecules. If the substrate is inert and flat, Pn tends to form crystalline domains regardless of the crystallographic orientation of the substrate.[32,41] The molecules prefer to stand nearly vertical and layer-by-layer growth occurs when the lateral Pn-Pn interactions are more important than either the Pn-substrate or Pn-Pn interlayer interactions.[21,42,43,44,45] Hence lattice matching is no longer a requirement for multilayer structures.

When Pn is deposited onto flat and inert substrates such as some of the oxides or polymeric dielectrics, or onto an appropriately passivated surface, the molecules stand nearly vertical on the substrate.[22,27,28,32,41,42,45] The (001) surface has the lowest

surface energy in Pn crystals. So when Pn-Pn interaction dominates compared with Pnsubstrate interactions then we get a thin film with the (001) plane parallel to the substrate. On the other hand with reactive substrate surfaces such as clean Si[42,46] or clean metals[47,48,49], the Pn-substrate interaction dominates and the molecules prefer to lie flat on the surface with possibility of charge transfer at the interface. These strong interactions lead to the formation of a large interface dipole at the substrate-Pn interface. This large interface dipole is known to increase hole injection barriers.[50,51] Beyond the first monolayer, however, the molecules continue their growth by standing nearly perpendicular to the surface. Among the most inert substrates the most common ones are SiO₂[22,27,28,42,44,56] or Si(001) surface passivated with self assembled monolayers such as styrene or cyclohexene.[42] A review of different growth modes with different substrates is given by Ruiz *et al.*[21], and Witte *et al.*[52] The thickness dependence of structural evolution is described in detail by Cheng *et al.*[53]

Two important growth parameters are substrate temperature and deposition rate; these are critical for the thin film morphology and thereby charge transport characteristics. Increasing the substrate temperature and lowering the deposition rate decreases the nucleation density thereby increasing the average grain sizes.[41,54,55,56] Purity of the source material used is also very important along with proper cleanliness of the substrate. These factors affect impurity concentration, which in turn affects mobility and in some cases even the polarity in transistors. For example iodine-doped Pn is a ptype semiconductor[57] while alkaline metal-doped Pn is an n-type semiconductor.[58]

It is generally expected that bigger grain sizes in thin films yield higher values of charger carrier mobility. This is observed in the case of polycrystalline oligothiophenes.[59] However in the case of Pn the opposite effect has been observed quite frequently.[60,61] For example, between 1 and 3 cm² V⁻¹ s⁻¹, collected literature reports seem to indicate increasing mobility with increasing grain size, but very high mobility films > 3 cm² V⁻¹ s⁻¹ suggests the opposite. These conflicting results on the importance of grain size on mobility underscore the point that the connection between dielectric surface energy, film morphology, and electrical properties in Pn is not yet fully understood.[62,63,64,65,66] The role of thickness of the deposited films on mobility if also of interest. It has been observed by Ruiz *et al.* that the field effect mobility saturates

when 6 ML of Pn are deposited on SiO_2 gate dielectric.[67] They ascribe this saturation of mobility to the fact that the transport of free carriers occurs in the first few layers adjacent to the gate dielectric, as predicted by electrostatic models.[68,69,70]

Scanning tunneling microscopy (STM), which was invented in 1982, allows investigators to "see" at a molecular level, and continues to be a key enabler providing fundamental information on the performance limitations of organic field effect transistors (OFETs) and organic light emitting diodes (OLEDs). STM studies on Pn have been reported by many groups. These studies primarily focus on growth and structural properties of Pn films metals well Si on as as surfaces.[71,72,73,74,75,76,77,78,79,80,81,82,83,84,85,86,87,88] Interface studies have also been performed including surface chemistry and reactions.[89,90,91,92,93,94,95,96] STM experiments on Pn based nanostructures have also been reported recently.[97,98,99] mapping of Pn molecules on insulating surfaces has been Wavefunction performed.[100,101,102,103] There have been many STM related experiments on organic semiconducting molecules as well as polymers; these reports are too numerous to list here. However there are only a few reports on charge injection by probe-tip and transport properties of organic semiconductors in general and Pn thin films[104,105] in particular. In particular s - V measurements where the tip-sample separation is varied with sample voltage has been performed by Alvarado et al. which was performed on copper phthalocyanine (CuPc). In those experiments the probe-tip physically makes contact and then gradually penetrates into the layered thin film structure, and from the results local electronic information about and transport properties are extracted.[106,107,108,109]

1.3 Quantum dots (QDs)

Chance discovery of the existence of coherent (i.e., defect free) three-dimensional (3D) islands in strained semiconductor epitaxy[110,111] has lead to a new area of research. These 3D islands known as self-assembled quantum dots (QDs) are interesting because they exhibit discrete atom like electronic levels.[112] Application in future devices based on these nanometer scale dots and novel properties due to charge carrier confinement in

all three dimensions are key driving forces behind growing interest of engineering and scientific community in this field.

In the following sub-sections some aspects of QD growth will be presented along with a discussion of the structural and electronic properties of QDs, focusing in particular on InAs dots in a GaAs matrix.



FIGURE 1.7: Spatial confinement in semiconductor heterostructures. Corresponding density-of-states are shown in the bottom row. Adapted from Ref [112].

1.3.1 Aspects of reduced dimensionality

Charge carrier motion in a solid is governed by its bandstructure. One will observe effects of size quantization in the solid if these carriers are restricted to move in a layer of a thickness of the order of the carrier de Broglie wavelength. With improved methods of epitaxial growth of semiconductors, it became possible several decades ago to insert well ordered thin films of materials having different properties than that of a host material. Due to the effects of quantum confinement along the growth direction, the electronic bandstructure as well as the density-of-states (DOS) gets modified significantly. Exploiting this modification in properties of such heterostructures, several novel optoelectronic devices like quantum well (QW) lasers were made possible with lower threshold currents. The advantage for applications of such quantum-size heterostructures due to confinement of electron gas attracted many scientists to reduce the dimensionality even further to one dimension (quantum wires) and zero dimensions (quantum dots). In quantum wires, carriers are localized in two directions and free to move only along the axis of the wire, and for QDs they are localized in all three directions giving rise to atomic-like discrete energy levels. The effects of this reduced dimensionality on the DOS as a function of energy is shown in Fig. 1.7. In bulk semiconductors the DOS increases with increasing energy separation from the band edges according to $E^{1/2}$. In QWs the possible energies are quantized in one direction and hence the DOS behaves like a step function (E^0 dependence). The quantization in two directions for quantum wires leads to variation of DOS according to $E^{-1/2}$, and ultimately for QDs the possible energy levels are completely quantized which corresponds to a δ -like DOS at discrete energies.[113] Due to this these quantized energy states, QDs are also called "artificial atoms"[114], and this energy quantization has made QDs a fascinating system for studying fundamental physics and an outstanding system for new electronic and optoelectronic devices.[115,116,117]

1.3.2 Fabrication of QD structures

Using epitaxial techniques such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD), growth of high quality defect free structures can be achieved. Although epitaxial growth of heteroepitaxial layers such as quantum well structures are fairly well established, growth of coherent QDs is more complex and demanding. A possible way to fabricate such structures is lithography and chemical etching. However a more direct way is by the self-assembled formation of dots through the Stranski-Krastanow growth mode, as explained below.

There are three well known modes of epitaxial growth of heterostructures near thermodynamic equilibrium. They are the Frank-van der Merwe (FM), Volmer-Weber (VW), and Stranski-Krastanow (SK) growth modes. They may be described as layer-by-layer growth (2D), island growth (3D), and a combination of layer-by-layer and islands. This is schematically shown in Fig 1.8. Complete wetting of the substrate is energetically favorable when the energy of the substrate surface $\sigma_{substrate}$ is larger than the sum of the

energies of the epilayer surface and the interface $\sigma_{\text{epilayer}} + \sigma_{\text{interface}}$, and then the FM growth mode occurs (at least for thin layers, where strain effects are not important).



FIGURE 1.8: Schematic diagrams of the three growth modes for heteroepitaxial systems: Frank-van derMerwe (FM), Volmer-Weber (VW), and Stranski-Krastanow (SK).

Alternatively, if $\sigma_{\text{epilayer}} + \sigma_{\text{interface}} > \sigma_{\text{substrate}}$ then we expect the VW growth mode to dominate and islands to form on the surface.

In the combination of both modes, islands can evolve only after an initial growth that occurs in a layer-by-layer mode where the initial layer is called the *wetting layer* (WL). This SK growth can occur in material systems with considerable lattice mismatch such as 7.2% for InAs on GaAs, where increasing strain in the growing epilayers induces inversion of the energetic situation. For these an systems. we have $\sigma_{\text{epilaver}} + \sigma_{\text{interface}} < \sigma_{\text{substrate}}$ as for the FM growth mode, but an additional term in the energetics is the strain energy in the growing film. At some *critical thickness* this latter term dominates, leading to the formation of 3D islands which can relax their strain (by elastic deformation). The critical thickness at which a transition from 2D layer-by-layer to 3D island growth occurs depends mainly on the lattice mismatch and the elastic constants of the material system. [118,119,120,121,122] Immediately thereafter the island formation is characterized by pseudomorphic growth, meaning that the lateral positions

of the atoms within the islands can be slightly shifted in respect to those of the WL and the bulk crystal, but the crystal lattice and symmetry are continued, each island atom is located at a lattice site defined by the underlying crystal. With further deposition, the size of the islands increases, until the strain gets too large for this pseudomorphic growth mode to continue even in these islands. At this stage dislocations may form to reduce the strain energy[123], disturbing the crystal lattice and therewith the electronic and optical properties of the nanostructures.

Within the large and complex parameter range of epitaxial growth, only small windows exist and have to be explored for each material system for the self-assembled SK growth of QDs. Moreover, the QD density, shape, stoichiometry and size critically depend on the chosen growth parameters.[124,125,126,127]

1.3.3 Structural properties of QDs

Determination of the precise shape of QDs is important for understanding its electronic and optical properties (i.e. as determined by its energy level structure arising from the quantum confinement) as well as for resolving the kinetics and mechanism of island growth.



FIGURE 1.9: Geometry of an InAs pyramid on an InAs wetting layer deposited on a GaAs(001) surface. Adapted from Ref. [112].

The structure of QDs is often analyzed for uncapped dots by local probes like scanning tunneling microscopy (STM) or atomic force microscopy (AFM). This yields information on typical shapes, density, size distribution, and evolution of QDs along with structure of the surrounding WL. The dots usually have a pyramidal shape with symmetry resembling the surface symmetry of the host material.[128,129,130,131,132,133] On a typical (001) growth surface, QDs exhibit the shape of a pyramid with a polygonal base, a (110) and a ($\overline{1}$ 10) symmetry plane and a clear apex as shown in Fig. 1.9.[130,134] Although this model is very often used for calculations it is only observed in case of smaller size QDs. In reality there can be many different facets, as revealed by STM on uncapped dots of different sizes.[128,129,135] Some examples of different facets are shown in Fig. 1.10. With increasing QD size relatively flat structure of the dots become unfavorable due to strong increasing strain of the lattice-mismatched material, and a shape evolution towards steeper structures occurs.



FIGURE 1.10: (a) Three dimensional STM image of an uncovered InAs QD grown on GaAs(001). (b) Height profiles and 3D images of a dot along $[1\overline{1}0]$ and [110] directions. (c) Extracted model of a dot. Adapted from Ref. [128].

The main driving force for the formation of QDs according to the SK growth mode, for the shape evolution of uncapped QDs, and also for structural changes upon overgrowth is the strain due to the lattice-mismatch between QD and host material. During growth of the WL the material has to adopt the lateral lattice constant of the host matrix and can only partly compensate this by an increased lattice constant in growth direction, leading to cumulative strain with increasing WL thickness. This situation changes in the QD, where only the bottom interface is defined by the material underneath, while towards the top the lateral lattice constant can also increase, hence providing additional strain relaxation.

Uncapped QDs are not used for device fabrication, as it is necessary to protect it from the ambient as well as minimize electron-hole recombination at an uncapped surface. Thus these QDs are capped normally, with the host material. However this process changes the strain distribution in the dots drastically as these dots are forced to fit into the host material from all sides. Hence the apex of the QD which is mostly strain relaxed gets strongly compressed, hence giving rise to truncated pyramidal shapes.[136] STM operating in a cross-sectional mode can image these capped structures, as explained in Chapter 2. The initial capping process and related shape changes have been studied by several authors.[137,138,139,140,141,142,143] The complex process of shape transition was divided into two different regimes, namely an initial, fast strain-driven material transfer, leading to QD shapes near thermodynamical equilibrium, which upon further capping was followed by kinetically limited surface diffusion.[136] Not only the shape, but also the stoichiometry of the dots can get rearranged upon overgrowth. This is true especially for larger structures, with an In-rich core being produced in an inverted-cone shape.[144,145,146,147,148]

Several other effects have also been found to occur during overgrowth process. For example, if there is a long growth interruption or annealing step, then complete dissolution of QDs can occur often accompanied by the formation of a second WL[149,150] or a partial dissolution with formation of nano-voids in the dot.[151,152] A second effect of growth interruption is that redistribution of material from the top can occur towards the surrounding matrix, producing so-called quantum rings.[142,153,154,155]

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1.3.4 Electronic properties of QDs

A band diagram for an InAs QD in a GaAs host matrix is shown in Fig. 1.13(a). InAs has a smaller bandgap of 0.35 eV whereas GaAs has a bandgap of 1.42 eV, with this difference in bandgaps leading to band offsets for both valence band (VB) and conduction band (CB) at the interface between the two materials.



