

Chapter 1

Introduction

Abstract This introductory chapter provides a brief survey on the development of epitaxial growth techniques and points out tasks for the epitaxy of device structures. Starting from early studies of alkali-halide overgrowth in the beginning of the 20th century, basic concepts for lattice match between layer and substrate were developed in the late 1920ies, followed by the theory of misfit dislocations introduced about 1950. Major progress in epitaxy was achieved by technical improvements of the growth techniques, namely liquid phase epitaxy in the early, and molecular beam epitaxy and metalorganic vapor phase epitaxy in the late 1960ies. Current tasks for epitaxial growth are often motivated by needs for the fabrication of advanced devices, aiming to control carriers and photons.

Most semiconductor devices fabricated today are made out of a thin stack of layers with a typical total thickness of only some μm . Layers in such stack differ in material composition and may be as thin as a single atomic layer. All layers are to be grown with high perfection and composition control on a bulk crystal used as a substrate. The growth technique employed for coping with this task is termed epitaxy. In the following we briefly consider the historical development and illustrate typical issues accomplished using epitaxy.

1.1 Epitaxy

1.1.1 Roots of Epitaxy

Crystalline solids found in nature show regularly shaped as-grown faces. The faces of a zinc selenide crystal grown from the vapor phase in the lab are shown in Fig. 1.1a. Mineralogists found that the angles between corresponding faces are always the same for different samples of the same type of crystal. They concluded already in the 18th century that such regular shape originates from a regular assembly of identical building blocks forming the crystal as indicated in Fig. 1.1b. In the early 19th century mineralogists noticed that naturally occurring crystals sometimes

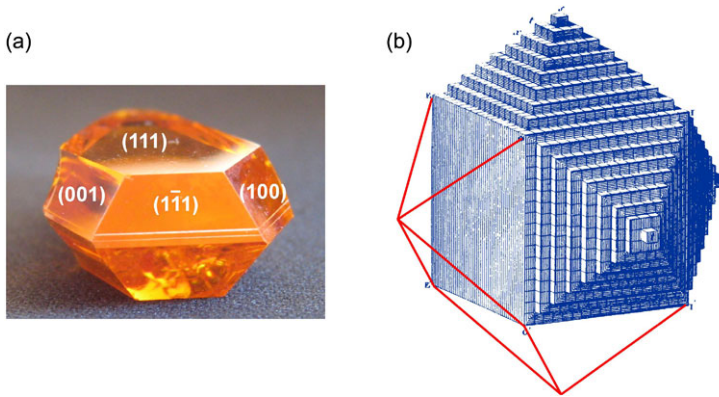


Fig. 1.1 (a) ZnSe bulk crystal with $\{100\}$ and $\{111\}$ growth faces. (b) Faces formed from regularly repeating building blocks described around 1800 [3]. The complete shape of the displayed rhomb-dodecahedron is indicated by *red lines*

grew together with a unique relationship of their orientations [1]. A first successful artificial reproduction of this effect in a laboratory was reported by Moritz L. Frankenheim in 1836 [2]. He demonstrated a parallel oriented growth of sodium nitrate NaNO_3 from solution on a freshly cleaved calcite crystal CaCO_3 .

First systematic studies on the crystal growth on top of another crystalline material were reported by Thomas V. Barker starting 1906 [4]. At that time growth from solution and optical microscopy were the only readily developed techniques for growth and characterization of samples, respectively. Baker investigated a large number of NaCl -type alkali halides like chlorides, bromides, iodides, and cyanides of, e.g., rubidium and cesium. He placed a drop of saturated solution of one halide onto a freshly cleaved surface of another halide and observed the nucleation of a crystalline structure under a microscope. Crystals of the solute appeared as a rule in a few seconds, but sometimes nucleation was too rapid to be observed or difficulties arose due to a greater solubility for the crystal than for the dilute dropped on top. He concluded that crystalline growth of alkali halides was more likely to occur if the molecular volumes of the two inter-growing materials were nearly equal. We note that such conditions often imply a similar size of the building blocks mentioned above and consequently a low misfit of the lattice constants of the two materials.

