Chapter 2

Self-assembled growth of nanostructures and different characterization techniques

"I'm here to do my best for the day"
— Kiran Bedi

2.1 Introduction

Nanoscience and nanotechnology constitute an active, frontier area of research worldwide. Research in this area promises to stimulate the exploration of new phenomena and to lead to the technological revolution to extend device physics to full two- or three-dimensional confinement (quantum wires and dots). It has long been predicted that the confinement in these low-dimensional structures will alter significantly the transport and optical properties, compared to bulk or planar heterostructures. The most important factor accelerating research in this area is the growth of lower dimensional structures by modern epitaxy, such as molecular beam epitaxy (MBE) and metallorganic chemical vapour deposition (MOCVD).
2.2 Epitaxial growth techniques

There are many varieties of epitaxial growth techniques used for the growth of thin films like chemical beam epitaxy, solid phase epitaxy and molecular beam epitaxy. In this section we discuss first very briefly about chemical beam epitaxy and solid phase epitaxy and then a brief overview on the molecular beam epitaxy will be presented. We have used molecular beam epitaxy for growing self-assembled nanostructures.

2.2.1 Chemical Beam Epitaxy

Thin film growth performed by means of surface chemical reactions is defined in general as chemical vapour deposition (CVD). In this technique, the source material is supplied to the sample surface in the form of its gaseous compounds. Precursor gas molecules decompose at the hot surface, leaving there the desired species, while the waste fragments of the molecules are desorbed from the surface. The group IV and the group V compounds are supplied usually as hydrides, such as SiH₄, GeH₄, AsH₃, PH₃ etc., while the group III components are supplied as metal-organic compounds, such as trimethyl gallium [Ga(CH₃)₃ (TMGa)], triethyl indium [In(C₂H₅)₃ (TEIn)], etc. Conventionally the term metal-organic CVD (MOCVD) refers to growth conducted at relatively high pressures (~ 1 – 760 Torr). If the growth is performed under ultrahigh vacuum (UHV) conditions, the technique is called metal organic MBE (MOMBE) or chemical beam epitaxy (CBE) (see ref.[1]). Due to a large mean free path of the gas molecules at low pressure, CBE growth is not affected by reactions in the gas phase and only surface chemistry here determines the growth process. In comparison to MBE, CBE is far more complex and conventionally requires higher temperatures. However, it provides higher growth rates with conservation of high film crystallinity.

2.2.2 Solid Phase Epitaxy

Solid phase epitaxy (SPE) [1] is a specific regime of MBE growth, in which an amorphous film is first deposited at a lower temperature and is then crystallized upon heating to a higher temperature. Generally, the crystallinity of films grown by SPE is
slightly lower than that of MBE-grown films. However, SPE might be advantageous over MBE in achieving abrupt doping profiles in epitaxial semiconductors films.

2.2.3 Molecular beam epitaxy

In molecular beam epitaxy (MBE) [1, 2], growth occurs under ultrahigh vacuum (UHV) conditions and the material for the growing film is delivered to the sample surface by beams of atoms or molecules, i.e., via deposition. During growth, the substrate is conventionally kept at a moderately elevated temperature, which is sufficient to ensure that the arriving atoms migrate over the surface to the lattice sites, but at the same time is not too high to induce diffusion intermixing between the substrate and the already grown film. Fig.2.1. schematically shows the process of MBE growth.

The non-equilibrium epitaxy of a solid, from its gas phase, which occurs in molecular beam epitaxy (MBE), and other epitaxial techniques leads to kinetic and/or thermodynamic instabilities of the growing front on the surfaces. Starting from low-index, high-symmetry substrates, the stochastic nature of the growth process brings almost an intrinsic instability for most of the semiconductors and metals leading to the
coarse-grained morphology of the terminating plane as observed in the AFM and STM topographies. The kinetic instabilities during growth can occur due to various factors like anisotropy of the diffusion current induced by the surface reconstruction [3], the presence of impurities [4, 5], asymmetry in the rate of attachment of atoms/molecules at step edges [6], elasticity [7] and electromigration [8]. They produce macroscopic roughening that can give rise to step bunching, step-edge meandering on vicinal orientations and mounds on the surfaces. An increase in the substrate temperature can lower kinetic instabilities; however, in the epitaxy of mismatched heterostructures, it may also increase thermodynamic instabilities like the formation of misfit dislocations, ‘coherent’ isolated clusters, wavy deformation of the surface, etc [9]. Various surface processes which occur during MBE growth are schematically shown in Fig.2.2. The roughening of a growing surface is of very general theoretical interest in addition to the obvious technological relevance for materials based on GaAs and Si. Growth models predict asymptotic dynamical scaling behaviour of the roughness, which may increase in time according to power laws defining universality classes [10, 11, 12]. Theoretical approaches are essentially of two types: atomistic models based on first-principles calculations providing the energetics of atomic motions, and continuum models based on linear or non-linear equations, whose predictions are generally limited to the large-scale, long-time macroscopic behaviour of the surface and to collective aspects of the growth. The most thoroughly studied continuum theory of

Figure 2.2: Schematic representation of various surface processes during film growth by solid source MBE.
kinetic roughening relies on the Kardar-Parisi-Zhang (KPZ) non-conserving equation [13] that is a valid description of the behaviour of a moving interface whenever the velocity normal to the average surface has a non-linear component dependent on the local orientation. Since the seminal paper of KPZ, many other theories have been developed to model a large variety of growth processes. The validity of such linear and non-linear continuum theories applied to MBE growth is amply discussed in the literature (see [10, 11, 12] and references therein).