FIGURE 1.13: (a) Schematic energy diagram of an InAs/GaAs QD. (b,c) Calculated energies and wavefunctions of confined states for pyramidal InAs/GaAs QDs of different size. Adapted from Ref. [155].

Different geometric structures of the dots give rise to different wavefunctions for both electrons and holes at different distinctive energies. In general there exists a range of energies from the ground state up to excited states of higher order with different symmetries as shown in Fig 1.13(b) and (c). There are many theoretical calculations of these energy states with the shape of their probability distributions.[156,157,158,159,160] It has been also shown that the electron ground state is mainly of *s*-like symmetry and hole ground state is *p*-like symmetry.[156,160] Also, since holes have larger effective masses compared to the electrons, the confinement energy and the energetic distance between excited states are larger for electrons than for holes.

The distribution of energy states of both the electrons and holes depend strongly on the QD size. This dependence is evident from simulations[156,157,159,161] as well as verified by experiments.[162,163,164,165] Not only does the size and shape of the quantum box influence the electronic states, but so too does the strain distribution[166,158,160] and the stoichiometry.[167,168,169,170] An exact knowledge of all these structural parameters is essential, and with such knowledge comes the ability to adjust the size, shape and stoichiometry of QDs in order to tune the energetic properties of the nanostructure devices.

1.4 Outline of the thesis

The research work described in this thesis deals with study of local electronic properties of two semiconductor systems: pentacene, which is an organic semiconducting molecule, and InAs quantum dots grown on GaAs. Both systems are studied by STM and scanning tunneling spectroscopy (STS). Various SiC surfaces have also been studied to have a broad understanding of electronic processes on a nano-scale in conjunction with STM/STS. A common theme in all the studies is the importance of *transport mechanisms* within the semiconductors, a topic which often is not discussed in the context of STM (since the rate limiting step is the transport across the vacuum barrier) but which turns out to play an important role in our measurements. Chapter 2 gives an overview of STM, which was the primary research tool used in this work.

In Chapter 3, electronic properties of Pn are described emphasizing nano-scale transport mechanisms. A home built deposition chamber specifically designed for deposition of Pn was used to deposit thin films of Pn molecules on oxidized SiC substrates. Pentacene samples thus prepared were then studied with STM/STS. Constant current imaging of the Pn films show high quality ordered surfaces of Pn thin films on which STS measurements were performed. Normalized conductance spectra were acquired to study local density of states (LDOS) of the Pn films. With systematic

variation of tip-sample separation different amount of charge carriers were injected in the film, thus enabling the study of local charge transport properties in the vicinity of the probe-tip. Saturation of tunnel current was observed for LUMO levels, which is direct evidence of transport limitations of the tunnel current. This nano-scale transport phenomenon was understood as an effect similar to space charge limited current as observed for charge injection into an insulator. We were able to deduce a hopping rate to characterize electron transport in the LUMO band.

We have applied the techniques developed for characterization of Pn films to other specific SiC surfaces. This work is described in Chapter 4. Highly conducting Crich graphene, and Si-rich 3×3 and $\sqrt{3} \times \sqrt{3}$ -R 30° surfaces which are Mott-Hubbard type insulators, were used to calculate decay constant κ (defined in Chapter 2). These results were compared with result from Pn surface to observe variation of κ with transport properties of semiconductor surfaces with varying degrees of conductivities. We concluded that, under severe transport limitation of the tunnel current, the decay constant collapses to zero indicating non-ideal behavior of the tunneling with transport limitations of the charge carriers.

As a further example of STM/STS study of nano-structures we have probed the electronic properties of InAs QDs grown in a GaAs matrix. Using tunneling spectroscopy we were able to identify localized states in the InAs QDs, albeit in the presence of other charge transport channels in the vicinity of the dots. These transport channels occur from defect related states. In our case step edges arising from the *in situ* cleavage process helped provide these transport channels. Only when the electron localized in the QD state leaks out of the dot with help from these transport channels does the conductance spectrum shows a direct signature of the QD states.

Several additional projects performed during this Ph.D. work are not discussed in this thesis. The first of these, published elsewhere, dealt with an STS study of the $Ge(111)c(2\times8)$ surface.[171] In that work, the influence of defects arising from the surface reconstruction of $c(2\times8)$ surface were studied using STS in a spatially resolved mode. Conductance spectra from these defect states were compared to spectra acquired from defect-free surface regions, in order to study the changes in local electronic properties of the surface due to the defects. A second project is a high resolution spatially

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resolved STS study of the SiC(0001) 3×3 reconstruction, with the goal of better understanding the variation of local electronic properties inside this unit cell with its complex atomic arrangement. That work wilsl be reported elsewhere as it is not directly related to the main theme of this thesis. An additional project dealt with cross-sectional STM (XSTM) studies of cleaved GaN surfaces. Although atomically flat cleaves were obtained, the resulting surface were found to be very reactive, thus appearing somewhat contaminated in STM image which prevented any detailed study of them. Finally we have successfully demonstrated the feasibility of combining porous SiC membrane with Si wafers using CYTOP which is a teflon like polymer. Thus we were able to demonstrate the possibility of making porous SiC based devices in combination with Si based electronics on a single chip using standard Si processing techniques. That work will be summarized elsewhere in report form.[172] Chapter 2

Experimental Setup and Introduction to STM/STS

2.1 Scanning tunneling microscopy (STM)

The principle behind the operation of STM is quite simple. A schematic diagram is shown in Fig. 2.1. A sharp metal probe-tip is brought into close proximity, e.g., 1 nm, to a sample surface under bias voltage between the tip and the sample. As a result a small electric current called tunneling current which is typically about 0.1 nA is established between the tip and the sample due to quantum mechanical tunneling of electrons though the vacuum barrier separating the tip and the sample. One important parameter is the tip-sample separation s on which the tunnel current depends exponentially as indicated in Eq. 2.1 below.



FIGURE 2.1: Schematics of principle of operation of STM. A metal probe-tip is raster scanned across a surface by piezoelectric actuators P_x , P_y and P_z . The control unit (CU) provides the tunnel voltage V_T as well as the feedback voltage V_P to the z-actuator P_z in order to maintain a constant tunnel current J_T while scanning. Voltages applied to P_x , P_y and P_z yield the topography of the surface at constant work function. The dashed line indicates the z displacement in a y scan at (A) a surface step, and (B) a contaminant spot, C, with lower work function. Apparent broadening of the step edge due to geometry of probe-tip is indicated by δ (from Ref. [3]).

$$I_{t} \propto \exp(-2\kappa s) \tag{2.1}$$

This exponential dependence of current on tip-sample separation gives rise to subangstrom level sensitivity in the z-direction as well as enhances lateral resolution which can be much smaller than the tip end.[173] The decay constant κ is a measure of the barrier height and is given by

$$\kappa = \sqrt{\frac{2m}{\hbar^2} \left(\overline{\phi} - \frac{|V_S|}{2} \right)} \quad . \tag{2.2}$$

Where $\overline{\phi}$ is the average work function between tip and sample, and V_S is the voltage between the tip and sample.

Apart from acquiring topographic images, STM can also be used to study local electronic properties of the sample surface. This is accomplished by varying the sample voltage and measuring the resulting variation in the tunneling current, i.e. scanning tunneling spectroscopy (STS). Tunneling between a probe-tip and metallic sample with a typical local density of states (LDOS) on the surface is shown in Fig. 2.2 with variation in sample voltages. As shown in the figure, the tunneling probability varies with change in sample voltage and is largest for electrons at the highest-lying Fermi level of the two electrodes.



FIGURE 2.2: Tunneling between tip and sample which is also a metal. An arbitrary LDOS is sketched for the sample surface. Tunneling probabilities are indicated by arrows (a) zero bias, no tunneling current, (b) for positive sample bias, current from occupied tip states to unoccupied sample states, and (c) for negative sample bias, current from occupied sample states to unoccupied tip states.

2.2 Tip-induced band bending in STM of semiconductors

In this section we describe some miscellaneous important observations regarding STM studies of semiconductor surfaces. These effects are frequently observed in the work presented in this thesis.



FIGURE 2.3: Schematic overview on typical regimes of tip-induced band bending at an n-type semiconductor. (a) No voltage applied. (b) Moderate positive sample voltage and (c) large positive sample voltage. (d) and (e) represent cases for moderate and large negative sample voltages. The arrows show tunneling of electrons. The dashed arrow in (e) shows tunneling through depletion region in the semiconductor. ϕ_t is tip work function and χ_s is the electron affinity of the semiconductor.

The metal semiconductor junction is in general defined by Fermi energies of the tip ($E_{F,t}$ and sample ($E_{F,s}$), metal work function (ϕ_t), semiconductor electron affinity (χ_s) and doping level of the semiconductor and the tip-sample separation. In the STM, the

proximity of a metal probe-tip to a semiconducting sample can lead to large amounts of tip-induced band bending (TIBB) in the semiconductor (arising from the continuity of the displacement field across the semiconductor-vacuum interface). The voltage drop between the tip and sample surface is thus less than the applied sample-tip voltage V_S , thereby affecting the accuracy of the spectroscopic energy scale $E - E_F(eV) = eV_S(V)$. For cases where the depletion region does not extend far into the semiconductor, then the potential barrier produced by band bending is partly transparent to electrons, in which case the band bending has a smaller influence on tunnel current. Band bending can also occur without any applied voltage in cases where existences of surface states or strong doping levels in the semiconductor create surface charges which in turn give rise to an electric field. Depending on the polarity and applied bias voltage, different regimes of TIBB can occur which are schematically shown in Fig. 2.3 for an n-type semiconductor.

2.3 Cross-sectional scanning tunneling microscopy (XSTM)



FIGURE 2.4: Comparison of STM in the (a) conventional plan-view arrangement with (b) XSTM. Samples are cleaved to expose (110) or $(1\overline{10})$ faces on which STM is performed. Cross-sectional features revealing the bulk (i.e. non-surface-specific) information can be images in this mode.

STM imaging of semiconductor nanostructures often performed in a plan-view configuration. This is very useful in studying nanometer scale features of the growth

surface and the details of the surface atomic reconstruction (a surface is said to be reconstructed when the geometric arrangement of the surface atoms is not the same as that of the truncated bulk). For the case of QDs they are typically measured in (001) growth direction and in plan-view STM is used to study the overgrowth process of these free standing dots. But most QD nanostructures in real devices are capped in order to protect it from environment and to minimize electron-hole recombination at an uncapped surface. This overgrowth changes many properties of these QD structures as explained in Chapter 5 on QDs.

These capped QDs (which are technologically more relevant) can be studied when STM is performed in a cross-sectional configuration. In XSTM the sample is cleaved, and the cleavage face is studied with STM tip. The advantage of using this method is that the sample can be capped as in real devices and studies can be performed independent of the history of the sample. Moreover, the cleaving process is usually done under UHV conditions thereby exposing fresh clean surfaces to be investigated. A schematic diagram of XSTM compared to conventional plan-view STM is shown in Fig. 2.4.

Several research groups in the world are currently investigating QDs with XSTM experiments, which are quite complex to perform. The earliest report to my knowledge was by W. Wu, and J. R. Tucker at University of Illinois at Urbana, USA, in 1997.[174] Later the groups of D. Stiévenard at the Institut d'Electronique et de Microélectronique du Nord in Lille Cédex, France[175,176,177], of R. S. Goldman at the University of Michigan, Ann Arbor, USA[178,179,180,181], of M. Dähne at the Berlin University of Technology, Germany[182,183,184,185,186,187,188,189], C. K. Shih at the university of Technology Eindhoven, The Netherlands[193,194,195,196,197,198,199,200,201,202], reported works various QD systems. More recent work is from the groups of E. Lundgren at Lund University, Sweden[203], A. Nakamura at Nagoya University, Japan[204] and W. W. Pai at the National Taiwan University.[205]

XSTM images contain both structural and electronic information about the sample being probed, just like common STM measurements. Remembering the tunneling current as representing integrated sample LDOS at the position of the tip, the topography of the sample will most directly influence the tip-sample separation and thereby the tunneling
current. The electronic properties of the sample surface and local variations are contained within the LDOS. Besides these general considerations, there is also a structural and electronic contrast mechanism specific for XSTM studies on cleaved QDs which will be briefly described in Chapter 5.

2.4 The STM and preparation chambers





The STM used in the studies described in this work is home-built. The principal setup of the chamber which includes a recent extension of a UHV sample preparation chamber is presented in the following sections.