The discovery of X-ray diffraction (1912) and electron diffraction (1927) by crystals had a strong impact on the knowledge about crystal structure. When Louis Royer made his seminal comprehensive studies with a wide variety of layers and substrate materials in 1928, he could precisely report on the effect of substrate crystal structure on the crystalline orientation of the layer [5]. Royer introduced the term *epitaxy* from the Greek $\varepsilon\pi\iota$ (*epi*, upon, attached to)— $\tau\alpha\acute{\xi}\iota\varsigma$ (*taxis*, arrangement, order) and concluded general rules for epitaxy. He noted that oriented growth occurs only when it involves the parallelism of two lattice planes which have lattice networks of identical or quasi-identical form and closely similar spacing. More

precisely, he found that the differences between the lattice-network spacing (lattice parameters) for growth of alkali halides upon other alkali halides or mica (minerals of the form $XY_{2-3}Z_4O_{10}(OH,F)_2$) should be no more than 15 %. Such geometrical considerations are still prominent today, though it was established later that epitaxy may also occur for much larger misfits.

In the 1930ies, G.I. Finch and A.G. Quarrell concluded from a study of zinc oxide on sputtered zinc that the initial layer is strained in order to attain lattice matching parallel to the interface [6]. The layer lattice-parameter vertical to the interface was also considered to be changed to maintain approximately the bulk density. They named this phenomenon *pseudomorphism*. Though later the experimental evidence was pointed out to be by no means conclusive [1], the concept of pseudomorphic layers proved to be of basic importance for epitaxial structures.

The introduction of the theory of misfit dislocations at the interface between the substrate and the layer by F.C. Frank and Jan H. van der Merve in 1949 [7–9] extended the pseudomorphism approach and predicted a limit for the misfit of pseudomorphic growth. The incorporation of edge dislocations allows to accommodate misfit strain and consequently makes epitaxy possible also for structures with larger misfit. Conclusive experimental evidence for this was provided by John W. Matthews and co-workers in the 1960ies [10, 11]. Thin metal layers on single crystal metals with low misfit proved to grow pseudomorphic, while misfit dislocations were generated in thicker layers with a density depending on layer thickness. Later also conditions not included in the mentioned concepts like, e.g., interface alloying or surface energies were found to significantly affect epitaxial growth.

The emerging semiconductor industry in the early 1960ies had a strong impact on the interest in epitaxy. In addition, advancements in the technique of producing high vacuum and pure materials, and progress in experimental techniques like electron microscopy and X-ray diffraction allowed to efficiently develop methods for epitaxial growth. Liquid-phase epitaxy enabled epitaxial growth of multilayered device structures of high complexity like separate-confinement semiconductor lasers. The advancement of this technology was facilitated by its similarity to the well-studied growth of bulk single-crystals from seeded solution. In the 70ies the more sophisticated methods of molecular beam epitaxy and metalorganic vapor-phase epitaxy emerged. These techniques opened up epitaxy far from thermodynamic equilibrium and hence fabrication of structures with atomically sharp interfaces, which cannot be produced near equilibrium. Understanding and control of the epitaxial growth techniques was significantly advanced by the application of in-situ studies of the nucleation and growth process, and by the development of computational techniques. In the late 80ies the modern techniques attained a maturity to get in the lead of device mass-production. Today a large variety of electronic, optoelectronic, magnetic, and superconducting layer structures are fabricated using epitaxial techniques, including structures of reduced dimensionality on a nanometer scale.

1.1.2 Epitaxy and Bulk-Crystal Growth

Crystal growth in an epitaxial process proceeds basically in the same way as conventional growth of bulk crystals. In epitaxy, however, layer and substrate differ in the nature and strength of the chemical bond. Moreover, both materials may have a different crystal structure and generally have an unequal lattice parameter—at least if the temperature is varied. We may therefore say that crystals differ *energetically and geometrically* in epitaxy [12]. Crystalline deposition of different materials on each other is also termed *heteroepitaxy*.

