CHAPTER 1

AN INTRODUCTION TO SEMICONDUCTOR MATERIALS

1.1. General outline

Semiconductor materials exist in many structural forms and therefore require a large range of experimental techniques for their analysis. The intention of this book is to allow the reader to obtain a good working knowledge of X-ray diffraction techniques so that he or she is fully aware of the possibilities, assumptions and limitations with this form of structural analysis.

The molecular structure of semiconductors is in general well known. Most materials of interest have been manufactured in some way, therefore an approximate knowledge of the elements and layer thicknesses and sequence is assumed and is the starting point for many of the approaches used. Most samples of interest, however, are not of a simple molecular form but are composite structures, commonly consisting of multiple thin layers with different compositional phases. There are many important structural parameters that can modify semiconductor device performance. These parameters include phase composition, micro-structural or layer dimensions and imperfections, etc. A description of how the properties are categorised and material form is given, since this largely determines the X-ray scattering experiment for the analysis, Fewster (1996).

The theory of X-ray scattering is presented from a physical basis and therefore naturally starts with dynamical theory and its extensions before describing the more approximate kinematical theory. The theories are largely considered at the single photon level. In reality the experiment collects many photons that are divergent and occupy a range of energies.

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These effects influence the experimental results and are covered in the description of the instruments. In general the scattering is three-dimensional because the sample is three-dimensional and this is born in mind throughout. The mapping of the scattering in three-dimensions is the most general experiment and all other approaches are obvious projections. The assumptions on moving to two-dimensional reciprocal space mapping and ultimately one-dimensional X-ray scattering, e.g. rocking curves will then appear more obvious and understandable. The assumptions associated with interpreting data collected in various ways will be discussed. This will then allow the reader to understand the subject conceptually and extend the techniques to his or her particular problem.

The concentration is on near-perfect semiconductor materials defined by the valence in the Periodic Table, that is group IV, III-V, II-VI, etc., since the available information is large as well as being commercially very important. The concentration on near-perfect materials is to contain the range of techniques and available information. The techniques will be considered in general terms so as not to limit the book to specific materials.

Interpretation requires understanding of the instrument aberrations, the assumptions in the methods and presumed details concerning the sample. Aspects of quality control with X-ray diffraction methods based on comparative measurements requires an understanding of the sensitivity of the conditions to the parameters of interest, these aspects will also be covered.

1.2. Semiconductors

Semiconductors range from the most perfect crystals available to amorphous materials. The sample dimensions can range from 12 inch diameter ingots of bulk Si to layers of partial-atomic coverage layers with nanometre scale lateral dimensions embedded in a multi-layer structure. The molecular structure of most common semiconductors is of a high symmetry extended lattice, for example Si has the space group (this represents the relative relationships between atoms) of $Fd3m$ and the space group for GaAs and InP is $F\bar{4}3m$. Both these space groups are simple face-centred cubic lattices, figure 1.1. Also the degree of complexity in semiconductor samples is increasing with the manufacture of laterally patterned or phase separated structures having dimensions

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sufficiently small to create "zero" dimensional quantum size effects. The list of structural parameters required to define these materials is increasing, although the basic definitions can be described quite simply, Table 1.1. Since these structures are manufactured the analysis has a good starting point in that an approximate understanding of the structure will exist. The challenge therefore is to determine these parameters more precisely, not only to aid the manufacturing process but also to analyse them for defects and structural quality, etc.

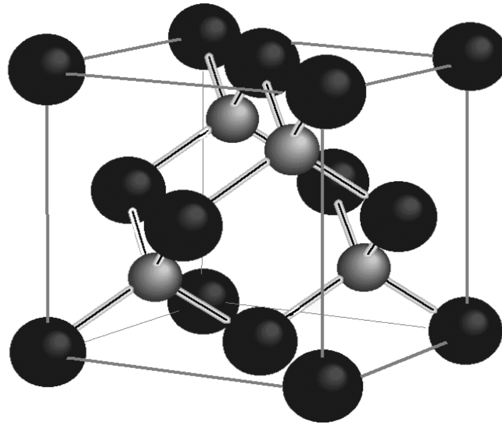

Figure 1.1 The arrangement of atoms in typical III-V semiconductor structures (e.g. GaAs, InP).

All physical properties, be they electronic or optical, rely in some way on the structural properties of the material. As the degree of device sophistication increases the structural tolerances are reduced. Therefore the necessity of accurate determination of the composition, thickness and defects, etc., becomes very important. X-ray analysis techniques are very well developed for obtaining this information and mature enough to recognise its weaknesses. Of course no technique should be used in isolation but compared and complimented with other methods. Most techniques measure something that does not compare directly with any other, this in itself gives valuable information not only on the assumptions in deriving the information but also the sensitivity of the technique.