MBE depositions are often carried out at temperatures where growth could be considered a conservative process dominated solely by surface diffusion, and non-linear mechanisms such as desorption and defect formation can be disregarded. Instabilities of the KPZ type, therefore, do not occur in the majority of MBE growth processes. Within the limit of an ideal conserving process, surface diffusion provides the mechanism for describing roughening and scaling properties of the growth at the coarse-grained length scale. The diffusion current $J$, driven by the gradient of the local chemical potential, must satisfy the continuity equation:

$$\frac{\partial h}{\partial t} = -\nabla \cdot J + F,$$  \hspace{1cm} (2.1)

where $h$ is the surface height at a given point at time $t$, and $F$ is the impinging flux inclusive of the stochastic noise. Since the growth equation cannot depend on the initial time or on the particular origin chosen on the surface for the description, it does not contain explicitly $h$ and $t$ but only linear and/or non-linear terms of $\nabla h$ describing the different processes involved. The equilibrium surface diffusion is accounted for by the linear term, $-K \nabla^4 h$, and the corresponding growth equation is stable. Yet in this case, instabilities may arise because of the non-equilibrium contribution to the diffusion current due to the stochastic nature of the impinging flux. In this case, the current itself may depend on the local curvature, i.e. $J \propto \nabla h$, and a non-equilibrium term, $-|v| \nabla^2 h$, adds to the growth equation leading to instability [10, 11].

The approach described above predict the scaling behaviour of a growing surface, such
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as roughness exponent, $\alpha$, growth exponent, $\beta$ and dynamic exponent, $z$. However, in the present thesis, we have not investigated these aspects for MBE growth. In a limited way we have explored the roughness exponent, $\alpha$, for the case of sputtering, which removes material from the surface instead of adding material to the surfaces as required for growth. However, these apparently opposite processes are thought to be similar in terms of their scaling behaviour, if the material removed by sputtering is not redeposited on the surface. These results are presented in chapter 7. For the MBE growth we have restricted our studies to the morphology, geometrical and electronic structures of the MBE grown nanostructures.

The work presented in this thesis mainly concerns nanostructures grown by MBE. A custom-made compact MBE system along with the capability to transfer the MBE-grown samples to a UHV transfer chamber/suitcase as well as to a commercial UHV variable temperature STM (VTSTM). This combined system is shown in Fig.2.3.

With the system shown in Fig.2.3 it is possible to grow and characterize thin epitaxial layers of metals and semiconductors on atomically clean surfaces of single crystal substrates. The MBE system has three effusion (Knudsen) cells, a low power electron beam evaporator, a quartz microbalance (QM) and a residual gas analyzer (RGA). There is also a reflection high energy electron diffraction (RHEED) equipment fitted to the MBE unit for monitoring surface reconstruction and growth. For sample cleaning it has direct heating as well as Ar ion sputtering facilities. The sample manipulator has a Z-translation (vertical) and X-, Y-translations (horizontal) and the azimuthal angle can be varied over 360°. It also has a resistive heating facility so that the substrate temperature can be raised up to 900°C by resistive heating. Also there is a possibility of direct heating where the temperature can be raised to 1200°C. Epitaxial growth of different materials are controlled by the substrate temperature and the rate of deposition. Out of the three Knudsen cells, one is capable of reaching 1400°C, the other two cells can reach 1700°C. The electron beam evaporator is used for deposition of silicon. With the option of three Knudsen cells and the electron beam
Figure 2.3: A custom-made compact MBE system (MBE chamber diameter: 250 mm) and a UHV variable temperature scanning tunneling microscope (VTSTM) attached to it. Different components are shown. QM: Quartz microbalance; RGA: Residual gas analyzer. ST: A port for attaching a small detachable UHV chamber for transferring the sample into it and carrying it away for other measurements.

evaporator, epitaxial multilayers can be grown. A load-lock chamber is attached with the main MBE chamber for initial sample mounting. A mounted sample in the load-lock chamber is transferred to the MBE chamber using a sample transfer mechanism on a magnetically coupled transfer rod. Using another transfer rod the sample can be transferred to the VT STM stage for STM studies without disturbing the UHV condition. The temperature range achievable in the VTSTM is 25 K–1400 K. The best base pressure achieved in the MBE chamber is $3 \times 10^{-11}$ mbar and that in the VTSTM chamber $2 \times 10^{-10}$ mbar. This combined MBE-VTSTM system and its initial performance have been described in ref.[14]
2.3 Self-assembled growth

Self-assembled growth is a bottom-up process, where nanostructures are formed from their basic building blocks, such as atoms or molecules. Self-assembled growth is associated with the growth of atoms or molecules that undergo exquisitely selective binding and obey highly specific rules for self-assembly. The general importance and desirability for advancement of technology requires a high degree of control of composition, size and structure. This is so critical to the area of nanostructure synthesis that self-assembly has been an increasing hallmark of this field. For epitaxial nanostructures the pseudomorphic growth of lattice-mismatched overlayer-substrate system and the drive of the system to minimize its free energy leads to the growth of self-assembled structures. Details of this growth process are discussed below.