The home-built STM chamber is designed for investigation of semiconductor surfaces both in plan-view and in cross-section mode. It has facilities for *in situ* sample and tip transfer, sample cleavage, and tip cleaning and inspection. It now includes a sample preparation chamber where thin films can be deposited by thermal evaporation under UHV conditions. Both the STM chamber and preparation chambers are kept in UHV by several pump stages and equipped with pressure gauges to measure base pressures.

2.4.1 The STM chamber

In addition to the STM, the chamber has a Low Energy Electron Diffraction (LEED) system for additional surface characterization. It is also equipped with a Quadrupole Mass Spectrometer to analyze the residual gas from time to time and also for leak detection. A Si e-beam evaporator is used to prepare various surfaces as described in Chapter 4. A scriber for cleaving cross-sectional samples, sample and tip storage systems and a tip cleaning filament are some other features of this chamber. Figure 2.5 shows the STM as well as the attached preparation chamber.

2.4.2 Preparation chamber

In order to investigate thin films of organic molecules, a separate preparation chamber was designed and installed which is connected to the current STM chamber though a gate valve. This chamber is pumped by separate pumps and the ultimate base pressure achieved was $< 1 \times 10^{-10}$ Torr. Two types of organic molecules can be deposited at the same time from two different crucibles mounted on a source flange. A quartz crystal thickness monitor is mounted close to the sample in order to measure thickness of the deposited films. The sample (substrate) can be heated resistively and simultaneously oxidized by leaking molecular oxygen in this compact system. A sample manipulator handles samples from the load-lock to the preparation chamber. This preparation chamber, which works quite well, was precisely designed to fit the limited space available near the STM chamber successfully.

2.4.3 The microscope

In our STM the x, y and z-drives arise from a hollow piezoelectric tube scanner with four quadrants. The inside of the scanner tube is grounded, while appropriate voltages are applied to the quadrants on outside. This is schematically shown in Fig. 2.6. The scanner is mounted on a slider which moves on a base plate on sapphire balls. Coarse positioning

of the probe-tip with respect to sample surface is achieved by two inch-worm motors. These motors are also used for systematic search of heterostructures in the XSTM mode. The entire STM assembly is suspended using four springs for vibration isolation. Further vibration isolation is achieved by eddy current damping. Various parts of the STM are shown in Fig. 2.7.

(a)



FIGURE 2.6: Schematic diagram of (a) STM and the (b) piezo tube scanner. Electrical connections for the scanner are also shown with voltage configuration for y-deflection.



FIGURE 2.7: Look from above of the STM assembly temporarily taken out of the STM chamber. Some important parts are indicated by arrows.

2.4.4 Sample holders

Different sample holders are used for plan-view and cross-sectional samples as shown in Fig. 2.8. Plan-view samples are resistively heated with the use of the wire clips as shown



FIGURE 2.8: Schematic diagram of sample holders in (a) plan-view and (b) cross-sectional STM configurations.

in the figure. The holder is made from two pieces of molybdenum (Mo), which serve as two electrodes for heating the sample. A slab of quartz is inserted between the Mo pieces and acts as an insulator. The wire clips are also made of Mo to hold the samples which are typically about $2 \text{ mm} \times 8 \text{ mm}$ in dimension. Electrical contact between the wire clips and sample is not well defined, and might be only a point. Thus there are often "hot-spots" under the wire clips. However at the center of the sample, the temperature is fairly uniform. The whole arrangement fits snugly into the STM with the help of Mo spring clips as shown in the figure.

The cross-sectional sample holders are usually made from Macor, a UHV compatible ceramic. Typical sample dimensions are $2 \text{ mm} \times 15 \text{ mm}$ which are mounted in such a manner that half of the sample protrudes outside which can then be cleaved in UHV to expose the desired surface. A small notch is made *in situ* by a diamond scriber to assist the cleaving process. The sample is fastened to the holder with the help of BeCu clips. The sample holder is mounted in STM with the help of spring clips as in the case of plan-view sample holders. However for these lighter sample holders, BeCu spring clips are often used.

Chapter 3

STM/STS Study of Pentacene Thin Films Deposited on SiC

3.1 Introduction

Nano-scale study of structural and electronic properties of organic semiconductors promises not only new applications, but also many novel physical phenomena. Among small semiconducting molecules, Pn in particular can be used as a model system for such type of nano-scale studies, especially for understanding electronic and charge transport properties in these small molecular systems in general. In this chapter, we discuss the use of STM/STS to probe nanometer scale electronic properties of Pn thin films and thereby study the problem of charge transport in the films.

There are two major advantages in our experiments on Pn thin films as described below. By ensuring clean UHV conditions for preparation of Pn films on SiC substrates we have eliminated unwanted effects of contamination which has a large effect on electronic properties of Pn. We will discuss effects of oxygen on the tunneling spectra and possible mechanisms in the later part of this chapter. A contamination free Pn film is essential for high quality reproducible results from experiments. The second unique advantage in our experimental method is in the use of the STM probe-tip as an electrode for efficient charge injection into the Pn films. The charge injection problem in Pn, which is relevant for other organic semiconductors as well, is briefly described below. Pentacene, like most other semiconducting molecules, has a low electron affinity value of about 3 eV. Most of the metals used as electrodes have work functions ranging from roughly 4 to 6 eV. Since Pn has a band gap of $\sim 2 \text{ eV}$, it is quite clear that the barrier for injecting electrons into the lowest-unoccupied molecular orbital (LUMO) is much higher than that for injecting holes into highest-occupied molecular orbital (HOMO) level. Consequently Pn behaves as a p-type semiconductor, not because of extrinsic doping as in the case of inorganic semiconductors, but because of the relative ease of hole injection into the HOMO level.

Using STM probe-tip for charge injection has two advantages over conventional metal contacts used as cathodes. First, any influence from the metal-semiconductor interface (such as intermixing at the interface) is avoided. Since Pn is quite reactive, the metal contacts can react with the molecules altering the electronic properties of the film considerably. Since STM probe-tip does not make contact in our experiments, we have



FIGURE 3.1: Schematic energy diagrams comparing situations of tip-sample contact [(a) with zero applied voltage and (b) with positive sample voltage] to tunneling through a vacuum barrier [(c) with positive sample voltage]. Tunneling through vacuum barrier makes LUMO states accessible.

completely eliminated these types of problems due to the metal-semiconductor interface. Secondly, states in the LUMO band become easily accessible by direct injection of electrons into this band. This situation is schematically illustrated in Fig. 3.1, comparing the cases of metal-semiconductor contact [panels (a) and (b)] with a vacuum tunneling barrier [panel (c)]. Under a positive sample bias the barrier height is very high for electrons coming from metal electrode in contact with the sample, Fig. 3.1(b), and states in the LUMO level are not accessible. However for a STM probe-tip most of the applied bias voltage drops in the vacuum junction since the dielectric constant of the semiconductor is large. Since the thickness of the vacuum barrier is quite small (~ 1 nm), the tunneling probability through the vacuum is large enough to yield an observable current, and the LUMO states become accessible as shown in Fig. 3.1(c). Exploiting this idea we can access both HOMO and LUMO states simply upon changing the bias voltage by using STM tip as an electrode for charge injection. We have also made use of the capability of STM to change tip-sample separation controllably thereby varying the amount of charge being injected into the sample. This enables us to observe new nanoscale phenomenon near the probe-tip as described in the next sections.

A limited number of tunneling studies on organic semiconductors and molecules have been reported previously. Kim *et al.* in 1996 used a thin insulating layer as tunneling barrier for efficient electron injection process into the sample.[206] However as explained earlier, in our experiments, interface effects from deposition of an insulating layer are eliminated in STM measurements since the thin insulator layer is replaced with a vacuum barrier between the tip and the sample. Similar STM studies as ours have been reported by Datta *et al.*[207] on self-assembled monolayers where a total voltage drop occurs between the tip and the sample and more recently by Ruppel *et al.*[208] on a Pn diode where they observed variation in I-V characteristics of Pn films with varying thickness of the films. However they did not perform any spectroscopic measurements by varying tip-sample separation thereby injecting different amount of charge carriers in the film. Other works in the literature include STM study by Alvarado *et al.*[209,210] and Kemerink *et al.*[211,212] on another semiconducting molecule CuPc. That work did investigate the variation of tunnel current with voltage and tip-sample separation, although those experiments relied on the tip and sample making physical contact and thus eliminating the vacuum barrier.

3.2 Experimental

Pentacene thin films were deposited in UHV conditions using a sublimation method. The substrate used was oxidized SiC which is a wide band gap semiconductor. The tunnel current spreads into the Pn film and provides us with a way to measure charge transport through these highly ordered molecular films. In the following sub-sections UHV deposition of Pn molecules and SiC substrate preparation by H-etching is described in detail, along with results from AFM and STM imaging of these thin films.

3.2.1 UHV deposition of Pn molecules

Pentacene molecules used in our experiments were bought from Aldrich. The Pn was deposited by sublimation from a pyrolytic boron nitride crucible under UHV conditions. The base pressure of our preparation chamber is less than 5×10^{-10} Torr. The crucible is capped with a perforated tantalum foil where the hole in the foil acts as a point source of Pn molecules. The crucible is wrapped with a tungsten filament for controlled heating. A type-K thermocouple is used to monitor the temperature of the crucible near the tantalum foil cap. The source/crucible temperature is typically kept at 210°C for Pn sublimation. In order to ensure the cleanliness of the deposited film the source was degassed at about

 120° C for about 12 hrs prior to deposition in order to get rid of low vapor pressure contaminants. During deposition process a typical pressure recorded in the ion gauge was around 5×10^{-8} Torr. Often to ensure further cleanliness of the whole process, a mock deposition step was performed prior to actual deposition to get rid of top layers of Pn molecules from the crucible. Deposition was monitored using a quartz crystal thickness monitor with a deposition rate of roughly 1 nm per minute. The substrate was kept at room temperature during deposition process. As presented below in Section 3.3, we were able to obtain 6-10 ML of Pn regularly in a typical deposition process with large domains of Pn showing a dendritic growth pattern, as observed by prior workers and indicative of high quality film growth.[213]

3.2.2 SiC substrate preparation

SiC, which is a wide band gap semiconductor, was chosen for use as the substrate material for the Pn thin film growth since its large band gap prevents transmission of the current into the SiC itself. Several poly-types of SiC exist. For our work we have used one of the most common, 6H-SiC, with the surface being (0001) oriented with nominally no miscut. The wafers were n-type doped having a doping density of about 10^{18} cm⁻³. By etching the as-received wafer with hydrogen, atomically flat SiC surface were prepared as described below.

The as-received wafers contain many scratches which arise from the polishing process and the surface is not suitable for thin film growth. In order to remove these scratches from the wafers, hydrogen etching is used.[214] We use a tantalum strip heater on which the SiC sample is mounted. By resistively heating such a foil to about 1650°C under a hydrogen environment we get atomically flat surfaces without any scratches, as seen from AFM images. The H-etching is performed using pure H₂ gas, at 1 atm pressure and with a flow rate of about 10 lpm. H₂ gas upon contact with the hot Ta foil dissociates into H atoms and reacts with SiC to produce the etching process. Figure 3.2 shows SiC surface before and after H-etching. After H-etching large atomically flat terraces with uniformly spaced steps are present on the surface, with the steps arising from unintentional miscut of the wafer. A typical terrace width is ~20 nm, which is large enough for STM experiments.



FIGURE 3.2: Comparison of as received SiC sample (left) with sample after H-etching (right). Images were acquired with contact mode AFM.

Following H-etching, the samples were cleaned using solvents and introduced into UHV. They were then thoroughly degassed at about 600°C for more than 2 hrs to eliminate any molecules adsorbed onto the surface during the sample transfer process from the H-etching chamber to the STM chamber through air. The substrates were then oxidized by leaking 99.995% pure molecular oxygen into the UHV chamber through a leak valve. The substrate temperature was held at 600°C during the oxidation process, and the substrate is exposed to ~5000 Langmuir of oxygen. This oxidation process is known to produce 1-2 ML of oxide on top of the SiC substrate, as verified by Auger electron spectroscopy. The oxide layers thus formed help in forming large domains of Pn as is typically observed in case of oxidized Si surfaces explained earlier in Chapter 1. The sample is then transferred *in situ* to the STM/STS chamber for further analysis.



FIGURE 3.3: (a) High resolution STM image of Pn thin film. Each protrusion represents a Pn molecule. The image was taken at -2.7 V sample voltage. A surface unit cell is marked by yellow lines. (b) Large-scale STM image of layer-by-layer growth pattern of Pn film. Image was acquired at -3.0 V. (c) A line scan of image in (b), taken along the dashed line in the image.