Such definition does obviously not apply for an epitaxial deposition on a substrate of the same material. The process is usually referred to as *homoepitaxy* (sometimes also *autoepitaxy*). Let us consider a simple example to illustrate that there may still be a difference to conventional crystal growth. Epitaxy of electronic devices is usually performed on doped substrates and often starts by depositing a layer of the same material termed homoepitaxial buffer layer. Doping often alters the lattice parameter without significantly changing the chemical bond in bulk material. A *p*-type doping of, e.g., silicon with boron to a level of $2 \times 10^{19} \text{ cm}^{-3}$ induces a change of the lattice parameter by -1% . An undoped layer on a doped substrate of the same material will hence not differ energetically but geometrically. This provides a clear distinction of homoepitaxy from conventional crystal growth. According this differentiation deposition of a layer of the same kind and doping like the substrate underneath should be termed crystal growth instead of epitaxy. Following the general usage we will, however, use the term homoepitaxy less strictly. Deposition of a layer of the same material as the substrate is usually just one of many layers to follow in the growth process of a device structure. Furthermore, fabrication of bulk crystals is usually performed applying a different growth regime than in epitaxy, allowing for much higher growth rates. Accordingly also different experimental set-ups are employed. The term homoepitaxy will be used here for deposition of the same material as the substrate, just to distinguish from heteroepitaxy.

1.2 Issues of Epitaxy

1.2.1 Convention on Use of the Term “Atom”

Solids are composed of atoms, which may be charged due to the character of the chemical bond. When used in a general way in this book, the word “atom” denotes both, an atom or an ion. Uncharged atoms are hence for simplicity usually not distinguished from charged atom cores in, e.g., ionic crystals or metals unless explicitly pointed out.

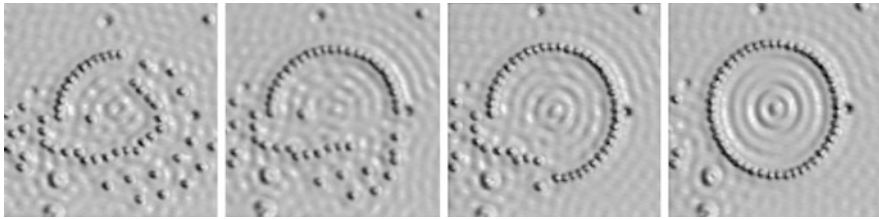


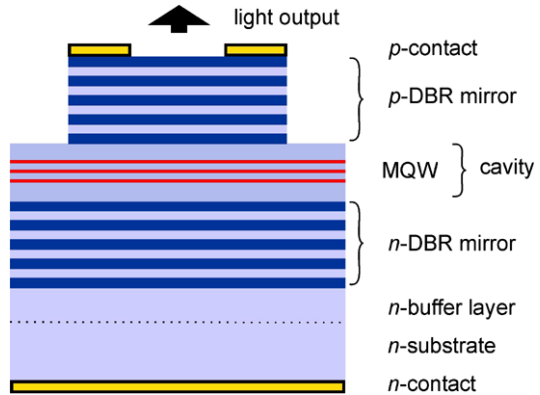
Fig. 1.2 Gradual circular arrangement of 48 iron adatoms on a copper surface assembled using a low-temperature scanning tunnelling microscope. Interference ripples originate from electron surface states. From [14]

1.2.2 Assembly of Atoms

Epitaxy denotes the regular assembly of atoms on a crystalline substrate. By inventing the scanning tunneling microscope (STM) a particular means has been developed to control the assembly of single atoms for forming an ordered structure. The method uses the finite force an STM tip always exerts on an adsorbed atom (adatom) attached to the surface of a solid [13]. The magnitude of the force can be tuned by adjusting the voltage and the position of the tip. Since generally less force is required to move an atom across a surface than to pull it away the tip parameters can be set to allow for positioning an individual adatom while it remains bound to the surface. The example given in Fig. 1.2 shows iron atoms on a (111) copper surface. The initially disordered Fe atoms were carefully positioned at chosen locations. May such procedure also be applied to deposit an epitaxial layer onto a substrate? Imagine a skillful operator placing one atom per second exactly on the correct site of a layer. For typically about 10^{15} sites per cm^2 such procedure requires 31 Mio. years for a single atomic layer being deposited on one cm^2 . The fabrication of epitaxial structures hence requires other methods.