2.4 Different growth modes

When a film is grown on a substrate by various methods, the film may be amorphous, polycrystalline or single crystalline depending upon the substrate, the substrate temperature, the material of the film and the method of deposition. In case of single crystallinity, the film may be epitaxial. One way to understand the epitaxial growth is to compare it with crystal growth. What differentiates epitaxial growth from crystal growth are the nature and the strength of the chemical bonds of both the substrate and the deposit crystal on one hand, and the crystal lattice parameters on the other. In other words, in epitaxial growth both crystals differ energetically and geometrically. If the two crystals do not differ simultaneously energetically and geometrically, which means that they are identical, we have the usual crystal growth [15]. Three principal growth modes [16, 17] of epitaxial growth are illustrated in Fig.2.4. These modes are named after their original investigators and are as follows:

- Layer-by-layer or Frank-van-der Merwe (FM) growth mode (Fig.2.4(a)) refers to the case when the film atoms are more strongly bound to the substrate than to each other. As a result, each layer is fully completed before the next layer
starts to grow, i.e., strictly two-dimensional growth takes place [18].

- **Island** or **Volmer-Weber (VW)** growth mode (Fig.2.4(c)) corresponds to the situation when film atoms are more strongly bound to each other than to the substrate. In this case, three-dimensional islands nucleate and grow directly on the substrate surface [19].

- **Layer-plus-island** or **Stranski-Krastanov (SK)** growth mode (Fig.2.4(b)) represents the intermediate case between FM and VW growth. After the formation of a complete two-dimensional layer, the growth of three-dimensional islands takes place. The nature and thickness of the intermediate layer (often called the **Stranski-Krastanov layer**) depend on the particular case (for example, the layer might be a submonolayer surface phase or a strained film several monolayers thick) [20].
The occurrence of different growth modes can be understood qualitatively in terms of the surface or interface tension or surface free energy $\sigma$. This is defined as the work that must be performed to build a surface (or interface) of unit area. $\sigma$ can also be interpreted as a force per unit length of boundary, considering the contact point of the film island and the substrate (Fig.2.5). If the island contact angle is $\phi$, the force equilibrium can be written as

$$\sigma_s = \sigma_i + \sigma_f \cos \phi$$

where, $\sigma_s$ is the surface free energy for the substrate surface, $\sigma_f$ is that for the film surface and $\sigma_i$ is the surface free energy of the film/substrate interface called interfacial energy. Monolayer-by-monolayer growth occurs only in the FM mode which is obtained when

$$\Delta \sigma(n) = \sigma_f(n) + \sigma_i(n) - \sigma_s \leq 0$$

for all $n$, where $n$ corresponds to the number of monolayers in the film [17]. Here the $n$-dependent strain energy in the film has been absorbed in $\sigma_i(n)$. $\sigma_f$ and $\sigma_s$ are the value for the semi-infinite crystals, and $\sigma_f(n)$ deviates somewhat from $\sigma_f$ due to $n$-dependent surface strain. The condition for the FM growth is rigorously fulfilled only for the growth of a material A on A (homoepitaxy) in which case $\sigma_f = \sigma_s$ and $\sigma_i(n) = 0$, or more generally for zero misfit, i.e., when the strain contribution $\sigma_i^e(n)$
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to \( \sigma_i(n) \) is zero and

\[
\sigma_f + \sigma_i^0(n) - \sigma_s \leq 0
\]

Here \( \sigma_i^0(n) \) is the zero strain contribution to \( \sigma_i(n) \) which depends on the specific chemical interaction between film and substrate atoms and rapidly approaches zero within the first few monolayers, depending upon the range of the interatomic forces.

![Diagram](image)

Figure 2.6: Illustration of strain of the overlayer due to the lattice mismatch of substrate and film material in heteroepitaxial growth modes (figures adapted from ref.[1]). Film lattice constant, is denoted as \( a_f \) whereas substrate lattice constant is \( a_s \). (a) \( a_f > a_s \) and (b) \( a_f < a_s \) show strained pseudomorphic growth. (c) Relaxed dislocation growth.

In all other cases the increase of the strain energy with \( n \) leads to an increase of \( \sigma_i(n) \) until at a given \( n = n^* \) the FM condition is not fulfilled any longer and three dimensional crystals form (SK mode). If the FM condition is not fulfilled from the very beginning (\( n = 1 \)) then three dimensional crystals form immediately on the substrate (VW mode). These three growth modes have also been subsequently [21] called class I, II, and III behaviour for the FM, SK, and VW modes, respectively, and have recently been studied in great details in the theory of wetting and layering transitions as complete wetting, incomplete wetting, and nonwetting cases [22, 23, 24]. It is evident that self-assembled epitaxial island growth can occur via SK or VW growth mode.
Let us discuss the role of lattice misfit between the film and the substrate which leads to a strain energy that serves as the driving force for island formation in almost every case. Strain in the epitaxial layer due to lattice mismatch is schematically shown in Fig.2.6. A surprising result is the fact that systems with strong film-substrate interactions do not, in most cases, produce uniform films of arbitrary thickness. The more common observation in this case is the Stranski-Krastanov configuration shown in Fig.2.4. The relative strength of the film-substrate potential (W) is defined as the ratio of the interfacial energy of the film-substrate interaction (\(\sigma_i\)) and the energy of the film-film interaction (\(\sigma_f\)), i.e.,

\[
W = \frac{\sigma_i}{\sigma_f}
\]

Large film-substrate interactions are represented by \(W >> 1\). The degree of misfit, \(\eta\), is defined as the difference between the film lattice constant (\(a_f\)) and the substrate lattice constant (\(a_s\)), normalized by the substrate lattice constant (\(a_s\)), i.e.,

\[
\eta = \frac{a_f - a_s}{a_s}
\]

Equilibrium growth modes [25], as a function of misfit (\(\eta\)) and strength of film-substrate interaction (\(W\)), are shown by the so-called phase diagram in Fig.2.7. From Fig.2.7, it is seen that the only driving force for uniform films (FM) is a strong interaction between the film and substrate which requires that \(W > 1\) and zero misfit. For zero misfit (\(\eta = 0\)) VW growth occurs for \(W < 1\). For non-zero misfit, VW growth occurs when \(W \leq 1\) for smaller misfit while \(W > 1\) corresponds to SK growth. For higher misfit, VW to SK transition may occur when \(W >> 1\).