3.3 Results from STM and AFM imaging of Pn

STM images were acquired in a constant current mode, using a constant current value of 0.1 nA unless otherwise specified and with sample-tip voltages specified below. Figure 3.3(a) shows a high resolution STM image of the Pn film, with a unit cell marked on the surface. Each lobe shows a single molecule. In the image the lobes are seen to be slightly elongated, resembling shape of a light bulb. This shape arises because the inequivalent Pn molecule at the center of the molecule is about 0.3 nm below the other 4 molecules, which are at the four corners of the unit cell. As shown in Fig. 1.5(b) the two types of inequivalent molecules make an angle of \sim 53° with respect to each other, hence giving rise to the "light bulb" shape. From the larger STM image of Fig. 3.3(b) it is clearly



FIGURE 3.4: (a) Large image of Pn film acquired using tapping mode AFM. The bright region indicated by an arrow reveals segregation of Pn molecules. (b) Multiple terraces are clearly visible in the close-up image.

observed that the Pn thin films growth in a layer-by-layer mode. In order to confirm the thin film structure in which the Pn molecules are expected to stand up with their long molecular axis almost perpendicular to the substrate, we took a line scan from the image and the result is shown in Fig. 3.3(c). The height of each layer is close to 1.5 nm which confirms the fact that the molecules do indeed align with their long axis almost perpendicular to the substrate surface. In order to characterize the large scale structure of the films, AFM images were acquired (using tapping mode as is normally used for

imaging soft organic molecules). These AFM images are acquired in air, after completing STM/STS studies in the UHV chamber. Figure 3.4 shows AFM images in which the dendritic growth pattern of Pn film is clearly observed. Large ordered domains of Pn are obtained, which are suitable for STM studies. These AFM images are usually acquired a few days after deposition and subsequent STM/STS measurements. Often times Pn molecules segregate during that time period, and show up in AFM images as bright spots. One such segregated region is marked by an arrow in Fig. 3.4(a).

3.4 Results from tunneling spectroscopy

Local electronic properties of Pn film can be obtained using STS techniques. Normalized conductance measurements yield information about the LDOS. Another important advantage of STM is that the tip-sample separation can be varied and different amount of charge can be injected into the sample. A new method for data acquisition was used for controllable variation of the tip-sample separation. Effect of transport properties of organic film on tunneling current was studied using these methods.

3.4.1 Normalized conductance measurements

Normalized conductance measurements $(dI/dV)/(\overline{I/V})$ were performed and a typical spectrum is shown in Fig. 3.5. Many such spectra are regularly acquired on different samples using different probe tips. Although a slight variation in the shape of these spectra is sometimes seen, the basic features are very reproducibly observed. The STS spectra reveal two peaks, as indicated by arrows in Fig. 3.5. The approximate locations of the peaks are at -2.25 and 0.80 V, respectively. The apparent width of the band gap is then found to be 2.1 ± 0.1 eV. For comparison, we examine band gap values reported in the literature. From STS on Pn films deposited on Cu(119) a molecular gap opening of 2.35 ± 0.05 eV has been reported.[215] The same value has also been quoted with STS on a monolayer of Pn on Ag/Si(111) substrate.[216] For thin films, gap values ranging from 1.97 to 2.68 eV have been obtained with optical measurements.[217,218,219] Moreover, the electronic properties of solid Pn for two different crystalline phases-S (solution phase crystallized) and V (vapor phase crystallized)-were determined using *ab initio* calculations[220] to be 2.2 and 1.9 eV, respectively. The phase with a higher



FIGURE 3.5: Normalized conductance spectra from a Pn thin film. HOMO and LUMO levels are indicated by arrows.

intermolecular overlap gives rise to a narrower molecular gap (1.9 eV) and larger bandwidth of the HOMO and LUMO. From the above discussion it is apparent that our result for band gap of about 2.1 eV matches well with earlier observations using both experimental and theoretical methods.

Nevertheless, as discussed in the following section, the shape of the STS spectra of Pn can potentially depend on the magnitude of the tunneling current used, because of transport limitations in the current flow. For this reason, we will revisit results obtained from normalized conductance spectrum in the Discussion Section later in this chapter.

3.4.2 Saturation of tunnel current in Pn thin films

In order to extract more information about the sample surface we have performed systematic measurements varying the set point current thereby changing tip-sample separations. The results are shown in Fig. 3.6. In this experiment, I-V curves were acquired at specific tip-sample separations as determined by the constant current value



FIGURE 3.6: I-V curves of Pn film acquired with different tip-sample separations. Δs is the relative tip-sample separation, with lower values meaning that the tip is moved closer to the sample surface.

(the so-called *set-point* current) prior to the I-V curve. By changing the set-point current, the relative separation Δs between the tip and the sample is changed. Values for Δs were determined after the I-V measurements by recording the variation of tunnel current with absolute tip-sample separation *s*, at a particular sample voltage. Results from such I-s curves, acquired at -3 V and -2 V respectively, are shown in Fig 3.7. From these curves



FIGURE 3.7: I-s measurements performed at different sample voltages as compared with ideal vacuum behavior shown with dashed lines. X-marks indicate set-point current values for which I-V curves were obtained as shown in Fig. 3.6.

we calculated the relative separation Δs between the probe-tip and the sample corresponding to the constant currents. These Δs values are shown in Fig. 3.6 and are also indicated with x-marks on the corresponding I-s curve shown in Fig 3.7.

The most interesting and surprising result obtained from the I-V curves shown in Fig. 3.6 is that the tunnel current strongly saturates at positive sample voltages. This saturation is direct evidence that the flow of the tunnel current is limited by some sort of charge transport mechanism in the sample. Moreover, from Fig. 3.7 it is seen that even for negative sample-tip voltage, there is significant deviation from the ideal vacuum behavior as the tip-sample separation is reduced. The ideal vacuum behavior, shown by dashed lines in Fig. 3.7, corresponds to $I \propto \exp(-2\kappa s)$ with an "ideal" value (appropriate to metal-vacuum-metal tunneling) for κ of 10 nm⁻¹ used in the figure. From Fig. 3.7 it is observed that, even at negative sample voltages, moving the probe-tip towards the sample does *not* produce an increase in the tunnel current by enough amount expected from ideal vacuum behavior; the slope of the log(I) vs. s curves for small s values in Fig. 3.7 are less

than half of the ideal curve, implying κ values less than 5 nm⁻¹. And, for the large positive voltages shown in Fig. 3.6 the current is completely saturated, implying a κ value of 0. Figures 3.6 and 3.7 thus provide the first evidence that charge transport properties of the sample do have significant effect on tunnel current. It should also be pointed out that using a single measurement technique we are able to see transport limitation in tunnel current for both filled (HOMO) and empty (LUMO) states.

It is important to note that, even in the absence of transport limitations in the semiconductor, tunneling characteristics of semiconductor-vacuum-metal junctions can be somewhat "non-ideal" in the sense that they differ from those of metal-vacuum-metal junctions. As already discussed in Section 2.2, some of the voltage drop across the junction can occur in the semiconductor itself, simply because of the electrostatics (continuity of the normal component of the displacement field across the vacuumsemiconductor interface). Such *tip-induced band bending* tends to produce I-V curve that are shifted to voltages with greater magnitude. This shift does produce associated changes in the κ value, but those changes are generally quite small (<10%) for voltages more than a few tenths of a V away from the band edges. In contrast, the large changes in the κ values seen in Figs. 3.6 and 3.7 imply not only a large voltage drop in the semiconductor, but one which increases as the current increases. Hence, we associate it with a transport-induced voltage drop in the semiconductor. This type of effect thus implies a transport limitation for the current that occurs in the semiconductor, rather than the usual situation in tunneling in which the limiting factor is in the transmission across the vacuum barrier itself.

The above measurements demonstrate transport limited tunnel current in Pn films conclusively. But, they suffer from several limitations. First it is not possible from the I-V curve alone to detect the saturation of the current for negative sample voltages. This limitation is because the changes in tip-sample separation are obtained in these measurements by varying the set-point current prior to acquiring each I-V curve. Also, the entire time scale over which the measurements are performed (in which the set-point current is progressively changed) is quite long, several minutes at least. During acquisition of such a set of I-V curves the probe-tip might drift away from the point of interest due to thermal effects. Also the electronic structure of the tip might change with

time, which makes the measurements process quite difficult to perform. Hence a faster and more reliable data acquisition was developed, as described below.



3.4.3 Spectroscopy with discrete Δs (tip-sample separation)

FIGURE 3.8: I-V curves obtained from a Pn thin film, by systematic Δs variation. Starting from red curve in the bottom, the probe-tip was consecutively moved by 0.05 nm to inject more current starting, from 10 pA (red) to about 1 nA (orange).

In this method we directly and systematically move the probe-tip closer to the sample surface, thereby injecting more charge carriers into the sample. For each I-V curve the STM feedback loop is opened, and current is measured by sweeping the voltage in the appropriate range. Then the probe-tip is automatically moved by a specified amount towards the sample typically (0.05 nm), and another I-V curve is obtained. One can continue this process till the point where the sample surface begins to show damage.

Once the appropriate range of Δs has been determined such that we can inject current without changing electronic properties of the sample surface, sets of spectra can be acquired easily and quickly. Additionally, images are acquired periodically to check the quality of the surface after each set of spectra. Figure 3.8 shows a set of spectra acquired using the method described above.

In Fig. 3.8 we again see saturation of the tunnel current at large positive sample voltages. These measurements, however, extend over a large range of Δ s values than those of Figs. 4.6 and 4.7, and a new feature appears in the data. When we move the probe-tip towards by more than 0.25 nm the current suddenly increases, and by moving it



FIGURE 3.9: Calculated κ values for negative (-2.4 V: blue) and positive (1.4 V: red) sample voltages plotted with magnitude of tunnel current. Results shown using triangle and circles are for two different probe-tips.

a little further by 0.05 nm it starts to decrease again. Those I-V curves are circled in the image. Usually this behavior is accompanied by a slight damage to the surface and we see a small dip in the accompanying STM images at the point where spectra were acquired. Observation of damage to the surface probably means that the vacuum barrier completely collapses and the probe-tip just starts touching the surface or forms a conducting bridge between the tip and the sample surface which results in a large increase in the tunneling

current. In this process the surface gets damaged and most likely the electronic as well as structural properties of the surface alter significantly. In this case, if the tip is moved even further the current is seen to decrease. In our analysis below we avoid this damaged threshold in the portions of the data that we analyze.

From the data of Fig. 3.8 we can deduce κ values as a function of voltage. Defining the κ value as that which gives a dependence of the current on separation of $I \propto \exp(-2\kappa s)$, then we have $\kappa = -0.5 d \ln I / ds$. From the neighboring I-V curves we compute $-0.5 \Delta \ln I / \Delta s$, and results are plotted in Fig. 3.9 for both negative (blue) and positive (red) sample voltages using two different probe tips. For positive sample voltage the tunnel current saturates and indeed κ rapidly decays to zero as seen from Fig. 3.9. For negative sample voltage, although there is some variation in κ values, it does not completely collapse to zero. These larger κ values are an indication that there is less transport limitation in tunnel current associated with the HOMO than the LUMO.

3.5 Discussion

In STS studies of semiconductors, transport of charge carriers within the semiconductors is not well understood. In most cases it is assumed that transport plays no significant role. This is because the resistance of the tunnel junction is about 1 G Ω which is many orders of magnitude higher than the resistance in the sample. A few prior studies have found evidence of transport limited tunnel current for some semiconducting surfaces. Low temperature STM studies on Si(001) $2 \times 1[221, 222]$ and H-covered Ge(111)c(2×8)[223] surfaces by Takanayagi et al. and Dujardin et al. lead to the suggestion that the transport of carriers in the semiconductor may be in some way affects the results.[221,223,224] Earlier, Ramachandran *et al.* had observed such effects on SiC(0001) $\sqrt{3} \times \sqrt{3} - R30^{\circ}$ surfaces using room temperature STS measurements.[225] Low temperature work on Ge(111) $c(2\times8)$ surface by Feenstra et al., following the work of Dujardin, showed evidence of transport limited current in the semiconductor and clarified the mechanism for this limitation as being associated with charging of midgap states arising from defects in the surface structure. [226] However, none of the above studies show nearly as much evidence of transport limitations as with our results for Pn, in which the tunneling current is completely saturated. Very recently, Berthe et al. [227] presented results on current



FIGURE 3.10: (a) Current injection from a STM tip and carrier confinement in a Pn film. (b) Constant potential contours (with potential rising towards the center) on Pn surface in the vicinity of probe-tip. (c) Schematic variation of band edge energy. V_1 and V_2 are the voltage drops in the vacuum and the sample respectively.

saturation in STS measurements for a single Si dangling bond on a B-doped Si(111) surface. At the end of this Section we analyze our results in a manner similar to that developed by those authors.

To introduce our discussion of transport limitations in the semiconductor current flow, Fig. 3.10 illustrates some aspects of the problem. The probe-tip injects current into the film. Some variation in the electrostatic potential will occur across the vacuum gap [voltage drop V₁ in Fig. 3.10(b)] as well as within the semiconductor [Fig. 3.10(c)]. For the situation of interest the Pn films are undoped. In a 3-dimensional model, the electricfield due to the probe-tip will fall off radially along the semiconductor surface due to the sharpness of the probe-tip. In the absence of any current flow, the electrostatic boundary condition across the semiconductor-vacuum interface will produce a variation in potential along the surface of the semiconductor qualitatively similar to that shown in Fig. 3.10(c).