The problem of growing a layer by the assembly of single atoms is comparable to the issue of describing the behavior of a gas by formulating the equation of motion for each atom. This cannot be accomplished for exceedingly large ensembles like a considerable fraction of 6×10^{23} atoms present in one mole. The approach of kinetic theory of gases hence solely describes averages of certain quantities of the vast number of atoms in the ensemble, concluded from the behavior of one single atom. These averages correspond to macroscopic variables. We will basically follow a comparable approach. In epitaxial growth we seek to establish favorable conditions for atoms of a nutrient phase to finding proper lattice sites in the solid phase. The macroscopic control parameters are governed by both thermodynamics and kinetics, and their effect depends on the materials and the applied growth method.

Fig. 1.3 Schematic of a vertical-cavity surface-emitting laser indicating the sequence of differently alloyed and doped semiconductor layers



1.2.3 Tasks for Epitaxial Growth

Semiconductor devices control the flow and confinement of charge carriers and photons. To fulfill its function a device is composed of crystalline layers and corresponding interfaces with different physical properties. Epitaxy is employed to assemble such layer structure. The precise control of the growth process in epitaxy requires the accomplishment of issues with quite different nature. We consider the example of a semiconductor device-structure to illustrate a number of tasks addressed during fabrication and indicate the connection to respective chapters of this book. The addressed concepts basically apply also for insulators and metals. In this book we focus on semiconductor materials.

The demand for increasing data-rate capacity in data-communication networks raised the need for suitable optical interconnects, particularly for light sources. Vertical-cavity surface-emitting lasers (VCSELs) have characteristics meeting ambitious requirements of fiber communication and recently emerged from the laboratory to the marketplace. VCSEL devices are also widely used in computer mice due to a good shape of their optical radiation field. A VCSEL is a semiconductor laser, which emits the radiation vertically via its surface—in contrast to the more common edge-emitting lasers. Like any laser it consists of an active zone where the light is generated, overlapping with a region where the optical wave is guided. Light is generated by recombination of electrons and holes which are confined in quantum wells (MQW, multiple quantum well). The generated photons contribute to the light wave which travels back and forth in an optical Fabry-Pérot resonator built by two mirrors, and a small fraction is allowed to emerge from the top mirror to form the laser radiation. Since the resonator in a VCSEL is very short, the reflectivity of the mirrors must be very high ($R > 99\%$) to maintain lasing oscillation. They hence are made from distributed Bragg reflectors (DBR) of many pairwise $\frac{1}{4}\lambda/n$ thick layers with a difference in the respective refractive index n , λ being the operation wavelength. If the index step Δn is low many pairs are required (a few tens). The basic design of a VCSEL is given in Fig. 1.3.

The realization of a semiconductor device is a complex process. The basic design layout is determined by a number of operation parameters like, e.g., the emission wavelength for an optoelectronic device. Already at this stage materials aspects play an important role. Obviously a wide-bandgap semiconductor material, e.g., must be used in the active region if the device is to radiate at high photon energy. The design stage comprises simulation work on electrical, optical, and other properties of the device depending on the employed materials and the specific purpose of the device. The design eventually yields a list of materials composition, thickness, and doping for each individual layer in the entire layer stack to be epitaxially grown.