In heteroepitaxy, a crystalline film of one material is grown on the crystalline substrate of another material. As the substrate and the film are of different materials, it is very rare that they have the same lattice constant and ideal lattice-matched, commensurate growth takes place. Most often the lattice parameters (and also the
Figure 2.7: Equilibrium growth modes, as a function of misfit ($\eta$) and strength of film-substrate interaction ($W$). The solid line separates the regions of VM mode and SK mode. FM mode is confined to the region $\eta = 0.0$ with $W > 1$.

Crystal structure) of the film and the substrate are different. Relatively low misfits can be accommodated by elastic strain, i.e., deformation of the lattice of the epitaxial film, in such a way that the strained film adopts the periodicity of the substrate in the interfacial plane, but can be distorted in the perpendicular direction in order to preserve the volume of the unit cell. This kind of growth, called pseudomorphic growth, is shown in Fig.2.6(a) and (b). At higher misfits, the strain is totally or partially relieved by the formation of misfit dislocations at the film/substrate interface as shown in Fig.2.6(c).

Recently, in theoretical studies another growth mode has been proposed. This mode appears to be induced by an electronic growth mechanism [26]. For the case of metal films on semiconductors it has been predicted that a uniform layer can be grown only over a thickness window, below or above which the metal film would be nonuniform [26, 27, 28]. A very thin film can be destabilized by charge transfer at the interface, films of intermediate thicknesses are stabilized by a quantum confinement and thick films are destabilized by stress. However, so far there is no convincing experimental
2.5 Characterization techniques

For characterizations of the MBE-grown structures we have used mainly scanning tunneling microscopy (STM) and spectroscopy (STS), reflection high energy electron diffraction (RHEED), high resolution x-ray diffraction (HRXRD) and transmission electron microscopy (TEM). In this section we shall discuss about these techniques.

2.5.1 Scanning tunneling microscopy (STM)

Scanning tunneling microscopy (STM) was developed in the early 1980s by Gerhard Binnig and Heinrich Rohrer, who were awarded the Noble Prize in Physics in 1986 for this invention.

The atomic resolution capability of STM directly in real space for surfaces of conducting materials has become the most important feature of STM. The extremely
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high lateral as well as vertical resolution makes STM an outstanding microscopy. In addition, the atomic resolution capability in real space has several important consequences.

1. Surface structures, either given by nature or artificially created, e.g. by MBE, can be monitored and controlled on the atomic scale.

2. Based on the atomic resolution capability, the tip can be positioned with atomic accuracy above a pre-selected atomic site and a local experiment can be performed. In this regard, electronic local density of states (LDOS) can be determined through I-V measurements using scanning tunneling spectroscopy (STS).

3. The capability of monitoring surface structures with atomic resolution combined with the ability to position the tip with atomic accuracy leads to the ability to perform direct and controlled manipulation at the atomic level, offering the opportunity to create atomic-scale devices.

The main components of a scanning tunneling microscope (STM) are discussed below. A block diagram of STM operation is shown in Fig.2.8.

- **Atomically sharp tip**: The STM tips are typically fabricated from metal (e.g. W, Pt-Ir, Au) wires. The preparation procedure of the atomically sharp tip includes preliminary *ex-situ* treatments, like mechanical grinding, cleavage, or electrochemical etching and subsequent *in-situ* treatments, like annealing, field emission/evaporation and even a "soft crash" of the tip by touching a sample surface.

- **Scanner**: To raster the tip over the area of the sample to be studied, a scanner is attached with the tip. Piezoelectric ceramics are used in scanners as electromechanical transducers, as they can convert electric signals of 1 mV to 1 kV into mechanical motion in the range from fractions of an Å to a few μm.

- **Feedback electronics**: This circuit controls the tip-sample gap.
Figure 2.9: Energy diagram of the tunneling contact of the STM tip and the metallic sample. $E_{F1}$ and $E_{F2}$ are the Fermi levels of the surface and the tip, $\phi_1$ and $\phi_2$ are the work functions of the surface and the tip, $\phi_B$ is the effective barrier height, $d$ is the effective tunneling gap and $V$ is the bias voltage. The diagram illustrates the situation when STM probes the empty states of the surface [1].

- Computer system: This is necessary to control the tip position, to acquire data and to convert the data into an image.

Apart from these, a course positioning system is attached with the scanner to bring the tip to within the tunneling distance of the sample and to retract it back to a sufficient distance (a few mm). For stable operation of the STM a vibration isolation system is essential. The changes of the tip-sample separation caused by vibrations should be kept to less than $\sim 0.01\text{Å}$. The required vibration damping is achieved by suspending the inner STM stage with the tip and sample on very soft springs and by using the interaction between the eddy current induced in cooper plates attached to the inner stage and the magnetic field of the permanent magnets mounted on the outer stage.