3.5.1 Simple resistance model

As a first step to understand saturation of the tunnel current in the sample is to treat the sample as highly resistive which simply limits the current flow. The model assumes that the tunnel current is proportional to the applied bias voltage according to the relation,

$$I = \frac{V}{R_t},\tag{3.1}$$

where, R_t is the resistance of the tunnel junction and depends exponentially on the tip sample separation s as,

$$R_t = R_t^0 \exp(2\kappa s) \tag{3.2}$$

Under an applied sample voltage, if the voltage drop in the sample is ΔV , the decay constant κ takes the form,

$$\kappa = \sqrt{\frac{2m}{\hbar^2} \left(\overline{\phi} + \frac{e\Delta V}{2} \right)}$$
(3.3)

We further assume that the voltage drop in the sample ΔV is related to the tunnel current and sample resistance R_S by $\Delta V = IR_S$. Using the relation $I \propto \exp(-2\kappa s)$ and Eqs. (3.1), (3.2) and, (3.3) we get,

$$I = \frac{V}{R_t^0} \exp\left\{-2s\sqrt{\frac{2m}{\hbar^2}\left(\bar{\phi} + \frac{e}{2}R_S I\right)}\right\}$$
(3.4)

We solve this equation for tunnel current I(s), and then compute the decay constant κ by the derivative $\kappa = -0.5 d \ln I / ds$. Figure 3.11 shows the results from the computation. The parameters used in the computation are |V| = 3.0 V, $R_t^0 = 10^7 \Omega$, $\overline{\phi} = 3 \ eV$, and the values of R_s ranging from 10^8 (red curve) to $10^{12} \Omega$ (cyan curve). Data points shown by triangles are for comparison.

It is clear from Fig. 3.11 that this simple model with constant sample resistance is insufficient and does not fully agree with the experimental spectroscopic results. The variation in the computed decay constant κ is much more abrupt than the variation of κ



FIGURE 3.11: Computed curves with different sample resistances R_s (10⁸ Ω shown in red to 10¹² Ω shown in cyan) are plotted by solid lines. Points shown with triangles are from experiments acquired at -2.65 V. These points are positioned on the x-axis to match the theoretical curves.

found in the experiments. Hence this model is inappropriate to completely explain the observed saturation of tunnel current in the Pn thin films, and additional physical effects must be considered. In the next sub-section we present a more detailed discussion of the electronic effects in the sample that occur in the vicinity of the probe-tip.

3.5.2 Space charge limited tunnel current

Now, to account for the transport of carriers in the undoped Pn films, we must treat them as insulators so that the carrier concentration will vary as a function of distance from the tip. The injected carriers move out into the sample from the region directly under the probe-tip. Considering the narrow HOMO and LUMO bands this transport process can be quite slow relative to the tunneling rate through the vacuum barrier. As a result there can be a charge buildup in the sample near the probe-tip. Hence the voltage drop in the sample increases and there is more band-bending in the sample with a corresponding decrease in voltage drop through the vacuum junction. This band-bending restricts more charges to be injected from the tip even if it is moved closer to the sample surface which results in saturation of tunnel current. This situation is analogous to space charge limited current (SCLC) observed for the case of charge injection into insulators through metal electrodes making ohmic contact with the sample.[228,229]

For organic semiconductors SCLC has been observed previously.[2] In a typical SCLC regime in a 1-dimensional geometry and with an electrode in intimate contact with the semiconductor a simple relationship $I \propto V^2$ exists between current and voltage. The field varies as $x^{1/2}$ where x is the distance from the electrode, and the carrier density varies as $x^{1/2}$. However in the case of charge injection by STM tip the physical situation is quite different. Charge is injected from the tip, and hence is mostly confined in the vicinity of the probe-tip in the nano-scale regime, and furthermore the voltage drop is split between the vacuum and the semiconductor. As a consequence, a simple relationship of $I \propto V^2$ which is observed under typical SCLC case is not appropriate in our experiments. A full description of the SCLC in our geometry involves a coupled solution of Poisson's equation and the current transport equation, in 3-dimensions, something that we have not yet achieved. Nonetheless we can estimate the number of charge carriers by few simple assumptions. Current density j is related to the number of charge carriers n, mobility μ and electric field E as,

$$j = ne\mu E. \tag{3.5}$$

We assume a carrier mobility of our Pn films to be of the order of about $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (as seen in prior experiments[230,231,232,233]) and assume a linear relationship to exist between mobility and electric field. In STM the electric field in the sample due to the probe-tip extends across the sample radially by tens of nanometers (of the order of the probe-tip radius of curvature). Hence, for a voltage drop in the semiconductor of 1V the field will be less than 0.1 V/nm, and for a current density of 1 nA/nm² we estimate a carrier density of ~ 10¹⁸ cm⁻³. If we compare this value with what occurs, at low current values, in doped semiconductors in which the doping density varies from 10¹⁸ cm⁻³ to much lower values, then we know that the band bending in the semiconductor does indeed significantly change over this range of charge densities. (It is important to note that, e.g. for n-type material and positive sample voltages, the space charge in the doped

case is positive, whereas the electron density in the SCLC case is negative, so the situations are not exactly analogous). Thus, a carrier density this large suggests that we can get into the regime where transport limitation starts to have significant effect on tunneling current.

We can use an additional argument to extract the hopping rate for carriers in the LUMO band for the situation where we see a clear saturation of the tunnel current. The argument is similar to that given by de la Broïse *et al.*[234] and Berthe *et al.*[235] for the case of tunneling current through a single Si-dangling bond on a Si(111) surface. Let us define W_t as probability per unit time for the tunneling of an electron between the tip and a LUMO state localized on a molecule opposite the tip. We are regarding the LUMO band to be formed by the overlap of such states on neighboring molecules, with hopping occurring between neighboring states (it is important to note that the known width of the LUMO band, 0.1 eV, is indeed quite narrow). We further denote by *f* the probability that the particular state is occupied. Then the expression for tunnel current can be written as

$$I = -e(1 - f)W_t, (3.6)$$

which simply expresses the fact that the electron tunneling is possible only when the state is empty. In the steady state regime the tunnel current must be equal to

$$I = -efW_{hopp}, \qquad (3.7)$$

where W_{hopp} is the probability per unit time for the emission process which is a hopping rate between the states localized on the molecules. Eliminating f between Eqs. (3.6) and (3.7) we obtain

$$I = e \frac{W_t W_{hopp}}{W_t + W_{hopp}}.$$
(3.8)

When rate of tunneling is much higher than the emission process i.e., $W_t >> W_{hopp}$ then we get the condition for space charge limited current and $I = I_{sat}$. Using this condition, Eqs. (3.8) is modified as,

$$I_{sat} = eW_{hopp} \,. \tag{3.9}$$

Using $I_{sat} = 25$ pA from Fig 3.8 we get a hopping rate of 1.6×10^8 s⁻¹.

Physically this hopping rate would determine charge transport at least in the vicinity of the probe-tip. The time scale is of the order of 10^{-8} s which is indicative of

strong polarization of the molecule[236] when it gets charged by an electron tunneling into it. As discussed by prior author,[236] a molecular ion is formed which in turn induces a lattice deformation and consequently there is a self-trapping type of effect in which the charge is strongly localized. This strong localization of charge leads to relatively low hopping rates, thus producing the space charge type of effect in the tunnel current.

The experimental method developed above for Pn can be used to look for evidence of transport limited tunnel current in other systems. We have performed similar measurements on SiC(0001) surfaces with different reconstructions. In particular we have focused on Si-rich SiC(0001) $\sqrt{3} \times \sqrt{3}$ –*R*30° and 3×3 reconstructed surfaces both of which are Mott-Hubbard insulators. Measurements on a graphene surface (C-rich surface of SiC) are also performed and a comparative study of all surfaces is presented in Chapter 4. In the next sub-section we return to re-examine the normalized conductance spectra of Pn (as already presented in Fig. 3.5), to see if the effects of transport/space charge limited tunnel current modify our conclusions of that data.

3.6 Effect of transport limitation on STS spectra

With observation of transport/space charge limited tunnel current we need to revisit the results obtained from the normalized conductance spectra. It is seen from the normalized conductance spectra shown in Fig. 3.5 that the so called LUMO level shows a sharp peak like feature. However if the tunnel current has limited transport in the semiconductor, then the current tends to saturate and thus they might affect the shape of this spectral feature. In particular, if less current is injected into the semiconductor during the measurement, then the peak should shift towards higher positive sample voltages. This is indeed what we obtain by injecting different amount of charge into the semiconductor by systematically varying the tip-sample separation. The results are shown in Fig. 3.12 are obtained by taking numerical derivative of some of the spectra shown in Fig. 3.8. The spectrum at the top was taken at a set point current of 10 pA. The next two spectra were taken by progressively pushing the probe-tip by about 0.1 nm each towards the sample (corresponds to set points of about 28 and 50 pA respectively). The spectrum at the bottom is the same spectrum as Fig. 3.5 taken at nominal set point current of 0.1 nA.



FIGURE 3.12: Series of tunneling spectra with varying tip-sample separation. Consecutive spectra are shifted upwards for clarity. The zero levels for $(dI/dV)/(\overline{I/V})$ are indicated by horizontal lines. Set point currents are indicated for each spectrum.

With increase in injected current the LUMO peak shifts as indicated by arrows. The shift is roughly 280 meV which is another, albeit indirect, signature of current being limited by electron transport in the sample.

3.7 Effect of oxygen on tunneling spectra

A disadvantage of using Pn in organic electronics is the susceptibility of the Pn molecules to degradation by several means, including oxygen, hydrogen and water impurities. In this section we describe effect of impurities on tunneling spectra for Pn thin film samples. In particular the effect of oxygen will be discussed.



FIGURE 3.13: STS spectrum of Pn films. Solid lines are spectra from "degraded" Pn films, illustrating (a) tailing of valence band edge, and (b) narrowing of band gap. Solid For comparison, the dashed line in both (a) and (b) show a spectrum from a pristine Pn films.

We regularly use pure dry molecular oxygen for oxidation of the SiC substrates in our preparation chamber. Typically oxygen is introduced by a leak value at a partial pressure of 1×10^{-5} Torr for 30 min to an hour for oxidation of the SiC. If we then immediately start the Pn deposition process, we find that the STS results show significantly different results as compared to the normalized conductance spectra described earlier.

Figure 3.13 shows various STS results from Pn, comparing spectra on the "degraded" (exposed to oxygen during deposition) Pn with conductance spectrum for "non-degraded" or usual Pn. The dashed lines indicate spectra on non-degraded Pn and solid lines are acquired for the degraded Pn case. Two distinct effects are seen which are shown in Fig. 3.13(a) and (b). A clear tailing of the band edge for valence band is observed in case of Fig. 3.13(a). Figure 3.13(b) shows another spectrum which shows considerable narrowing of the band gap compared with a normal spectrum. Since most of the narrowing is in the valence band side, means more acceptor like character for these degraded Pn films. Hence oxygen acts as a p-type dopant for Pn. It should be made clear that these spectra were acquired on different samples using different probe tips. We almost always obtain tunneling spectra which can be broadly classified into two different categories as shown in Fig. 3.13(a) and (b). In one case, tailing of the valence band edge

into the band gap is obtained as shown in Fig. 3.13(a). In the second case the band gap narrows considerably than that of pristine Pn films which is shown in Fig. 3.13(b).

In order to understand the variation in spectra, we have to know if oxygen reacts with Pn to create complex species or simply gets trapped in the film and retains its molecular form. We can rule out the later case as it is known that in vacuum, oxygen molecules simply diffuses out of the Pn film without leaving behind electrically active electronic states that would lead to a doping of the film.[237] In order to check the effect of oxygen we prepared thin films in an oxygen free environment in UHV. Then we exposed the sample to several Langmuirs of molecular oxygen. STS observation in those samples (not shown here) does not show any change in conductance spectra due to the oxygen exposure. Since those spectra remains unchanged we can safely conclude that in our case the surface of Pn film does not simply react with molecular oxygen (it can react with *atomic* oxygen, but that was not used in our experiment). Our conclusion is supported by observations of Vollmer et al. [237] where ultraviolet photoelectron spectroscopy (UPS) was used for surface characterization of Pn films. Hence we conclude that *during deposition* (i.e. in the gas phase, or due to the enhanced energy of the hot molecules that are being deposited) oxygen probably forms some sort of complex species of Pn and gets incorporated into the film and it does not prefer to stay in molecular form. The differences between spectra shown in Fig. 3.13(a) and (b) are further explained below.