The crystalline epitaxial growth on a single crystalline substrate requires a well-defined relationship of the substrate structure with respect to that of the layers grown on top. For this purpose the spacing of the atoms parallel to the interface between substrate and the layers of the device structure on top has to accommodate. Since the lateral lattice constants never match perfectly and the total layer thickness of the device structure is generally much below the substrate thickness, epitaxial layers are elastically strained. *Chapter 2* introduces into the structural and elastic properties of epitaxial layers and points out a critical limit for such strain. As a consequence of overcritical stress, plastic relaxation occurs by the introduction of misfit dislocations. Prominent species of such dislocations for the important crystal structures zincblende and wurtzite are treated. Prior to the growth of the device layers usually a buffer layer is grown on the substrate. This layer is introduced to keep defects located at the interface to the substrate and dislocations originating from large misfits away from the device layers. A further challenge occurs from a large change of composition within a layer sequence. The device depicted in Fig. 1.3 comprises Bragg mirrors, which require a large step of the refractive index between consecutive quarter-lambda thick layers. A large index step of the layer pairs in the mirror stack is connected not only to a large difference of the fundamental bandgap of the layers, but usually also to a large difference of lattice constants. To keep the strain below the critical limit, layers with a composition mix of materials are used to maintain the lattice constant while changing the refractive index. The change of lattice constant in mixed layers and means to compensate the total strain in a layer stack are also considered in Chap. 2.

Strain and interfaces between layers with different bandgap affect the electronic properties of the layer structure. In *Chapter 3* the effect of strain on valence and conduction-band states is outlined. Furthermore, the consequence of alloying on the fundamental bandgap is considered. The contact of two semiconducting layers raises the question how the uppermost valence bands mutually align. Models treating this problem and effects of interface composition are reviewed in Chap. 3. The band discontinuities determine the confinement of charge carriers in a sandwich structure and are also affected by strain. This is particularly important for the active layers which are usually formed by quantum wells as depicted in Fig. 1.3. Structures with a reduced dimensionality—quantum wells, quantum wires, and quantum dots—form the active core of many advanced devices. Chapter 3 points out the basic electronic properties of such quantum structures to indicate the required dimensions, which have to be realized in the epitaxial growth process.

Growth occurs at some deviation from thermodynamic equilibrium. Epitaxy is a controlled transition from the gas or liquid phase to a crystalline solid. The nature of the driving force depends on the particular material system and growth conditions. *Chapter 4* introduces into the thermodynamics of growth for simple one- and two-component systems. Nucleation of a layer, epitaxial growth modes, and a thermodynamic approach to surface energies is described. Even though epitaxial growth processes may occur under conditions far from equilibrium, thermalization times of atoms arriving from the nutrition phase on the surface can be much less than the time required to grow a single monoatomic layer. In such cases thermodynamic descriptions are often successfully applied to model the growth process. For the device structure illustrated in Fig. 1.3 thermodynamics may constitute limits for the stability of mixed crystals used to meet the requirements for lattice constants, bandgaps, band alignments, and doping. In such cases epitaxy may still be possible in a restricted temperature range.

The fabrication of atomically sharp interfaces between two dissimilar solids requires a significant deviation from equilibrium to suppress interdiffusion. This is particularly important for quantum structures like the active layers in the VCSEL structure shown in Fig. 1.3, usually realized using multiple quantum wells. Under such nonequilibrium conditions growth is strongly affected by kinetic influences. Kinetics and atomistic aspects of epitaxial growth are addressed in *Chapter 5*. A kinetic description of nucleation and layer growth accounts for the detailed steps atoms experience on the growing surface. They depend on the structure of the surface, where the arrangement of atoms may differ strongly from that found in the solid bulk underneath. Such surface reconstructions are specific for the given material and change with growth conditions—they are pointed out for specific examples. Growth modes depending on strain or specific surface states are often employed in epitaxy to fabricate low-dimensional structures by self-organized processes. The basics of such self-organized formation of quantum dots and quantum wires is considered in Chap. 5. VCSEL devices like that depicted in Fig. 1.3 are also fabricated using quantum dots in the active region, formed in the self-organized Stranski-Krastanow growth mode.