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Amorphous semiconductors are important in the areas of large area electronics, although because of the low free-carrier mobility some of the associated circuitry requires re-crystallisation. This change of structural form improves the mobility and device speed. The sizes of the crystallites, the location of crystallite boundaries with respect to the device active region are all-important parameters. As we increase the degree of perfection the long-range structural order gives rise to well defined electronic band structures. This leads into the possibilities of band structure engineering. The variables that the device engineer has are composition, shape and orientation to create structures with the required optical or electronic responses. Control over the growth of these structural parameters at the required level, sometimes at the atomic level, is not a trivial task. The growth of these structures is dominated by epitaxy either from the liquid phase (LPE), chemical vapour deposition (CVD), molecular beam epitaxy (MBE) or extended forms of these; metal organic CVD (MOCVD), metal organic MBE (MOMBE), etc. These growth methods require very careful control and therefore careful analysis (in-situ and ex-situ) to ensure the structural parameters are those wanted. Also different compositional phases have different interatomic spacings and therefore these must be accommodated either by elastic strains or plastic deformation. Plastic deformation exists in the form of cracks and dislocations, which can act as charge carrier recombination centres and alter the device performance. It is therefore very necessary to have knowledge of the defects in the active region of the device that controls their behaviour. Again very careful structural analysis is required. All these properties can depend strongly on the quality of the substrate material, i.e. its defect density, orientation and surface strains, etc.

It should be clear that these semiconductors cannot be grown by pressing a few buttons and achieving the performance expected. A very good and thorough understanding of the materials and the growth method are required. In-situ analysis methods to monitor the growth are developing but generally the most thorough analysis are performed ex-situ. The in-situ methods generally rely on a detailed understanding from post-growth analysis that of course can be very exhaustive. X-ray diffraction methods are sometimes used in-situ but in general contribute to improving yield by analysing material at various stages in manufacture, help in controlling the growth process and for detailed materials analysis ex-situ.

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Table 1.1 Definition of the structural properties of materials.

Type of property	General property	Specific property
Macroscopic	*Shape*	Layer thickness Lateral dimensions
	Composition	Structural phase Elements present Phase extent
	Form	Amorphous Polycrystalline Single Crystal
	Orientation	General preferred texture Layer tilt
	Distortion	Layer strain tensor Lattice relaxation Warping
	Homogeneity	Between analysed regions
	Interfaces	Interface spreading
	Density	Porosity Coverage
Microscopic	*Shape*	Average crystallite size Crystallite size distribution
	Composition	Local chemistry
	Orientation	Crystallite tilt distribution
	Distortion	Crystallite inter-strain distribution Crystallite intra-strain distribution Dislocation strain fields Point defects Cracks Strain from precipitates
	Interface	Roughness laterally
	Homogeneity	Distribution within region of sample studied

The X-ray analysis technique to apply depends on the material quality, the level of detail and precision required. This book will describe all the levels of precision and assumptions made to carry out certain types of analysis. Because the crystalline quality of many semiconductors is very high the diffraction process cannot be treated in a simple way. Most analyses require the application of the dynamical diffraction theory and therefore an understanding of this and the assumptions involved are important and described in Chapter 2. The development of instrumentation

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for collecting the scattered X-rays has also created new possibilities in analysis that make X-ray methods a very versatile tool in probing the structure of materials.

1.3. Method

In this section a brief description of the accessible information to X-ray diffraction techniques will be given. How and why this following information is possible to extract will become clear in later chapters. Table 1.1 presents the definition of various structural parameters used to define a material. The first subdivision of the structural properties is into macroscopic and microscopic. These are X-ray definitions and can be considered respectively as aspects that define the major features of the diffraction pattern (peak position and intensity) and those that alter the pattern in a more subtle way (peak shape and weak diffuse scattering).

Table 1.2. Definition for structural types.

Structural type	Definition
Nearly perfect epitaxial	A single extended crystal having near perfect registry with the same orientation as the underlayer, which is also nearly perfect.
Textured epitaxial	The layer orientation is close to registry with the underlayer, both normal and parallel to the surface plane. The layer is composed of mosaic blocks.
Textured polycrystalline	Crystallites preferentially orientated normal to the surface, but random in the plane. They have a distribution in sizes.
Nearly perfect polycrystalline	Random orientated crystallites of similar size and shape.
Amorphous extended lattice	Similar strength interatomic bonds but no length scale correlation greater than this.
Random molecules	Essentially amorphous structure with weak interlinking between molecules, possibly giving some ordering.

X-ray diffraction is a very sensitive structural analysis tool and the extent to which detailed information can be obtained depends on the sample itself. Suppose that the sample is poorly defined and contains numerous crystallites, with a distribution of structural phases, sizes, orientations and strains, then separating the various contributions is not trivial. However if

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certain properties can be determined rather precisely then others can be determined by extending the range of experiments. Clearly therefore, the initial assumptions concerning the sample will define which structural details can be obtained readily. At this stage we should define the sample since these will define the likely information that can be determined by X-ray methods and the type of instrumentation that is applicable, Table 1.2.