During imaging the STM tip is placed very close to the surface. In this condition the wave functions of the closest tip atoms and the surface atoms overlap. The typical
tip sample gap is about $\sim 5 - 10\text{Å}$. If one applies a bias voltage $V$ between the tip and the sample, a tunneling current will flow through the gap. In simplified form, the tunneling current density $j$ is given by:

$$j = \frac{D(V)V}{d} \exp\left(-A\phi_B^{1/2}d\right)$$

where, $d$ is the effective tunneling gap, $D(V)$ reflects the electron density of states, $A$ is a constant and $\phi_B$ is the effective barrier height of the junction [1]. A schematic of energy diagram for the tunneling process is shown in Fig.2.9.

The sharp dependence of the tunneling current on the gap width determines the extremely high vertical resolution of STM. Typically, a change of the gap by $\Delta d = 1 \text{Å}$ results in a change in the tunneling current by an order of magnitude or if the current is kept constant to within 2%, the gap width remains constant to within 0.01 Å. As for the lateral resolution of STM, this is determined by the fact that up to 90 % of the tunneling current flows through the gap between the "last" atom of the tip and the atom of the surface, which is the closest to it. Surface atoms with an atomic separation down to $\sim 2\text{Å}$ can be resolved.

Tunneling through the barrier is due to the overlapping of the wave functions of tip and surface atoms. So STM topography is sensitive to LDOS. When the tip bias voltage is positive with respect to the sample, the STM image corresponds to the surface map of the filled electronic states. With a negative tip bias voltage, the empty-state STM image of the surface is obtained. The basic parameters for STM operation are the lateral coordinates, $x$ and $y$, height $h$, the bias voltage $V$ and tunneling current $I$. There are different modes of operation of STM depending on the manner in which these parameters are varied. In the next section we shall discuss about the constant current mode and constant height mode of operation of STM. Apart from these two modes there is scanning tunneling spectroscopy (STS) which is rather a series of various modes in which $V$ is varied.
2.5.1.1 Constant-Current mode

The first and the most widely used mode of STM operation is the constant current imaging (CCI) mode as illustrated in Fig.2.10(a). In this mode, the tip is scanned across the surface at constant voltage and current. To maintain the tunneling current at a preset value, a feedback system continuously adjusts the vertical position of the tip by variation of the feedback voltage $V_z$ on the $Z$-piezoelectric driver. In ideal circumstances of an electronically homogeneous surface, constant current essentially means constant gap. The height of surface features are derived from $V_z$. Though the contour map $z(x, y)$ is often referred to as the 'topographic image' of the sample surface, it is generally not solely the arrangement of atoms on a surface which determines $z(x, y)$. The contour map $z(x, y)$ rather reflects a constant current surface according to the experimental measurement procedure. The advantage of this mode resides in the possibility of probing surfaces which are not necessarily atomically flat. The disadvantage is the limited scan speed due to the finite response time of the feedback system.
2.5.1.2 Constant-Height mode

In this mode the tip is scanned across the surface with $V_z$ kept constant and the variation of current are recorded as a function of the tip position as illustrated in Fig. 2.10(b). A significant drawback of the constant current imaging (CCI) mode lies in the finite response time of the feedback loop which limits the scan speed and data acquisition time considerably. In principle the tip can be scanned faster than the feedback can respond. In this mode feedback loop can be switched off completely or slowed down. Then the rastering of the tip can be much faster than the constant current mode as scanning system does not have to respond to the surface features passing under the tip. This mode is very much useful to collect STM images at real-time video rates, offering the opportunity to observe dynamical atomic-scale processes at surfaces, such as surface diffusion. The disadvantage is that this mode is applicable for relatively flat surfaces.

2.5.1.3 Scanning tunneling spectroscopy (STS)

Due to the bias dependence of the tunneling current, STM can be used as a spectroscopic tool to probe the electronic structure of the surfaces. For tunneling between metal electrodes in the low bias (millivolt) limit, the tunneling current is found to be linearly proportional to the applied bias voltage. For higher bias (volts) and particularly for semiconductor samples, the bias dependance of the tunneling current generally does not exhibit Ohmic behaviour. As a result the constant current STM images depend on the applied bias [30]. Studying this bias dependence in detail allows extraction of various spectroscopic information of high spatial resolution down to the atomic level. Applying this feature of STM, semiconductor surfaces have been widely investigated.

Simplified one-dimensional potential energy diagram at zero temperature for the system consisting of the tip (left electrode) and the sample (right electrode) which are separated by a small vacuum gap is shown in Fig. 2.11. For zero applied bias [Fig. 2.11(b)] the Fermi levels of tip and sample are at equilibrium. When a
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(b)
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Tip Sample
bias voltage $V$ is applied to the sample, a shift of the energy levels downward or upward in energy by an amount $|eV|$ occurs depending on whether the polarity is positive [Fig.2.11(c)] or negative [Fig.2.11(d)]. For positive sample bias, the net tunneling current arises due to the electrons which tunnel from the occupied states of the tip into unoccupied states of the sample [Fig.2.11(c)]. For negative sample bias, electrons tunnel from the occupied states of the sample to the unoccupied states of the tip [Fig.2.11(c)]. Consequently, the bias polarity determines whether unoccupied or occupied sample electronic states are probed. The equation for the tunneling current is given by,

$$I \propto \int_{0}^{eV} n_t(\pm eV \mp E) n_s(E) T(E, eV) dE$$

(2.2)