This presence of oxygen in the film is expected to alter the properties of the film as observed in the STS experiments. This is because the pristine $\pi - \pi^*$ bonds gets disrupted by the formation of C – O bonds. These types of chemical defects are known to produce gap states in Pn band gap shown by theoretical calculations [238,239] as well as affect recent experiments[240,241] and is known to electronic transport properties.[242,243] For a simple case in which oxygen forms a bridge between neighboring Pn molecules is known to produce gap states located at about 0.33-0.4 eV above the valence band edge. However more complex configurations contribute to shallower states in the gap. Hence our observation of amorphous like band tails can be explained by the fact that the oxygen indeed produces some complex species in the film to create shallow states near the valence band leading to band tailing. We also observe considerable band gap narrowing for these "degraded" Pn films as shown in Fig. 3.13(b). This narrowing of the band gap can also be explained from the above arguments. The onset of HOMO and LUMO states occur at lower voltages because of the gap states introduced in the sample by oxygen. Hence we conclude that oxygen does play an important role in Pn films even under UHV conditions by doping the sample thereby creating acceptor states and also localized states are formed closer to the valence band edge giving rise to band tailing and band gap narrowing.

3.8 Summary

To summarize work done on Pn thin films, we have used Pn as a model system for study of organic semiconducting molecules by using STM and STS. By varying tip-sample separation, different amounts of charge carriers were injected into the sample. Thereby we were able to observe transport/space charge limited tunnel current in the Pn thin films. Charge injection to empty (LUMO) and filled (HOMO) states was found to be different, with the intrinsic mobility for holes greater than that of electrons. A simple model of the charge transport process for LUMO states was used to estimate the hopping rate. We get evidence of strong charge localization at least in the vicinity of the probe-tip. Oxygen induced defect states and their influence on tunneling spectroscopy was also studied. We found amorphous like density of states signature in the normalized conductance spectra. The change in spectra is attributed to oxygen being incorporated in the Pn film with formation of some complex species of Pn molecules. Future work might involve detailed theoretical understanding of correlation of transport of charge carriers near the probe-tip to that of further away from it. This might shed light on intrinsic transport mechanisms in Pn and related materials. Also low temperature STM can be used to see temperature dependence of the spectra which would be quite useful to study intrinsic transport and thermally activated process in Pn films.

Chapter 4

Scanning Tunneling Microscopy and Spectroscopy of SiC Surfaces

SiC is a wide band gap semiconductor with properties suitable for making high temperature, high power and high frequency electronic devices. It exists in a variety of polytypes (different stacking arrangements of the atomic planes), and has many different surface reconstructions which have been a focus of numerous studies. In this chapter we present STM/STS work on 6H-SiC, one of the most common hexagonal polytypes. In particular we will describe tunneling current measurements by using the variable tip-sample separation method previously developed for the Pn films described in Chapter 3. We have used different SiC(0001) surfaces with considerable variation in conductivities for these STS measurements. Hence we were able to obtain some variation of the inverse decay constant κ for these surfaces, providing a basis for comparison of our results for the Pn films.

Two different Si-rich surfaces were used for our experiments, namely, the SiC(0001) 3×3 and the $\sqrt{3} \times \sqrt{3}$ -R30° surfaces. As described below both of these surfaces are Mott-Hubbard insulators, so that we expect relatively low surface conductivities for them and hence possible transport limitations (which, were already reported for the $\sqrt{3} \times \sqrt{3}$ -R30° surface[244]). We have compared results obtained for these Si-rich surfaces with a graphene monolayer on SiC(0001), which is a C-rich surface having a relatively high surface conductivity. Data for the graphene was provided by Shu Nie, and is gratefully acknowledged. All details relating to the graphene surface preparation have been previously provided in her thesis,[245] and will not be repeated here.

4.1 Structure and surface reconstructions of 6H-SiC

In SiC each atom is covalently bonded to four atoms of the other chemical species in a tetrahedral coordination. These tetrahedral Si-C bonds are arranged in a hexagonal bilayer with carbon and silicon in alternating position with single bonds pointing upwards and downwards perpendicular to the bilayer plane. The bilayers are stacked together, and depending on the stacking sequence in a unit cell we get different polytypes. For 6H-SiC there are 6 bilayers as shown in Fig. 4.1. SiC is polar along the c-axis where the Si



FIGURE 4.1: Stacking sequence of 6H-SiC. (a) Top view of hexagonal bilayer, and (b) side view. In (b), a single bilayer of Si and C atoms is shown. (c) Unit cell of 6H-SiC. Red line indicates the bilayer stacking sequence, ABCACB.

terminated face is labeled (0001) and the C terminated face as $(000\overline{1})$. We will focus our attention to the (0001) face called the Si-face for the remainder of the discussion.

The Si-face of 6H-SiC has a rich variety of surface reconstructions.[246] These surface reconstructions include Si rich surfaces such as $\sqrt{3} \times \sqrt{3}$ -R30°, 3×3, $6\sqrt{3} \times 6\sqrt{3}$ and 6×6. These surfaces can be produced by thermal treatment with or without presence of a flux of reducing agent such as Ga or As. An easier method is to use a Si beam to compensate for the Si loss during high temperature treatment of SiC.



4.1.1 $\sqrt{3} \times \sqrt{3}$ -R30° surface reconstruction

FIGURE 4.2: The atomic arrangement the $\sqrt{3} \times \sqrt{3}$ -R30° surface. Each Si adatom (larger filled circles) is located at the T₄ sites on top of a C atom (open circles) and is bonded to three Si atoms (filled circles) in the underlying plane. The dotted lines show a unit cell.

The atomic arrangement of the $\sqrt{3} \times \sqrt{3}$ surface has been determined using a grazing incidence X-ray diffraction.[247] This arrangement is shown in Fig. 4.2. Si adatoms reside above the top surface plane, in so-called T₄ sites. The adatoms are each bonded to three Si atoms located in the underlying plane. There is 1/3 monolayer of Si adatoms, which fully saturates all the bonds to the Si atoms in the underlying plane. The adatoms each have one half-filled dangling bond remaining, extending into the vacuum. These remaining dangling bonds have relatively little overlap with each other (being on fourth-nearest-neighbor sites), and the system thus forms a Mott-Hubbard insulator with a filled band and empty band separated by a band gap.[248,249]



FIGURE 4.3: Atomic arrangement of the 3×3 surface. Si adatoms (larger circles), Si trimers (mid-sized circles), and remaining Si atoms (small circles) form the Si underlayer shown as open rectangular background. Si bilayer is shown as filled rectangular background. Note that the Si atoms (small circles) in the outermost Si underlayer are significantly distorted from their sites in the 1×1 structure. The dotted box is a unit cell.

4.1.2 3×3 surface reconstruction

The 3×3 surface has a complex reconstruction and has been investigated by using STM, LEED holography, and density functional theory by Starke *et al.*[250,251] They proposed a so-called twist model consisting of a Si tetramer on a twisted Si adlayer with cloverlike rings, which is favorable in energy compared to other models. Figure 4.3 shows the model schematically. In this model, there are several different types of Si atoms, namely the Si adatom, Si trimers, Si atoms in the adlayer, and Si atoms in the SiC bilayer underneath the topmost adlayer. A Si tetrahedral adatom cluster consists of a Si adatom and a Si trimer. The Si adlayer is distorted remarkably when the Si tetramers are formed producing six Si atoms displaced towards the two undistorted Si atoms. (See Fig. 7 of Ref. [250]). The electronic structure of this 3×3 structure is very much more complicated than for the $\sqrt{3} \times \sqrt{3}$ surface, but the end result is that a band consisting of half-filled
dangling bonds is formed, and due to the small overlap between neighboring bonds this band again splits into two, forming a Mott-Hubbard insulator.[252]

4.2 Surface preparation

6H-SiC samples were hydrogen-etched as described in Chapter 3, and were then loaded into the UHV chamber. These samples were then degassed at ~ 600°C for a few hours and then heated up to ~ 800°C in presence of Si flux for about 15 mins. Si was evaporated from a UHV e-beam evaporator which was at a distance of about 15 cm from the sample. The surface was monitored with a LEED in the same chamber until a sharp 3×3 pattern was observed. The sample was then cooled down and loaded to the STM stage for further measurements.

After characterization of the 3×3 surface, the sample was again heated without any Si flux to about 1000°C in front of the LEED system until a sharp $\sqrt{3} \times \sqrt{3}$ -R30° pattern was observed. Temperature is a crucial parameter in the thermal treatment of the sample as it removes the native oxide layer deposited on the surface by transfer of the sample through air after H-etching. Si flux helps remove this oxide layer by compensating for the Si loss during annealing.[253] However a balance between Si gain from the flux and Si loss caused by annealing should be maintained to obtain appropriate surface reconstructions.



FIGURE 4.4: Large scale image of the 3×3 reconstructed surface. The dark region in the upper right corner is due to a step edge. Dark spots are missing Si atoms.

4.3 STM imaging

Reconstructed SiC(0001) surfaces were imaged with STM at a constant current and sample voltages specified below. Figure 4.4 shows a large scale 3×3 STM image acquired at 20 pA constant current and -2.5 V sample voltage. STM images of the SiC(0001) $\sqrt{3} \times \sqrt{3}$ -R30° and graphene surfaces can be found elsewhere.[244,245]

4.4 Tunneling spectroscopy

We obtained normalized conductance spectra for both 3×3 and $\sqrt{3} \times \sqrt{3}$ surfaces and the results are summarized in Fig. 4.5.



FIGURE 4.5: Normalized conductance spectra of (a) SiC 3×3 and (b) SiC $\sqrt{3}\times\sqrt{3}$ -R30° surface reconstructions. Arrows indicate states in the band gap.

Both the 3×3 and the $\sqrt{3} \times \sqrt{3}$ surfaces show states within the bulk SiC gap, as indicated by arrows in Fig. 4.5. Both the surfaces are found to be Mott-Hubbard insulators. The arrows in the spectra those point to the separate completely-filled and completely-empty bands of states that are formed on the surface. The insulating nature of both surfaces was experimentally determined by a combination of photoemission and inverse photoemission.[248,249,252] For the case of the $\sqrt{3} \times \sqrt{3}$ surface, STM/STS was also used to confirm the existence of two separate bands on the surface by Ramachandran *et al.*[254] It was observed in that prior work that the spectra showed considerable evolution depending on the current set-point, varying from that shown in Fig. 4.5(b) as relatively high set-points (0.1 nA) to something with a much sharper surface bands and more well-defined gap between the surface band at low set-points (1 pA).

In addition to local conductance measurements, we have performed spatially resolved spectroscopy with extremely high resolution to map electronic properties of a unit cell of 3×3 surface. However the results will not be presented in this thesis as we limit our attention to transport limited tunnel current for this surface as is discussed in the next section.

4.4.1 Spectroscopy using variation in tip-sample spacing

Multiple I-V curves were obtained for Si-rich and C-rich surfaces by changing the tipsample separation sequentially, in the manner described in Chapter 3 for Pn films on SiC. The results are shown in Fig. 4.6.

It is immediately clear that from Fig. 4.6 that the Si-rich surfaces, for which we expect relatively low surface conductivity, show indications of transport limited current. The data for both 3×3 and $\sqrt{3} \times \sqrt{3}$ surfaces reveal that the current does not increase in appropriate proportion as the probe-tip is moved towards the sample surfaces, particularly for positive sample voltages. This behavior is in clear contrast to the case of graphene, where current could be injected into the sample without any indication of a transport limitation. This point will be further discussed in the following section by computation of the decay constant κ and a comparison of the results with those from the Pn films.



FIGURE 4.6: I-V curves taken at different tip-sample separations for (a) 3×3 (b) $\sqrt{3} \times \sqrt{3}$ -R30° and (c) graphene surfaces. For the curves shown in each set, the tip was moved towards the sample surfaces in increments of 0.05 nm.



FIGURE 4.7: Comparison of decay constants calculated from I-V curves of different surfaces specified in the plot. Voltages at which the results are shown are Pn, at 1.4 V, $\sqrt{3} \times \sqrt{3}$ -R30° surface at 2.9 V, 3×3 surface at 1.5 V, and graphene at 1.5 V respectively.

4.5 Comparative study of decay constant, κ

In order to study the effect of transport limitation of charge carriers on various surfaces we have computed the decay constant κ . The results of the calculation are summarized in Fig. 4.7.

Since I-V curves for Pn showed complete saturation (See Fig. 3.6) for voltages above about 2 V in the LUMO band, the κ values are essentially zero in that region. For the purpose of computation, we have chosen a somewhat lower bias voltage of 1.4 V for calculating κ . Hence we observe some nonzero values for the κ value for Pn, as shown in



FIGURE 4.8: (a) Calculated κ values for negative sample voltages plotted with magnitude of tunnel current. (b) Normalized conductance spectrum indicates states associated with the 3×3 surface.

Fig. 4.7, with κ dropping from about 3 nm⁻¹ to 0 over a narrow current near 0.01 nA. This behavior is in sharp contrast to that of graphene, which is a highly conducting material with no expected limitation in transport. In that case we find that even for currents an order of magnitude higher current than that of Pn, κ stays close to the ideal value of 10 nm⁻¹. The Si-rich SiC surfaces with conductivities intermediate to that of Pn and graphene have κ values that lie within the ranges of Pn and graphene. The above result is conclusive evidence that for STS studies on different surfaces, the surface conductivity (i.e. hopping rates) do influence the decay constant κ , which in turn modifies the tunneling spectra.