Orientation in this context refers to the alignment of low index atomic planes (these are planes separated by distances of about one unit cell spacing) to some other reference, e.g. the surface. These definitions concentrate on laterally extended homogeneity and therefore can be expanded to included patterned structures and random structural variations in the lateral plane by considering them as columns.

Since any structural probe will determine an average of a region or analyse an unrepresentative region of an inhomogeneous sample, it is clear to see that the useful information may be limited to some average parameter and its variation. For structural types that are highly inhomogeneous, e.g. random molecules and textured polycrystalline materials, then X-ray diffraction will average some long-range order, orientation distribution and their variations. This is where it is important to link the physical or chemical property of the material to the structural property, for example is it the macroscopic average or the microscopic details that determines the property of interest? The next question may well be the scale of the variation; is it homogeneous at the micron or nanometre scale? X-ray diffraction averages in several ways, within a coherently diffracting volume and the X-ray beam dimensions on the sample. Controlling the beam divergence can modify the former and the latter can be subdivided by analysing the scattered beam with an area detector as in X-ray topography. The range of X-ray analysis techniques therefore cannot be simply categorised into finite bounds of applicability but depend upon the material, the property of the material of interest, the versatility of the diffractometer, the X-ray wavelength, etc. Understanding the details of diffraction process, the nature of X-rays and assumptions concerning the sample are all-important to making a good and reliable analysis.

Some typical macroscopic and microscopic properties are given in figures 1.2 and 1.3 respectively. The important aspect here is the X-ray probe dimension with respect to the properties. Clearly the probe is not simply defined two dimensionally but also has some depth into the figures,

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consequently we must be aware how this probe brings all this information together to create a signal which is then interpreted. Having defined some basics concerning the sample we shall consider some basic information about the X-rays used to extract this information.

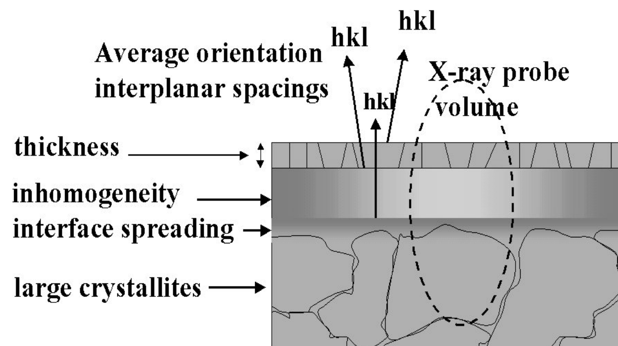

Figure 1.2 The main macroscopic parameters that characterise a layered structure.

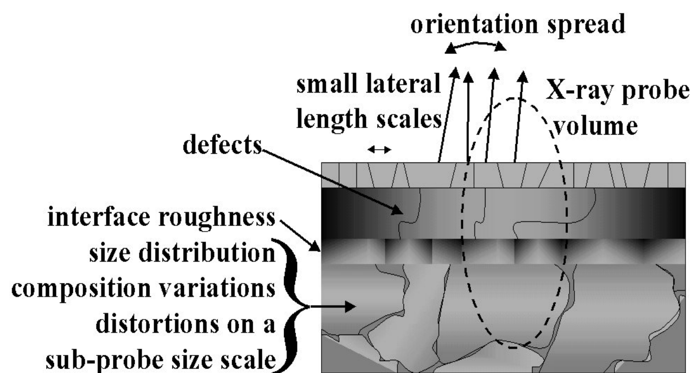

Figure 1.3 The main microscopic parameters that characterise a layered structure.

1.4. Properties of X-rays

X-ray wavelengths compare with the energy transitions of inner electron orbitals in atoms. It is this property that is used to create laboratory monochromatic X-rays. High energy decelerating electrons will also emit X-radiation and this is the reason for the continuum of radiation from

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laboratory sources and the emission from synchrotron sources. A laboratory source is shown diagrammatically in figure 1.4 with an accompanying spectrum. The radiation from a laboratory source is not very uniformly distributed and in general much of the radiation is not used. However the intense characteristic lines act as a good internal standard and it is these lines that are used in the majority of laboratory experiments.