Here $n_t(\pm eV \mp E)$ and $n_s(E)$ are the density of states of the tip and the sample surface, respectively; energies are with respect to Fermi level and $T(E, eV)$ is the bias dependent transmission coefficient. So, the electronic structure of the tip enters in the tunneling current. By varying the applied bias voltage, the electronic states can be selected that contribute to the tunneling current and this, in principle, measures the local electronic density of states. For instance, the current increases strongly if the applied bias voltage allows the onset of tunneling into a
maximum of the unoccupied sample electronic density of states. Therefore, the first derivative $dI/dV(V)$ reflects the electronic density of states to a first approximation. However, we also have to consider the energy and bias dependence of the transmission coefficient $T(E,eV)$. Since, electrons in states with the highest energy 'see' the smallest effective barrier height, most of the tunneling current arises from electrons near the Fermi level of the negatively biased electrode. This is indicated in Fig.2.11 by arrows of differing size. The maximum in the transmission coefficient $T(E,eV)$ given in Eq.(2.2) can be written as [32, 33],

$$T_{\text{max}}(V) = \exp\left\{ -2(s + R) \left[ \frac{2m}{\hbar^2} \left( \frac{\phi_t + \phi_s}{2} - \frac{|eV|}{2} \right) \right]^{1/2} \right\} \quad (2.3)$$

The bias dependence of the transmission coefficient typically leads to an order-of-magnitude increase in the tunneling current for each volt increase in magnitude of the applied bias voltage. Since, the transmission coefficient increases monotonically with the applied bias voltage, it contributes only a smoothly varying 'background' on which the density-of-states information is superimposed. As an important consequence of the dominant contribution of tunneling from states near the Fermi level of the negatively biased electrode, tunneling from the tip to the sample [Fig.2.11(c)] mainly probes the sample's empty states with negligible influence of the tip's occupied states. On the other hand, tunneling from the sample to the tip is much more sensitive to the electronic structure of the tip's empty states which often prevents detailed spectroscopic STM
studies of the sample's occupied states [34].

(i) Voltage dependent STM imaging:
The simplest way of obtaining spectroscopic information consists of sequentially recording conventional constant current topographs (CCT) at different applied bias voltages followed by comparison of the experimental results. However, thermal drift, creep of the piezodrives and tip changes during scanning often make direct comparison between successive STM images difficult. Voltage dependent STM imaging as a spectroscopic method relies on the fact that, at a particular chosen bias voltage, only the electronic states between the Fermi levels of the tip and the sample can contribute to the tunneling current. This method often provides a quick and simple way to assess whether there are many interesting differences between different bias voltages, particularly at different polarities. The major drawback in this technique is that the constant current topotgraphs generally reveal both geometric and electronic structure information which cannot easily be separated.

(ii) Scanning tunneling spectroscopy (STS) at constant current:
Another way to extract the spectroscopic information from the surface is to superimpose a high-frequency sinusoidal modulation voltage on the constant d.c. bias voltage applied between tip and sample. The modulation frequency is chosen higher than the cut-off frequency of the feedback loop which keeps the average tunneling current constant. By recording the tunneling current modulation, which is in-phase with the applied bias voltage modulation, by means of a lock-in amplifier, a spatially resolved spectroscopic signal $dI/dV$ can be obtained simultaneously with the constant current image [35, 36, 37]. Based on the expression (Eq.2.2) for the tunneling current and by assuming $dn_t/dV \approx 0$, we obtain [38],

$$
\frac{dI}{dV}(V) \propto e n_t(0)n_s(eV)T(eV,eV) \\
+ \int_{0}^{eV} n_t(\pm eV \mp E)n_s(E) \frac{dT(E,eV)}{dU}dE
$$

(2.4)
At a fixed location, the increase of the transmission coefficient with applied bias voltage is smooth and monotonic, as mentioned earlier. Therefore, structure in $dI/dV$ as function of $V$ can usually be attributed to structure in the state density via the first term in Eq.(2.4). However, the interpretation of the spectroscopic data $dI/dV$ as a function of position $(x, y)$ is more complicated.

There are also other drawbacks of the STS technique. Measurements of $dI/dV$ [Eq.(2.4)] at constant average tunneling current contain a strongly voltage dependent background originating from the voltage dependence of the transmission coefficient. In the low bias limit where the tunnel junction exhibits Ohmic behavior, it is found that

$$\frac{dI}{dV} = \frac{I}{V}$$

For constant tunneling current $I$, the quantity $dI/dV$ therefore diverges like $\frac{1}{V}$ as $V$ approaches zero. This $\frac{1}{V}$ background, on which the desired electronic structure information is superimposed makes it difficult to observe structure in the $dI/dV$ data at low bias voltages, thereby preventing investigation of the electronic structure near the Fermi level. However, this problem can be solved by operating the STM at a constant tunneling resistance $\frac{V}{T}$ instead of constant tunneling current $I$ [39]. Usually electronic structure information can then be obtained close to the Fermi level.