Having found a strong dependence of κ on tunnel current for several surfaces, the next question to ask if there is any voltage dependence associated with κ . By changing the sample voltage different energy states become accessible, which in turn modifies the tunnel current. Hence κ will also be modified especially for samples with many states in the band gap such as SiC 3×3 surface. We present the results of variation of κ with voltage in Fig. 4.8.

We see some variation in κ from Fig. 4.8(a). More variation is seen for voltages at -0.5 V and -0.9 V. For positive voltages similar results were obtained, but not shown here. This change in κ with bias voltage then gives a measure of transport properties of the sample surface, resolved in energy.

4.6 Conclusion

We have performed STS measurements on surfaces with varying conductivities and compared the results with results from Pn. We were able to extract information about the decay constant κ and found that the ideal κ value of 10 nm⁻¹ in STS experiments is *not* always found, with the actual value depending strongly on the sample electronic properties. Nevertheless, for highly conducting surfaces, such as graphene, κ does have values close to the ideal one. But, for other surfaces for which the surface conductivity is low (Mott-Hubbard insulators), it was observed that κ tends to collapse to zero, similar to the case of organic semiconducting molecules such as Pn, which is indicative of severely transport/space charge limited tunnel current in the sample.

Chapter 5

Cross-sectional STM/STS on InAs Quantum Dots



FIGURE 5.1: Bulk lattice constants, band gap energies, and corresponding luminescence wavelengths of various binary and ternary III-V semiconductors. From Ref [255].

5.1 Introduction

Among III-V semiconductors, InAs has a 7.2% lattice mismatch with GaAs. Growth of coherent (i.e., defect free) self-assembled InAs QDs on GaAs is possible because of the resulting strain due to this large lattice mismatch. Since InAs has a band gap of 0.36 eV as compared to GaAs which has a band gap of 1.42 eV, QD structures which are confined in all three directions are potential candidates for laser and photodetectors. A general overview of variation of band gap with lattice constant for all III-V semiconductors is shown in Fig. 5.1.[255]

In this chapter we present XSTM work on InAs QDs grown in a GaAs matrix (i.e. the InAs dots are grown on a GaAs surface, and then overgrown with GaAs). Some



FIGURE 5.2: Detailed sample heterostructures. Diagram not to scale.

structural aspects of these dots will be described and an important distinction between different contrast mechanisms in STM image will be made on these cleaved heterostructures. We have focused primarily on electronic characterization of single dots using tunneling spectroscopy of buried QDs exposed by cleaving. Results from tunneling spectroscopy measurements will be presented, and effects of tip-induced band bending will be discussed. Finally the effects of nearby step edges on the tunneling spectra will be shown and the effects on tunneling spectra will be elaborated.

5.2 Experiment



FIGURE 5.3: Schematic of GaAs surfaces. (a) Surface unit cell is marked with red dashed lines. (b) Atomic rearrangement in (110) plane. (c) Cleavage lines along [110] and $[1\overline{1}0]$ directions. Circles representing surface atoms are larger than those for lower level atoms. (d) Zigzag III-V chains forming (110) and $(1\overline{1}0)$ surfaces are mirror images of one another.

The InAs QD samples studied were grown on a heavily doped n-type GaAs(001) substrate using molecular beam epitaxy by J. Walker in the group of E. Towe at Carnegie Mellon University.[256,257,258,259] We have used 100 μ m thick heavily doped GaAs substrates for growth of InAs QDs. A GaAs buffer layer ~ 200 nm thick was grown at a substrate temperature of 580°C. Then 5 periods of InAs QD layers were grown keeping the substrate at 490°C. Each layer was covered with 50 nm of GaAs. After growth of the final GaAs layer in the InAs/GaAs superlattice, a 200 nm GaAs cap layer was grown. All the epitaxial layers were undoped. The growth process is schematically shown in Fig. 5.2.

5.2.1 XSTM and cleaved {110} surfaces

Usually in order to obtain XSTM data the samples were cleaved *in situ* to expose {110} planes. These planes are non-polar and contain the least density of unsaturated bonds making it easier to cleave along these planes. Although there is no surface reconstruction meaning no rearrangement of atomic bonds, there is a small shifting of atomic positions, the so called buckling as experimentally shown using STM on the GaAs(110) surface.[260] In Fig. 5.3 we schematically show various GaAs surfaces.





A top-view of (110) surface shows zigzag atomic chains along the [110] direction which consist of alternating Ga and As atoms. However in STM images only Ga or As atoms can be imaged, depending on the sign of the voltage used. Also it is important to note that in STM data on zinc-blende {110} surfaces, only every second atomic ML in the typical epitaxial growth direction is imaged. An example of atomically resolved image is shown in Fig. 5.4. The image was acquired at -2 V sample voltage meaning only As atoms corresponding to filled As dangling bonds are seen. The surface unit cell and the distances between the neighboring surface As atoms are indicated in the image.

An important distinction must be made while deciding the cleavage plane between the equivalent $[1\overline{10}]$ and [110] directions. Although they have identical geometry, they are inequivalent with respect to the cleavage direction used to form the surface. The reason that $(1\overline{10})$ cleavage surface is preferred in our experiments over the (110) is that, more often than not, $(1\overline{10})$ surfaces are atomically flatter (i.e. fewer steps) than (110) surfaces. Although those surfaces are electronically and geometrically the same, the cleavage direction for one face is directed along bonds which extend from Ga atoms to As atoms while for the other, the direction is opposite. Hence even though the bonds are equivalent, during cleaving process the order in which bonds are broken is different.

After cleavage of the QD samples, optical inspection shows a clean and flat surface suitable for further study by XSTM. But due to strain in the heteroepitaxial layers, steps with height of one or more atomic layers are frequently observed in the STM images. Often times the step edges will run parallel to a row of dots. Also many times these steps form right at the QD layer, which in turn makes it impossible to correctly locate the dots and continue the experiment. These steps seem to have a significant effect on the tunneling spectra, as will be further discussed below.



FIGURE 5.5: (a) XSTM image of a QD row, acquired at -2 V sample voltage. (b) Same image after high pass filtering in order to improve contrast. (c) Image after further contrast enhancement to emphasize the isolated In atoms. A step edge which runs parallel to the QD row is apparent. The [001] growth direction is indicated by the arrow.



FIGURE 5.6: Sketch of differently cleaved QDs. The cleavage positions are indicated with respect to the QD extension in the [110] direction. From Ref [261].

5.3 XSTM results

Figure 5.5 is a large scale STM image showing several dots in the epitaxial layer, appearing as the bright regions in the image. A step is also apparent on the far left side of the image, running parallel to the QD row; such steps form as a result of *in situ* cleavage process as described earlier. The size of the dots as seen in XSTM can vary significantly depending on where the cleavage plane intersects a QD, as schematically shown in Fig. 5.6. However a completely buried dot can also in principle be seen in the images because of the surface deflection from the strain (discussed in more detail in the following section), provided that the QD is not too deep inside the bulk. Prior work indicates that if the cleavage position of the QD, indicated by the percentage of its lateral extensions, is somewhere between 0% (completely cleaved) to 120% (20% of the diameter underneath the cleavage surface), it can be detected.[261]

In addition to the QDs, Fig. 5.5 also reveals the bright atomic rows between the dots. These rows contain In atoms, and they arise from the so-called *wetting layer* (WL), which is a layer of InAs that forms on the GaAs surface prior to the QD formation. After the InAs growth it terminated and the structure is overgrown by GaAs, the In atoms in the wetting layer segregate somewhat, thus ending up being distributed over several atomic layers. Individual In atoms are visible, appearing bright in the STM image for the reasons discussed in the following section.



FIGURE 5.7: Two contrast mechanisms occurring in XSTM experiments. (a) Electronic contrast, which affects all experiments on different materials because of their differing band gaps. (b) Structural contrast due to strain relaxation, which only contributes in the case of strained systems, in particular at low spatial dimensions such as QDs.

5.3.1 Origin of contrast in XSTM images

The band gap of InAs at room temperature is 0.36 eV as compared to 1.42 eV in case of GaAs. The electronic structure of InAs and GaAs are different, which leads to different tunneling probabilities for InAs and GaAs. In case of InAs, with its smaller band gap, more states are accessible for tunneling and hence the tip retracts from the surface in order to maintain a constant current. As a result InAs appears brighter in STM images as compared to GaAs. In general, materials of different electronic properties lead to

different tunneling probabilities which lead to different apparent heights in a constant current STM image.[262] This situation is shown schematically in Fig. 5.7(a).

This effect persists in the case of InAs dots, where despite of the quantization of the energy levels, a great local-density-of-states is accessible for tunneling at the InAs region than GaAs. Even for a single In atoms in a GaAs matrix, the energy positions of the atomic orbitals from In results in an increase of the tunneling probability.[263]

Unlike a *lattice matched structure* such as AlGaAs/GaAs heteroepitaxial layers, InAs is compressively strained on GaAs due to a 7.2% lattice mismatch. After cleaving, this strain will result in a strong structural relaxation effects.[264,265] This relaxation leads to an outward relaxation of the atoms at an InAs QD and in its close environment, as shown in Fig. 5.7(b). Even single In atoms in a GaAs matrix slightly relax outward upon cleavage because of their larger back-bonds as compared with the Ga atoms.[266] It is clear from the above discussion that contributions to contrast in both cases have the same sign for InAs QDs and it thus appears brighter in XSTM images.

Since image contrast is dependent on both electronic and structural properties of nanostructures, it is useful to understand the contributions in typical XSTM experiments. Usually for constant current images we prefer to have voltages with magnitude between 2 to 2.5 V for both positive and negative voltages. It is found that in many cases STM images yield more structural contrast due to strain variation and electronic contributions are relatively smaller.[267] The relatively small size of the electronic contribution to the tunnel current then enables the possibility of quantitatively determining strain variations in the nanostructures from the observed strain-induced displacement of the cleavage face.

5.3.2 Shape, size and composition of the dots

Since the QDs have a flat top surface as seen in the XSTM images, we consider these dots to be of truncated pyramid type. As seen from the images, atomic corrugations are better resolved in the QD than the GaAs matrix. This is because the InAs bond lengths (in a non-strained state) are larger than those of GaAs by 7.2%. Also after cleaving, the QDs relax outward as seen from Fig. 5.7(b) which makes it easier to see atomic resolution clearly at least near the top of the dot looking down in the [110] direction. In our experiments we use Pt-Ir probe tips which have been thoroughly cleaned by heating, and

their sharpness is thus not always the highest possible. Atomic resolution is therefore somewhat compromised. However we prefer such tips for STS measurements since they tend to give more reproducible spectra presumably because the DOS of the probe-tip is featureless. The resolution of Fig. 5.5 is relatively high, revealing details of the distribution of In atoms in the wetting layer. Nevertheless, even higher resolution image have been obtained by other workers, [268] that revealed even more detail concerning the composition of the WL as well as compositional variations within the QDs themselves.



FIGURE 5.8: Base length distribution of the XSTM images of the analyzed quantum dots.

As shown earlier in Fig 5.6, depending on where the cleavage plane intersects a given dot we see a variation in dot sizes from XSTM images. In our experiments we have probed 10 dots and measured their base lengths carefully. The largest base length was found to be 10.2 nm which is the diagonal of the square base. So the actual base length is estimated to be 9.7 ± 1 nm. Heights of the dots are measured by counting the number of zigzag atomic rows and then multiplying it by the distance between the rows which from XSTM measurements is every second [001] oriented monolayer. For GaAs this distance between rows is 0.565 nm. For all the dots measured we find five to six of these zigzag

rows and hence the estimated heights of the dots are about 2.8 ± 0.6 nm. A histogram plot of the variation in base lengths is shown in Fig. 5.8.

5.3.3 Tunneling spectroscopy on QDs

As described in Chapter 2 tunneling spectroscopy can be used to probe local electronic properties of nanostructures under investigation. Traditional spectroscopic methods such as photoluminescence measurements yield data which is averaged over many QDs. By using STS we have successfully determined electronic structure of many QDs individually. In a typical experiment spectra were taken on a dot by placing the probe-tip on top of the QD. We then compare that spectra to spectra acquired on GaAs at least ~15 nm away from the dot. This was repeated for in a given experiment for a number of QDs. One such observation is shown in Fig. 5.9.



FIGURE 5.9: (a) High resolution XSTM image of InAs QD. A x-mark denotes the position where a spectrum was acquired. The image was acquired at -2 V sample voltage. (b) Normalized conductance spectra. The solid line is the spectrum from the dot and the dashed line is the spectrum from the GaAs. The inset shows a straight line fit used to estimate band edge position (shown for conduction band minimum of GaAs).

Figure 5.9(a) shows a high resolution QD image. We carefully position the tip on top of the dot, at a position indicated by the x-mark in the image. The normalized conductance spectra shown in (b) by the solid line is obtained by averaging several spectra taken on the same spot. In order to quantify the results thus obtained, we compare this spectrum with a similarly acquired spectrum on GaAs obtained with the same probetip positioned far from the dot. It is well known that the (110) surface of GaAs has no surface states lying in the band gap.[269] Hence by fitting the band edges of the GaAs spectrum to a straight line we determined the conduction band and valence band onsets, as shown by tic marks in Fig. 5.10(b). For the QD spectrum, these apparent band edges correspond to quantum confined energy levels formed within a dot as a result of the strong quantum confinement.