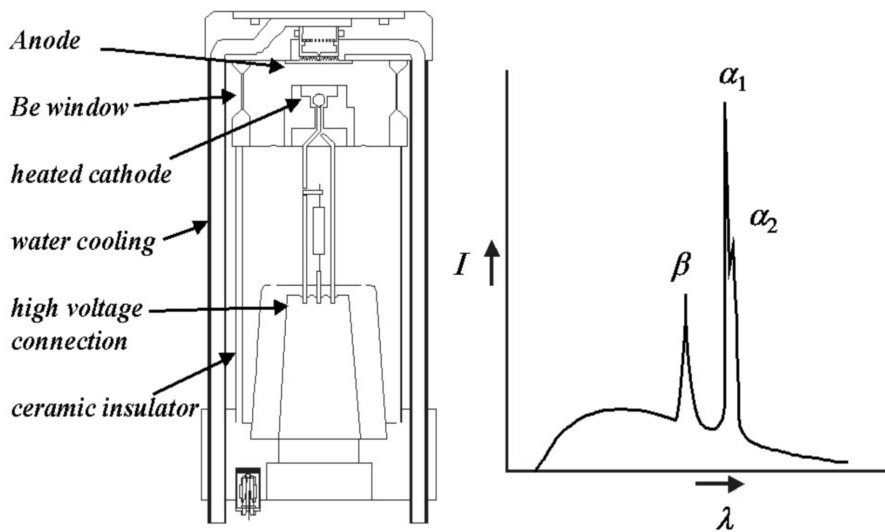

Figure 1.4 The interior of a modern sealed source X-ray tube and the spectral variation with intensity for a typical anode material

Synchrotron radiation sources work on a very different principle. A synchrotron is really a storage ring for electrons, which are contained by magnetic fields to prevent excessive divergence and consequent energy loss. When the electrons are deviated from a straight line using so-called bending magnets, wigglers and undulators, the consequent acceleration towards the centre of the curve creates an energy orbital jump thus producing electromagnetic radiation. If this energy change is large (i.e. high speed electrons and small bending radius from intense magnetic fields) then X-rays can be produced. The X-rays from the synchrotron are emitted tangentially from the radius and concentrated into a narrow cone with the electric field vector predominately confined to the plane of the orbit; i.e. the

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beam is horizontally polarised. However it is possible to rotate this plane of polarisation but in general this aspect does restrict most experiments to scattering in the vertical plane. This can lead to extra tolerances required for mechanical movements of diffractometers because of the gravitational pull. Another aspect to consider is the wavelength calibration; this has to be done before any experiment since the emission is smooth and there are few reference lines except at absorption edges. Laboratory sources are rather less efficient at producing X-rays. The emerging X-rays are randomly polarised and almost radially symmetric, yet only a small percentage of this divergent source can be used.

Because of the method of injecting electrons into a synchrotron they are arranged in bunches and therefore the consequential X-ray emission will have a time structure. This can prove useful for some experiments especially when only a single bunch is injected, if the X-ray pulse can be synchronised with some dynamic experiment, (Barrington-Leigh and Rosenbaum, 1976, Whatmore, Goddard, Tanner and Clark, 1982). Third generation sources are also increasing the brilliance level. This gives rise to very small source sizes that can create some phase coherence across the whole source leading to observable interference effects when the beam travels along different optical paths (phase contrast topography and tomography, Cloetens et al, 1999). This coherence over the source can also create routes to reconstructing the scattering object (Miao, Charalambous, Kirz and Sayre, 1999). Laboratory X-rays from similar sized sources have very low power output. However there are methods of effectively moving the source close to infinity with crystal optics: the phase front formed from an object containing several different optical paths can then be separated with an analyser crystal (Davis, Gao, Gureyev, Stevenson and Wilkins, 1995). It is clear that the developments and possibilities continue and this is far from a static subject. These developments will then lead to new possibilities in analysis.

The highly directional aspects of the synchrotron generated X-rays leads to very intense sources compared with laboratory sources. However the convenience and improvements in intensity output makes the laboratory sources suitable for most experiments. One of the earliest methods of increasing the intensity in the laboratory was achieved by rapidly rotating the anode (rotating anode source) to distribute the heat. This has lead to increases in intensities by almost an order of magnitude for 15kW sources,

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although 60kW sources are available. However there are many other ways of improving the intensity and whatever method is used it has to be related to the problem to be solved, since the intensity output should be qualified with flux, divergence, wavelength distribution, etc.

Since X-rays are primarily generated from inner atom core transitions the photon wavelengths are in the region of 0.1nm, which is of the order of the interatomic spacings in materials. Bragg's equation (derived in Chapter 2) indicates that the difference in the scattering angle of two interatomic spacings of 0.14 and 0.15 nm determined with a 0.15 nm X-ray wavelength is ~2.4^0. As will be seen later the peak widths of diffraction maxima can be located within about 0.0002^0. This gives X-rays the high strain sensitivity at the part per million level and sensitivity to atomic scale spatial resolutions.