(iii) Local I-V measurements at constant separation:

Another way to eliminate the $\frac{1}{V}$ divergence and additionally the influence of the $z$-dependence of the transmission coefficient is based on measuring local $I - V$ curves at a fixed tip-sample separation. This can be achieved by breaking the feedback circuit for a certain time interval at selected surface locations by means of a sample-and-hold amplifier while local $I - V$ characteristics are recorded [40, 41, 42]. The $I - V$ characteristics are usually repeated several times at each surface location and finally signal averaged. Tunneling current may be assumed as a convolution of density of states (DOS) of tip and LDOS of sample surface. Since the feedback loop is inactive while sweeping the applied bias voltage, the tunneling current is allowed
to become extremely small. Therefore, band gap states in semiconductors, for instance, can be probed without difficulties. The numerical differentiation of tunneling current \( \frac{dI}{dV} \) corresponds closely to the sample density of states assuming the DOS of tip is relatively featureless over the energy range being studied. The dependence of the measured spectroscopic data on the value of the tunneling conductance \( I/V \) can be compensated by normalizing the differential conductance \( \frac{dI}{dV} \) to the total conductance \( I/V \). Feenstra et al. [41] showed that the normalized quantity \( \left( \frac{dI}{dV} \right) \left( \frac{I}{V} \right) = \frac{(d\ln I)(d\ln V)}{d\ln V} \) reflects the electronic density of states reasonably well by minimizing the influence of the tip-sample separation. However, the close resemblance of the \( (d\ln I)(d\ln V) \) vs. \( V \) to the electronic density of states is generally limited to the position of peaks while peak intensities can differ significantly. This measurements allow the probing of electronic properties of a very local preselected area, even of an individual adatom at the surface. Another way is to measure the tunneling current at each point of the scan by varying the bias voltage \( V \) at constant tip-sample separation. By calculating \( \frac{dI}{dV} \) one can map the spatial distribution of particular states. This technique is referred as current-imaging tunneling spectroscopy (CITS) [43].

2.5.2 Reflection high energy electron diffraction (RHEED)

Diffraction techniques utilizing electrons or X-ray photons are widely used to characterize the structure of surfaces. The structural information is gained conventionally from the analysis of the particles/waves scattered elastically by the crystal. The intensities of the diffracted beams contain information on the atomic arrangement within a unit cell. The spatial distribution of the diffracted beams tells us about the crystal lattice. The evaluation of the crystal lattice is straightforward, as the diffraction pattern is directly related to the crystal reciprocal lattice by the condition:

\[
\mathbf{k} - \mathbf{k}_0 = \mathbf{G}_{hkl}
\]

where \( \mathbf{k}_0 \) is the incident wave vector, \( \mathbf{k} \) is the scattered wave vector, and \( \mathbf{G}_{hkl} \) is a reciprocal lattice vector. As scattering is elastic,
from the laws of conservation of momentum and energy. This condition may be satisfied by an infinite number of \( \mathbf{k} \) vectors pointing in many directions. Diffraction is often discussed with the help of an Ewald sphere. An Ewald sphere is a sphere with its centre as the origin of \( \mathbf{k}_0 \) and its radius \( |\mathbf{k}_0| \). Hence the Laue condition may be re-formalized as diffraction occurs for all \( |\mathbf{k}_0| \) connecting the origin of the sphere and a reciprocal-lattice point [44, 45].

The magnitude of \( |\mathbf{k}_0| \) from the relativistic expression is:

\[
|\mathbf{k}_0| = \sqrt{\frac{2\pi}{\lambda} \left( 2m_0qV + \left( \frac{qV}{c} \right)^2 \right)}
\]

where \( m_0 \) is the electron rest mass, \( q \) is its charge and \( V \) is the accelerating potential.

Reflection high energy electron diffraction (RHEED) is a widely used technique to study the growth and the structure. Although high-energy electrons are used for RHEED, it is very surface sensitive as the incidence and detection angles are grazing (\( \sim 1 - 3^\circ \)). As a result, on its relatively long mean free path through the sample, high-energy electrons still keep in the near-surface region of only a few atomic layers deep. The geometry of RHEED is such that the electron gun and the screen are placed far apart from the sample. Thus the front of the sample is open for the deposition process. Therefore, RHEED can be used as an in-situ technique to study the structure of a growing surface directly during growth.

The Ewald sphere construction in RHEED conditions and the schematic of the experimental arrangement are illustrated in Fig.2.13. A flux of high energy electrons from the electron gun is incident under grazing angles and diffracted beams produce a RHEED pattern on a fluorescent screen. Our RHEED system has a 30 keV electron gun.

The reciprocal lattice for a two dimensional layer is a set of one dimensional rods along the perpendicular to the surface. Since the reciprocal rods are continuous rods,
Figure 2.13: Ewald sphere construction and diffraction geometry of RHEED. Intensity maxima on the screen correspond to projected intersection of Ewald sphere with the reciprocal lattice.

every rod produces a reflection in the diffraction pattern as shown in Fig.2.13. The reflections occurs on Laue circles of radius $L_n$ with $n=0,1,..$, centered at $H$. The origin of the reciprocal lattice is projected onto $I$. The reciprocal rod separations $G_\parallel$ and $G_\perp$ are along the parallel and perpendicular to the beam direction, respectively. Apart from the structural information, RHEED provides additional information which appear to be specifically useful for studying thin film growth and monitoring the formation of multilayer epitaxial structures. By monitoring the intensity of the diffracted spot(s) one observes the intensity oscillation during the layer-by-layer growth. If 3D crystalline islands form on the surface, they can be readily identified by the appearance of new spots in the RHEED pattern.
Although we do not present any RHEED experiment/result in this thesis, it was important to give a brief introduction about this characterization tool which is attached with our MBE growth chamber and occasional experiments have also been performed though not presented here. After cleaning the substrate surface and prior to deposition of materials on the substrate, RHEED pattern from the substrate surface was determined in order to check the cleanliness of the surface. We mainly used various surfaces of Si [e.g. (111), (100) and (110)]. Clean surfaces of these orientations have characteristic surface reconstructions and RHEED patterns. We checked for these characteristic RHEED patterns in each case.