Using the method described in Fig. 5.9(b) we determine the GaAs apparent bandgap to be $1.88 \pm 0.04 \text{ eV}$ which is significantly larger than the known gap of 1.42 eV. We attribute this difference to tip-induced band bending (TIBB) in the semiconductor.[270] In order to estimate physical quantities such as the energy level gap of InAs QD we need to include consideration of this effect in our energy determinations. It has been demonstrated previously, that a first-order method for accomplishing this is to apply a linear scaling to the observed energy difference for a *known* spectrum in order to match the known gap, and them apply the same scaling for neighboring spectra acquired from a region of *unknown* gap.[271] Thus, for the spectra of Fig. 5.10(b), we determine a scaling factor for the GaAs of 1.42/1.88=0.76, and applying the same correction to the spectrum from the QD we determine a band gap for the dot of $1.10 \pm 0.04 \text{ eV}$. This value provides an initial estimate of the energy gap for the dot, although as discussed below we find that it is not sufficient to explain all the spectra we have obtained on different dots using different cleavage surfaces and different probe-tips.

5.3.4 Effect of steps on tunneling spectra

We have performed measurements as described above on about 13 QDs of similar sizes. However, in many cases we find InAs QD energy level gap much smaller than 1.10 eV (by about 30%). A few representative spectra taken on different samples are shown in Fig. 5.10. These spectra show a multitude of effects such as different offsets from GaAs conduction band sometimes accompanied by appearance of peaks in the gap region of the spectra. A careful observation of all the images accompanying the entire spectra shows steps (similar to Fig. 5.5) near each QD. These steps, found at distances ranging from about 5 nm to 10 nm from the QDs, arise from the cleavage process and have a



FIGURE 5.10: Various spectra acquired on different cleaved samples using different probe tips, plotted in the same manner as Fig. 5.9(b) (solid lines on QD, dashed lines on GaAs). A shift is seen in the Fermi level position between different sets of spectra, presumably due to different contact potentials between the tip and sample.

significant effect on spectra. For the case of Fig. 5.9, there were no atomic steps occurring within 50 nm of the QDs, and the resulting spectral features of the dot were confined to within 0.4 eV of the GaAs conduction band edge. However, when a step is present nearby the QD then often time additional spectral features, located more towards the middle of the gap, are observed.

In order to further investigate the effect of steps on the tunneling spectra, we have performed spatially resolved spectroscopy on single QDs along a line passing though the dots. A typical result is shown in Fig. 5.11. Considerable changes in the spectra occur as we move from the GaAs region, spectrum (l), to a point directly on the QD, spectrum (f), to a point off the dot but near a step edge, spectrum (a). Far from the step edge the spectrum has pure GaAs character, with the relatively large gap and well defined band edges. As the dot is approached, nonzero conductance first appears near the conduction band edge, and then an intense state near midgap (at about 0.5 V) forms. Then, as we move off the dot towards the step edge, the evolution is quite different. The conductance

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FIGURE 5.11: STM image and the corresponding spatially resolved spectra. Points a though l are locations of spectra. Consecutive spectra are shifted up for clarity. A step edge is indicated on the bottom left of the image by an arrow.

near the conduction band edge is seen to decrease in an analogous manner as it increased when we approached the dot, but conductance features near midgap persist. Spectrum (a)shows two midgap features, marked by arrows. These features have evolved from the midgap states seen directly on the dot, spectrum (f). Most importantly, the midgap features seen in spectrum (a) are not present on the other side of the dot, e.g. in spectrum (k) or (l). We therefore conclude that the step edge is affecting the wavefunction of the states associated with the QD. The features seen in spectrum (a) would thus be an admixture of states from the dot with those from the step edge, i.e. involving the overlap of the wavefunction tails from the dot and the step edge. In this way, the step edge states couple to those of nearby dots, thus allowing current to flow through the dots. Hence, when steps are located sufficiently close to the dots, we are able to see the lowest-lying quantum states of the dots, something that was not seen in the spectrum of Fig. 5.9(b) for which no step was located nearby.

5.4 Discussion

Figure 5.12 shows a summary of our experimental results. Tunneling spectra from two QDs which illustrate the two possible cases in STS experiments are shown. For comparison, the GaAs spectrum is shown as a dashed line. For the spectrum acquired



FIGURE 5.12: I-V curves for two QDs shown as solid lines as compared to that of GaAs shown as a dashed line. The spectrum shown in blue was acquired from a QD which was located far from any step edges, and the spectrum shown in green was acquired from a QD that did have a step edge located nearby.

from a QD located nearby a step edge, as shown by the green curve in Fig. 5.12, we observe discrete midgap features. In contrast, for the spectrum acquired from a QD

located far from any step edges, as shown by the blue curve in Fig. 5.12, no such midgap features are seen.

We interpret these midgap features as arising from the low-lying quantum states of the dot. In the presence of a nearby step, the QD state can couple to states associated with the step and thereby current is able to flow through the QD state. But in the absence of a step, there is no path through which the current can flow, and hence the QD states do not appear in the spectrum. These two possible situations are illustrated in Fig. 5.13.

According to the above interpretation, when the QD state is occupied with an electron then this state becomes invisible to the probe-tip as electrons from the tip cannot further occupy this QD state. Hence this occupied state in the QD does not contribute to the tunnel current. In such tunneling spectrum acquired on the QD, we only observe a shift in the conduction band edge as compared to the GaAs spectrum. No peak associated with the QD state is observed. Figures 5.9(b) and 5.10(b) and (c) are examples where we observe these effects. However it is possible that the electron localized in the QD state may leak out into the bulk GaAs or recombine with a hole from the valence band states. But this process can only occur when assisted by external means such as presence of a defect state near the vicinity of the electron. The electron can then leave the QD state and electrons from the probe-tip can then tunnel into the QD state. The QD state then contribute to the tunnel current and we can see peaks in the tunneling spectra associated with the QD states. Figures 5.11 and 5.10 (a) and (c) clearly show peaks associated with QD states.



sample voltage > 0

FIGURE 5.13: Schematic of various tunneling situations at a QD, depending on whether or not a path for the electrons to escape from the dot is present. The QD state is indicated with a blue line. In (a) tunneling into the QD state is allowed. In (b) this process is not allowed since the QD is occupied by an electron (present from an earlier tunneling event).

In our experiments the defect states are created as a consequence of the cleaving process which results in formation of steps near the QDs. The electronic states from these steps extend towards the rows of QDs and couple with the states of the dots to create new conductance/transport channels for the tunnel current. In the absence of the steps, QD states are invisible to STM due to the absence of a pathway for charge carriers to be transmitted from the dot into the substrate. However, in presence of steps, they can now be seen in the spectra since they contribute to the tunnel current through the new transport channels. Hence the peaks as shown in Fig. 5.11 by arrows are actually indicative of discrete states in the dot. For different spectra, some variation in the energetic location of the states is observed. This variation can be explained by the fact that the QDs are not identical and each dot is different than the other in structure and also composition. Also depending on the height where the QDs are cleaved the nature of the states can differ from dot to dot.

5.5 Summary and conclusion

In summary, we have measured tunneling spectra on cleaved InAs QDs grown in GaAs. States related the QDs can be seen in the normalized conductance spectra, but only in presence of defects. These defects produce conductance channels for the electrons localized in the QD state to leak out into the substrate and the corresponding spectrum then show signature of the QD state. In our case these defects arise from step edges that run nearby the QDs.

Chapter 6

Summary and Conclusion

In summary, the work described in this thesis deals with the study of nano-scale electronic properties of organic semiconducting molecules such as Pn and semiconductor nano-structures such as InAs QDs. The primary research tool used to study the nano-scale electronic and charge transport properties was STM and STS. Electronic properties of the sample surfaces under investigation were found to strongly influence the behavior of the tunnel current. This so called "non-ideal" nature of tunnel current is actually helpful in extracting some physical properties of the sample surfaces at least in the vicinity of the probe-tip. In this chapter we summarize our results and suggest some future research goals.

6.1 Tunneling spectroscopy of Pn

Among small organic semiconducting molecules Pn has some unique advantages including high charge carrier mobility and ease of preparation using sublimation in UHV conditions. Hence we have used Pn as a model system to study electronic and charge transport properties at the nano-scale utilizing STM and STS. The Pn thin films were deposited in UHV by sublimation of the molecules on suitably prepared oxidized SiC substrates. We have used the STM probe-tip in order to efficiently inject charge carries in both filled (HOMO) and empty (LUMO) states. By varying the tip-sample separation, different amounts of charge carriers were injected into the sample. Thereby we were able to observe transport limitations, interpreted as space charge limited tunnel current, in the Pn thin films. Charge injection to LUMO and HOMO states was found to be different, with the intrinsic mobility for holes greater than that of electrons. A strong saturation of tunnel current was seen for the LUMO states, which is indicative of the collapse of the decay constant κ to zero. We were able to explain this behavior of κ in which it strongly deviates from the ideal value of 10 nm⁻¹ and sharply drops to zero by treating the Pn thin film as an insulator. The injected carriers then move out into the sample from the region directly under the probe-tip. This transport process can be quite slow relative to the tunneling rate through the vacuum barrier as the HOMO and LUMO bands are very narrow. As a result there can be a charge buildup in the sample near the probe-tip. Hence the voltage drop in the sample increases, which results in more band-bending in the sample along with a corresponding decrease in voltage drop through the vacuum junction. This band-bending restricts more charges to be injected from the tip even if it is moved closer to the sample surface, which then results in saturation of the tunnel current. A simple model of the charge transport process for LUMO states was used to estimate the hopping rate of charge carries in the sample. We get evidence of strong charge localization at least in the vicinity of the probe-tip.

In a related study we observed effects of oxygen induced defect states on tunneling spectroscopy. Normalized conductance spectra showed amorphous like band tailing and band gap narrowing of the spectra as compared to oxygen free Pn samples. The change in spectra is attributed to oxygen being incorporated in the Pn film, with resulting formation of some sort of complex species of Pn molecules.

Detailed theoretical understanding of the transport of charge carriers both near the probe-tip and further away is required in order to correctly predict the non-ideal tunnel current. This theoretical modeling is in progress, and it is expected to yield further unstanding of the intrinsic transport mechanisms in Pn and related materials. By using low/variable temperature STM, intrinsic transport and thermally activated processes in Pn films could also be studied in detail with increased energy resolution of the spectra.

6.2 **Tunneling spectroscopy of SiC surfaces**

STS measurements similar to that on Pn thin films were performed for various SiC surfaces with varying conductivity values. We have used SiC 3×3 and $\sqrt{3} \times \sqrt{3}$ -R30° surfaces both of which are Mott-Hubbard insulators. We have also used epitaxial graphene surface which is basically a monolayer of graphite on SiC and is highly conducting. Different amounts of charge carriers were injected into these samples in order to study charge transport on these surfaces and the results were compared with the results from Pn. We have calculated values for the decay constant κ for these different samples and found significant variation in κ depending on the conductivity of the samples. It was observed that the ideal κ value of 10 nm⁻¹ in STS experiments is *not* always found, with the actual value depending strongly on the sample electronic properties. Nevertheless, for highly conducting surfaces, such as graphene, κ does have values close to the ideal value. But, for other surfaces for which the surface conductivity is low (Mott-Hubbard insulators), it was observed that κ tends to collapse to zero, similar

to the case of organic semiconducting molecules such as Pn, which is indicative of severely transport/space charge limited tunnel current in the sample. This observation of the variation of κ is conclusive evidence that transport properties of samples play a large role in tunnel current and hence spectroscopy results.

6.3 Tunneling spectroscopy of InAs QDs

Tunneling spectra on cleaved InAs QDs grown in GaAs were obtained using the STM in cross-section mode. Spectra were acquired for about 13 QDs by putting the probe-tip at the center of the cleaved dots. These spectra were compared with spectra taken on GaAs roughly 15 nm away from the respective dots. We observed a large tip-induced band bending effect for the GaAs spectra and corrected for the same by a linear scaling of the data which is appropriate in our experiments. Steps were seen in most of the STM images in close proximity to the QDs. These steps, which arise from the *in situ* cleaving process, were found to have significant effect on the tunneling spectra. Depending on the strength of coupling between the states corresponding to the step edges and that of the QD states, tunneling spectra were found to be significantly different from dot to dot. When the coupling is relatively weak, then the states from the step are believed to provide produce conductance channels for the electrons localized in the QD state, thereby enabling the electrons to leak out into the substrate. The corresponding spectrum then shows the signature of the QD state. In order to understand this effect more carefully we obtained high resolution spatially resolved spectra which show significant variation of spectra depending on the distance from step edge. In the future we plan to do experiments in which more of these spatially resolved spectra would be acquired, including spectra exactly on a step edge. Also voltage depending imaging and wave function mapping of the dot states will be performed to see correctly identify the QD states in the spectra.

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reliable measure of the band edge energy.