1.5. Instrumentation

There have been considerable developments in new instrumentation. The power of laboratory X-ray sources have increased and various focusing mirrors and X-ray lenses can recover the divergence of laboratory X-ray sources with considerable intensity enhancements. The degree of sophistication is increasing with the various components recognising each other (i.e. exchanging the X-ray tube will be recognised by the system, thus limiting the power delivered, etc.). Computer automation has made considerable improvements in time and freed user involvement and this will continue. This has considerably helped in the thinking to doing ratio.

The mechanical stability has also improved with optical encoding on the axes, allowing fast movement to very high precision. Interchangeable components (monochromators, X-ray mirrors, slits, etc.) increase the versatility of diffractometers and can be pre-aligned so that several very different experiments can be performed on one instrument with a simple change. The experiment can now be fitted to the sample and property of interest instead of the former more established approach of having an array of instruments for each experimental technique.

The choice of instrumental configuration and its consequential influence on the information required from the sample will be covered in Chapter 3.

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1.6. Sample definition

The various sample types have been described in section 1.2 and 1.3, but here the description will be defined more closely to that required for X-ray diffraction. These definitions also indicate the information of importance in analysis, Table 1.3. Basically any structure will be an arrangement of atoms. However a crystal is defined as "any structure having essentially a discrete diffraction pattern." This is the accepted definition (Acta Crystallographica **A48** 928, 1992). To have a diffraction pattern that is observable with X-rays in the simplest case requires some form of periodicity or repeat unit cell.

A semiconductor, for example GaAs, Si, GaN, consists of an extended periodic array and would fit into the above categories of perfect epitaxy, textured epitaxy and possibly textured polycrystalline in thin layer form. Although material with no dislocations (missing lines of atoms) can be grown, most do have dislocations threading through them. The generation of convection currents during growth can create mosaic blocks (crystallites surrounded by defects) that can be tilted with respect to each other. These are all fairly typical features found in bulk material and thin films. One of the most fundamental problems in thin films is that the atomic spacing of the layer differs from that of the underlying material. This will cause either elastic distortion or, if the internal stress exceeds that which can be accommodated by elastic strains, plastic deformation occurs and misfit dislocations are generated. Misfit dislocations can be formed from the high stress levels and imperfections at the growing surface nucleating dislocation loops that glide to the interface or by turning a threading dislocation to lie in the interface plane. Knowledge of the state of strain, the number of defects, etc., can be very important for device performance and X-ray diffraction methods are very sensitive to these effects.

Figure 1.5 gives a three dimensional view of the structural properties of a thin film. Basically we have a unit cell repeat that can vary laterally and in depth, having parameters a,b,c,α,β and γ. Within this there are relative rotations between regions and layers, defects (dislocations and point defects (atomic site errors, e.g. interstitials, vacancies and impurity atoms)). These features all influence the diffraction pattern of X-rays. The creation of the scattering pattern from X-rays is one thing but to interpret the features is quite another and a reasonable understanding of the sample in question is necessary. The important aspects will now be considered

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here. The very high strain sensitivity can allow measurement of x <1% (absolute) composition variations in $Al_xGa_{1-x}As$ alloys, <0.1% (absolute) composition variations in $In_xGa_{1-x}As$, etc., for peak shifts of 0.001° or 3.6 seconds of arc. However to achieve this the strain has to be related to the composition using some assumptions. As discussed above a thin layer grown epitaxially on a substrate will distort either elastically or plastically. In both cases we need to determine the unit cell parameters of the layer of interest and calculate how this would change if it were free standing. Clearly we have to include the influence of elastic parameters.

Table 1.3. A broad overview of the structural parameters that characterise various material types. Those parameters that have meaning in the various materials are given with filled diamonds, those that could have meaning are given by open squares.

	Thickness	Composition	Relaxation	Distortion	Crystallite size	Orientation	Defects
Perfect Epitaxy	♦	♦				♦	
Nearly perfect epitaxy	♦	♦	❐	❐	❐	♦	♦
Textured epitaxy	♦	♦	♦	♦	♦	♦	♦
Textured polycrystalline	♦	♦	❐	♦	♦	♦	❐
Perfect polycrystalline	♦	♦		♦	♦		❐
Amorphous layers	♦	♦					

The arrangement of atoms in silicon is similar to that given in figure 1.1, except that all the atoms are identical. If we try and compress the structure along the bonds, [111] type directions then it will be much more difficult to do so than along a [100] direction where we would distort angles, for example. So although the structure is of high symmetry, its elastic properties are very anisotropic. Compression along one direction will necessitate an expansion in another. This can be characterised by examining the relationship between stress and strain. Initially we can

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suppose that the strain is elastic until the internal stress is too large and plastic deformation occurs. The plastic deformation will occur as cracks or dislocations, however the strain parallel to any interface will be related to the degree of alignment of the atoms in a layer with that underneath. Hooke's law gives the relationship of stress to strain, but because we are considering an anisotropic medium we have to generalise the problem and the elastic stiffness to fourth rank tensors, Nye (1985). This is all rather unwieldy and can be simplified to a 6 × 6 matrix when equivalent coefficients are considered