Electronic and optoelectronic devices require control of charge carriers in semiconductors and a contact of the semiconductor structure to a metal for a connection to the electric circuit. *Chapter 6* gives a brief introduction to problems in epitaxy connected to doping and contact fabrication. For a given semiconductor material thermodynamics may impose limits in the doping level originating from restricted solubility of the dopants, an amphoteric behavior of the dopants, or compensation by native defects. Nonequilibrium epitaxial growth may relieve some restrictions. Growth far from equilibrium also enables delta-like doping profiles, used to fabricate devices employing a two-dimensional electron gas with a high mobility. Doping and heterostructure composition profiles may be affected by redistribution of atoms due to diffusion phenomena. Mechanisms of diffusion in semiconductors are considered and examples are given for dependences on the ambient atmosphere and on doping. Ohmic contacts between semiconductor and metal are a classical subject, but epitaxy also enables the growth of specific contact structures to achieve a low contact resistance. Some examples are outlined in Chap. 6.

Various techniques for epitaxial growth have been established and are described in *Chapter 7*. The first method which attained maturity to produce complex devices was liquid-phase epitaxy. It operates close to thermodynamic equilibrium and may hence be well described by thermodynamics. More versatile control is achieved using the more sophisticated methods of molecular-beam epitaxy and metalorganic vapor-phase epitaxy, which both operate far from thermal equilibrium. They hence both allow for a control of layer thickness down to a fraction of a single atomic layer and are used to fabricate devices with quantum structures in the active region. The two methods are also employed in VCSEL production on a large scale.

References

1. D.W. Pashley, A historical review of epitaxy, in *Epitaxial Growth (Part B)*, ed. by J.W. Matthews (Academic Press, New York, 1975), pp. 1–27
2. M.L. Frankenheim, Über die Verbindung verschiedenartiger Kristalle. *Ann. Phys.* **113**, 516 (1836) (in German)
3. M. L'Abbé R. J. Haüy, *Traité élémentaire de physique*, 3rd edn. (Mme. V. Courcier, Libraire Pour Les Sciences, Paris, 1821) (in French)
4. T.V. Barker, Contributions to the theory of isomorphism based on experiments on the regular growths of crystals on one substance on those of another. *J. Chem. Soc. Trans.* **89**, 1120 (1906)
5. L. Royer, Recherches expérimentales sur l'épitaxie ou orientation mutuelle de cristaux d'espèces différentes. *Bull. Soc. Fr. Minéral. Cristallogr.* **51**, 7 (1928) (in French)
6. G.I. Finch, A.G. Quarrell, The structure of magnesium, zinc and aluminium films. *Proc. R. Soc. Lond. A* **141**, 398 (1933)
7. F.C. Frank, J.H. van der Merve, One-dimensional dislocations. I. Static theory. *Proc. R. Soc. Lond. A* **198**, 205 (1949)
8. F.C. Frank, J.H. van der Merve, One-dimensional dislocations. II. Misfitting monolayers and oriented overgrowth. *Proc. R. Soc. Lond. A* **198**, 216 (1949)
9. F.C. Frank, J.H. van der Merve, One-dimensional dislocations. III. Influence of the second harmonic term in the potential representation, on the properties of the model. *Proc. R. Soc. Lond. A* **200**, 125 (1949)
10. W.A. Jesser, J.W. Matthews, Evidence for pseudomorphic growth of iron on copper. *Philos. Mag.* **15**, 1097 (1967)
11. W.A. Jesser, J.W. Matthews, Pseudomorphic growth of iron on hot copper. *Philos. Mag.* **17**, 595 (1968)
12. I.V. Markov, *Crystal Growth for Beginners* (World Scientific, Singapore, 2003)
13. D.M. Eigler, E.K. Schweizer, Positioning single atoms with a scanning tunnelling microscope. *Nature* **344**, 524 (1990)
14. Details and the last STM image are reported in M.F. Crommie, C.P. Lutz, D.M. Eigler, Confinement of electrons to quantum corrals on a metal surface. *Science* **262**, 218 (1993). Image originally created by IBM Corporation, accessible at <http://www.almaden.ibm.com/vis/stm/corral.html>



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