2.5.3 X-ray diffraction (XRD)

Almost a century after the discovery of x-ray diffraction (XRD) by crystals in 1912, XRD has been proved to be one of the most useful diffraction techniques to study the crystal structures. X-ray photons with energy $\sim 10$ keV have the wavelength $\sim 1\text{Å}$, which is the order of atomic spacings in solids. This makes XRD a powerful tool to study crystal structure, defects, stress etc.

When x-rays are scattered from a crystal lattice, constructive interference occurs when Bragg’s law is satisfied:

$$2d \sin \theta = n \lambda$$  \hspace{1cm} (2.6)

where $\lambda$ is the wavelength of the x-rays; $2\theta$ is known as the scattering angle (half of the scattering angle is known as the Bragg angle: $\theta_B$), $d$ is the spacing of lattice planes responsible for diffraction (not necessarily planes parallel to the surface) and $n$ is the order of diffraction. Above equation allows us to calculate the crystal structure. The value of $d$ is determined by the Miller indices of the family of planes. For a cubic crystal with lattice constant $a$, the interplanar spacing for planes of Miller indices $h$, $k$, $l$ is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$  \hspace{1cm} (2.7)
For high resolution x-ray diffraction (HRXRD) we use our laboratory rotating anode (Mo) x-ray source with a Si(111) monochromator [46, 47]. The incident beam on the sample contains only the Mo Kα1 line (λ = 0.709 Å). In our system the sample is mounted on a four-circle diffractometer. For some experiments we have also used synchrotron radiation (SR). The energy tunability of SR allows one to select x-rays with an appropriate wavelength for specific experiments. In epitaxial growth one often encounters d-spacings with very small differences in the same sample. In such a situation the separation between Bragg peaks increases when x-ray with a larger λ are chosen. This is helpful for the detection of these Bragg peaks when the peak separation is close to the angular precision of the diffractometer.

For epitaxial layers, the substrate planar spacing is usually known. The epilayer planar spacing (d_e) can be determined from the separation between the Bragg angles for diffraction from the substrate (θ_B^s) and from the epilayer (θ_B^e) and the planar spacing of the substrate d_s. The difference in planar spacing (Δd = d_e - d_s) is given by

$$\Delta d = -d_s \cot \Delta \theta$$

(2.8)
where $\Delta \theta = \theta^*_B - \theta^*_B$. This relationship is obtained by differentiating Eq.(2.6) (with $n = 1$).

Figure 2.15: A GIXRD experimental set-up with simultaneous fluorescence detection is schematically shown.

A typical experimental set up for XRD experiments using synchrotron X-radiation is shown in Fig.2.14. Grazing incidence XRD (GIXRD) experiments are performed in order to investigate the diffraction planes perpendicular to the sample surface. A typical experimental geometry for a GIXRD experiment is shown in Fig.2.15, which also shows an additional fluorescence detector. In some cases simultaneous detection of fluorescence and the diffracted beam can provide additional information about the sample under investigation.

2.5.4 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is based on the diffraction of electrons when they pass through a very thin sample. The principle of the transmission electron microscope is almost the same as an optical microscope, using magnetic lenses instead of glass lenses and electrons instead of photons. An electron beam from an electron
gun is focused by a condenser lens onto a small spot (~ 2 – 3 μm) on the sample and after passing through the sample is focused by the objective lens to project the magnified image onto a screen. A very essential element is the aperture located at the back focal plane of the objective lens which determines the image contrast and resolution limit of the microscope.

In the simplest view, electron diffraction from a crystalline lattice can be described as a kinematical scattering process that meets the wave reinforcement and interference conditions given in the Bragg equation. As in the case of x-ray diffraction, the electron diffraction patterns are spot patterns form single crystal films, ring patterns from fine-grain randomly oriented crystallites, and superimposed ring and spot-patterns from larger grain polycrystalline films containing some preferred orientation (texture films).

Our equipment is a 200 keV (JEOL 2010) high resolution transmission electron microscope (HRTEM) [14] with point-to-point resolution of 0.19 nm and lattice resolution of 0.14 nm. A camera consisting of a yttrium-aluminium-garnet (YAG) scintillator that is fibre-optically coupled to an image intensifier, connected to a high-resolution television tube camera, provides a total magnification of 30 million (microscope magnification: $1.5 \times 10^6$ and the camera magnification: 20). This magnifying system outputs a video stream that is acquired in a computer with a frame-grabber. An option of using films is also available.

Due to a limited penetration depth of electrons in solids, the sample should be very thin: the acceptable thickness is about 100–1000 Å. To facilitate sample preparation, an ultrasonic disc-cutter, a dimpler, a precision ion-polishing system (all from GATAN, USA), a grinder/polisher unit and wire saw are available. For studying buried interfaces, cross-section TEM observations are widely used. For this purpose, the sample is cut normal to the surface and thin slices are prepared by chemical etching and ion milling. With high-resolution TEM lattice images can be obtained directly. We have used transmission electron diffraction (TED), plan view TEM and
cross-sectional TEM (XTEM) for the work presented in this thesis.

2.6 Conclusions

Different techniques for the growth of epitaxial layers have been discussed in this chapter. Molecular beam epitaxy is the most important technique for growing epitaxial nanostructures with precise control over growth. Self-assembled growth of epitaxial nanostructures and different growth modes have been discussed. Self-assemble growth of islands occur via Stranski-Krastanov or Volmer-Weber growth mode depending on the combination of materials for the overlayer and the substrate. Principles of operation of different characterization techniques used in this work, such as STM, STS, RHEED, XRD and TEM, have been discussed.
Bibliography


Characterization techniques