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} c_{11}c_{12}c_{13}c_{14}c_{15}c_{16} \\ c_{21}c_{22}c_{23}c_{24}c_{25}c_{26} \\ c_{31}c_{32}c_{33}c_{34}c_{35}c_{36} \\ c_{41}c_{42}c_{43}c_{44}c_{45}c_{46} \\ c_{51}c_{52}c_{53}c_{54}c_{55}c_{56} \\ c_{61}c_{62}c_{63}c_{64}c_{65}c_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{xz} \\ \varepsilon_{xy} \end{pmatrix} \qquad 1.1$$

c_{ij} are the stiffness coefficients, where c_{11} is the stiffness along the a axis and c_{46}, etc., give rise to shear. σ_{ij} and ε_{ij} represent the stresses and strains along various directions. This is the general case for triclinic structures. For higher symmetry many of these coefficients become zero and some become equivalent.

Suppose we consider the growth along the z <001> direction then the layer will be constrained in the plane of the interface and the stress will be zero normal to this direction, i.e. the top surface is unconstrained then

$$\sigma_{zz} = 0 = c_{31}\varepsilon_{xx} + c_{32}\varepsilon_{yy} + c_{33}\varepsilon_{zz} + c_{34}\varepsilon_{yz} + c_{35}\varepsilon_{xz} + c_{36}\varepsilon_{xy} \qquad 1.2$$

Now for a cubic system $c_{31} = c_{32} = c_{13} = c_{23} = c_{12} = c_{21}$, $c_{22} = c_{33} = c_{11}$ and $c_{34} = c_{35} = c_{36} = 0$, therefore

$$\varepsilon_{zz} = -\frac{c_{12}}{c_{11}}\{\varepsilon_{xx} + \varepsilon_{yy}\} \qquad 1.3$$

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Hornstra and Bartels (1978) have solved the condition for the general case of cubic systems, giving the calculation procedure and some examples for the GaAs phase. Any solutions of the cubic system will just include combinations of the coefficients c_{11}, c_{12} and c_{44}.

Figure 1.5 The range of structural parameters accessible to X-ray methods for imperfect (real) samples.

As the degree of anisotropy decreases a Poisson ratio can be used (in fact a Poisson ratio can be used for any system except that it varied with direction). The equivalent Poisson ratio for the above example with the <001> direction normal to the surface direction is therefore

$$\nu = \frac{\varepsilon_{\perp}}{\varepsilon_{\perp} - 2\varepsilon_{//}} = \frac{c_{12}}{c_{11} + c_{12}} \qquad 1.4$$

where

$$\varepsilon_{//} = \frac{1}{2}\{\varepsilon_{xx} + \varepsilon_{yy}\} = \frac{1}{2}\left\{ \frac{{}_{L}d_x - {}_{L0}d_x}{{}_{L0}d_x} + \frac{{}_{L}d_y - {}_{L0}d_y}{{}_{L0}d_y} \right\} \qquad 1.5$$

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and

$$\varepsilon_{\perp} = \varepsilon_{zz} = \frac{{}_{L}d_z - {}_{L0}d_z}{{}_{L0}d_z} \qquad 1.6$$

where ${}_{L}d_x$, etc., are the actual atomic plane spacings along x and ${}_{L0}d_x$ are the unstrained or free standing atomic plane spacings along x, etc. Since we wish to know the strain normal to the interface due to the strain parallel to the interface we can write the general case (remembering that ν is a function of direction)

$$\varepsilon_{zz} = \frac{-\nu}{1-\nu}(\varepsilon_{xx} + \varepsilon_{yy}) \qquad 1.7$$

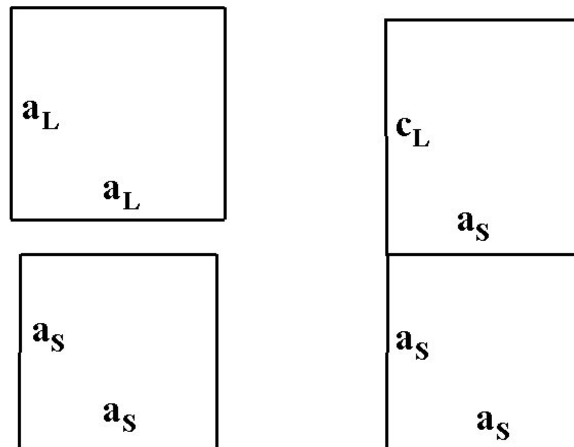

Figure 1.6 The undistorted (before deposition) and a distorted (after deposition) unit cell for a simple cubic layer on a cubic substrate; both are orientated along a cubic edge direction.

If constant volume is maintained during distortion then Poissons's ratio is simply 0.5, however most materials, especially the structural form of typical III-V semiconductors this is much closer to 0.3. Clearly as the molecular form becomes more complicated and the bond directions more random this anisotropy will decrease. Additional shear actions come into

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effect along directions of lower symmetry, however these may be of less concern in a homogeneous thin layer of large lateral dimensions.

Let us firstly consider a cubic (001) GaAs substrate with a thin film of cubic AlAs on top. Both structures have the same space group, the same arrangement of atoms, but slightly different lattice parameters and elastic parameters. If a thin layer (~0.2 μm) is deposited then the atoms will align with those of the substrate and the structure will appear as a continuous lattice with an abrupt change in lattice parameter and composition at the substrate interface. The alignment of the atoms in the interface plane will define the lattice parameter of the layer in the interface plane and through the appropriate Poisson ratio or elastic stiffness combinations will define the lattice parameter normal to the interface plane, figure.1.6.

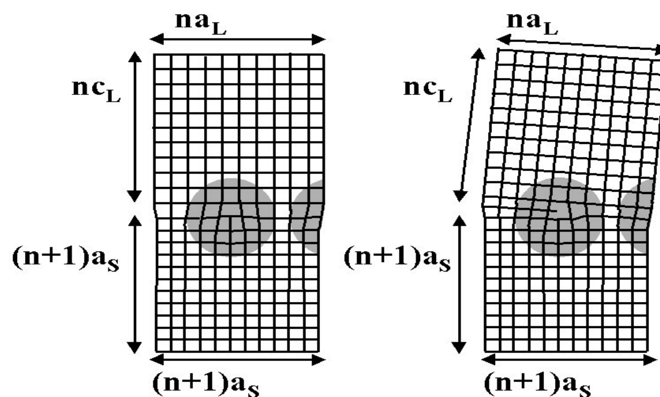

Figure 1.7 The problems that occur when the elastic parameters are incapable of accommodating the distortions necessary for perfect epitaxy.

As the thickness of the layer increases the layer will become progressively more reluctant to distort. Eventually the elastic limit will be reached and only partial registry will exist. When this situation arises there will be more rows of atoms in the substrate than in the layer (the lattice parameter of GaAs is less than that of AlAs). The average lattice parameter in the plane of the interface will therefore differ and some distortion will extend into the layer and substrate with possible tilting between the two, figure.1.7. Clearly the structure becomes quite complex even for this simple system. For perfect epitaxy we are trying to match the layer

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interatomic spacings to that of the layer or substrate below, ${}_{S}d_x$, etc., however if the layer has partially relaxed back to its strain-free state then we can rewrite equation 1.5 as

$$\varepsilon_{//} = \frac{1}{2}\{\varepsilon_{xx} + \varepsilon_{yy}\} = \frac{1}{2}\left\{\frac{{}_{S}d_x - {}_{L0}d_x}{{}_{L0}d_x}[1 - R_x] + \frac{{}_{S}d_y - {}_{L0}d_y}{{}_{L0}d_y}[1 - R_y]\right\} \tag{1.8}$$

where R_x is the relaxation in the misfit along x, etc. The relaxation is then zero for perfect matching and unity when the layer relaxes to its unconstrained shape. Substituting equation 1.8 into 1.7 will therefore give the perpendicular strain from knowledge of the original lattice parameters of the component layers and the degree of relaxation in two orthogonal directions.

$$\varepsilon_{\perp} = \frac{-\nu}{1-\nu}\left\{\frac{{}_{S}d_x - {}_{L0}d_x}{{}_{L0}d_x}[1 - R_x] + \frac{{}_{S}d_y - {}_{L0}d_y}{{}_{L0}d_y}[1 - R_y]\right\} \tag{1.9}$$

When the unit cells of the two materials differ significantly then the registry of the atoms becomes very complex. Consider for example (0001) GaN on (0001) sapphire, both are hexagonal structures but the lattice parameters differ quite considerably. The atom arrangement of both materials is given in figure.1.8. The best atomic match appears when the two lattices are aligned along different directions, i.e. the x-direction is rotated through 90^0 with respect to the other. However we can see that this gives approximate alignment of the Al in the sapphire to the Ga in the GaN. The mismatch is so large however that the GaN is very heavily relaxed towards its unstrained state and will be full of defects associated with this poor match.

Pashley (1956) has given a very full account of the possibilities in epitaxy and the accounts of the early theories. A full all-encompassing theory explaining the nucleation and orientation dependence is still elusive, but there are some general guidelines that can be given. Generally an orientation dependence occurs when the mismatch (the fractional difference in the lattice plane spacing in the plane of the interface) between the

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overlayer and underlayer is less than ~14%. Theoretical models and experimental evidence on a wide range of systems support this. The orientation depends on the relative alignment of atoms in the overlayer and underlayer and is not governed by integer relationships of atomic plane spacings of the two lattices. The thickness of the layer influences the extent to which the elastic distortion can be accommodated, the greater the misfit the thinner the layer should be to maintain good epitaxy. Once epitaxial growth is established in the fabrication of a structure then a full understanding of these nucleation processes may seem irrelevant, however new structures are emerging that make use of some of the nucleation properties of certain materials.

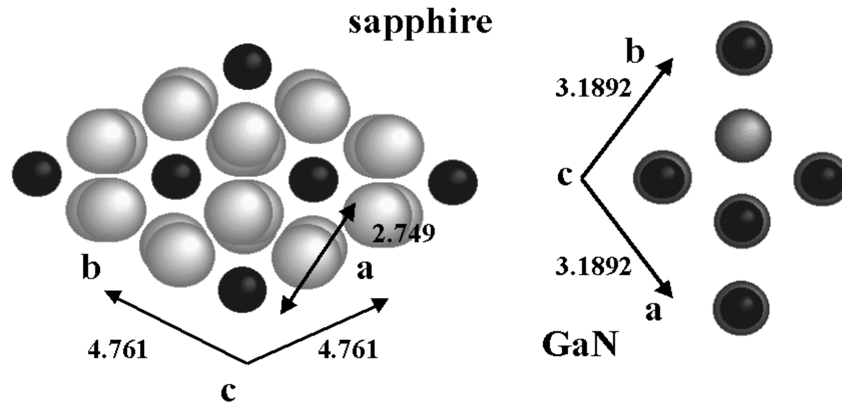

Figure 1.8 The basal plane view of GaN and sapphire; this indicates the rotation necessary to accommodate the alignment of atoms for epitaxy. Al and Ga are coloured black.

We can consider growth to occur in three principle ways. The first is a two-dimensional mechanism, i.e. the layer is built up atomic layer by atomic layer, and this relies on the atoms migrating across the surface and preferring to locate at atomic layer steps. A complete atomic layer coverage will create a very smooth surface, whereas for intermediate coverage the surface is atomically rough. This oscillation in smooth and rough surfaces explains the oscillating specular reflectivity observed in Reflection High Energy Electron Diffraction (RHEED) during growth by Molecular Beam Epitaxy (MBE), Neave, Joyce, Dobson and Norton (1983). When the surface does not "wet" easily with the deposited atoms of the overlayer, the

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growth can occur in distinct islands that gradually enlarge and eventually coalesce. This is termed three-dimensional growth and can lead to mosaic or columnar growth with defects concentrated at the boundaries. Another interesting growth mode is a mixture of both three- and two-dimensional growth first described by Stranski and Krastanow (1938). This mechanism is characterised by the initial formation of a wetting layer (two-dimensional growth) that is very thin (no more than a few atomic layers) and the subsequent growth of islands. Examples of these mechanisms can be seen in semiconductor materials. InGaAs deposited on GaAs at low In compositions, <10%, will grow two-dimensionally up to about 70nm before misfit dislocations are formed at the interface, whereas InAs will grow by the Stranski-Krastanow mechanism. These differing growth modes may appear troublesome but can be used to advantage in creating structures defined in all three dimensions by optimising the growth method. These can have very special properties and offer another challenge to analytical methods.

Determining the growth mode can only be accomplished with precise surface diffusion data and bond strengths, etc. It is then possible to construct a surface by modelling the whole process and extracting a statistical significance. These approaches have been very successful at predicting some of the general observations of surface topography, Itoh, Bell, Avery, Jones, Joyce and Vvedensky (1998).

Predicting the situation when defects form at the interface between two materials, i.e. when the elastic limit has been exceeded, has been the subject of many studies. This of course is a very important parameter because defects in general are detrimental to semiconductor devices and knowledge of the bounds of lattice parameter misfit and thickness define whether a device is possible to fabricate. Hull and Bean (1992) have reviewed the mechanisms of dislocation generation and propagation and discussed the definitions and derivation of the "critical" thickness defining their onset. Of course there are many experimental studies that have questioned the theoretically derived values. Dunstan, Kidd, Howard and Dixon (1991) have taken a very pragmatic approach to the evaluation of critical thickness and compared the residual strain as a function of thickness. The resulting curve is remarkably predictable for a large range of material systems and offers a very quick procedure for predicting the onset of relaxation.

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If the mismatch is large or the substrate is amorphous then the orientation dependence of the layer can be governed by very different criteria and the layer can become essentially textured polycrystalline or even random polycrystalline. Knowledge of the likely form of these materials will define the type of experiment necessary to obtain detailed structural information.

Chapter 2 will describe the theoretical basis of scattering from various structures typically encountered in the field of semiconductor physics. These materials represent the case when a large amount of information is available, although the techniques are applicable to any material and not specific to semiconductors.

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