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Molecular beam epitaxy

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Abstract

Molecular beam epitaxy (MBE) is a process for growing thin, epitaxial films of a wide variety of materials, ranging from oxides to semiconductors to metals. It was first applied to the growth of compound semiconductors. That is still the most common usage, in large part because of the high technological value of such materials to the electronics industry. In this process beams of atoms or molecules in an ultra-high vacuum environment are incident upon a heated crystal that has previously been processed to produce a nearly atomically clean surface. The arriving constituent atoms form a crystalline layer in registry with the substrate, i.e., an epitaxial film. These films are remarkable because the composition can be rapidly changed, producing crystalline interfaces that are almost atomically abrupt. Thus, it has been possible to produce a large range of unique structures, including quantum well devices, superlattices, lasers, etc., all of which benefit from the precise control of composition during growth. Because of the cleanliness of the growth environment and because of the precise control over composition, MBE structures closely approximate the idealized models used in solid state theory.

This discussion is intended as an introduction to the concept and the experimental procedures used in MBE growth. The refinement of experimental procedures has been the key to the successful fabrication of electronically significant devices, which in turn has generated the widespread interest in the MBE as a research tool. MBE experiments have provided a wealth of new information bearing on the general mechanisms involved in epitaxial growth, since many of the phenomena initially observed during MBE have since been repeated using other crystal growth processes. We also summarize the general types of layered structures that have contributed to the rapid expansion of interest in MBE and its various offshoots. Finally we consider some of the problems that remain in the growth of heteroepitaxial structures, specifically, the problem of mismatch in lattice constant between layers and between layer and substrate. The discussion is phenomenological, not theoretical; MBE has been primarily an experimental approach based on simple concepts.

Keywords: Models of surface kinetics; Molecular beam epitaxy; Reflection high-energy electron diffraction (RHEED); Epitaxy; Single crystal surfaces; Heterojunctions; Quantum wells; Superlattices

1. Introduction

As scientists have learned how the properties of materials depend on their microstructure, there have been ever increasing efforts to design the structure to produce the desired behavior. While the fraction of the atoms in a solid that lie on the

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surface is very small, the formation of that solid has been critically dependent on processes occurring on the surface. Crystal growth involves surface processes, whether it takes place from the vapor or from a melt. The better we can understand these processes, the more we can control the manner in which the solid is formed and its subsequent properties.

The invention of the transistor and the beginning of the computer age had an enormous impact on the science of materials. The new semiconducting devices were critically dependent on the availability of very perfect and extremely pure semiconductor crystals. The economic importance of the semiconductor revolution quickly stimulated researchers to develop a variety of new methods of growing crystals in order to produce the purity and perfection demanded by the new devices. One approach was to use a slice of semiconductor as the seed on which to deposit additional material in the form of a thin film in order to obtain electrical properties in the film that were superior to those of the starting substrate material. If the film had a crystalline structure that was ordered with respect to that of the underlying substrate, it was described as "epitaxial". Epitaxial films could be grown on a substrate of the same material, in which case the film was "homoepitaxial"; alternatively, if grown on a substrate of a different material, the film was "heteroepitaxial".

Epitaxial films of semiconductors have continued to play a major role in device processing because they can be produced with electrical properties different from those of the substrate, either higher purity, or fewer defects or with a different concentration of electrically active impurities as desired. By depositing a sequence of epitaxial layers with specific properties, specialized device structures can be realized without the need for processing steps involving the diffusion of impurities to produce doped layers.

Many semiconductor materials can be grown epitaxially by allowing a suitable mixture of gaseous vapors containing the constituent elements to react with a heated seed or substrate crystal, a process known as vapor phase epitaxy (VPE). Alternatively, placing a seed crystal wafer in contact with a liquid solution saturated with the semiconductor constituents can be used to grow an epitaxial layer by liquid phase epitaxy (LPE) as the solution is very slowly cooled. Each of these methods has advantages, e.g. VPE is a relatively rapid method of film growth which is readily scaled to manufacturing volume, and LPE produces relatively pure films; however each has disadvantages as well, e.g. VPE takes place at relatively high temperatures which can enhance bulk diffusion, and LPE does not produce films of uniform thickness.

Recently I listened to a radio program on the Public Broadcasting Network in which a group of experts presented brief statements describing their work in "Nanotechnology". While the presentations left me a bit impatient because of the heavy emphasis on the more flamboyant future possibilities that research may provide, there was some brief, but interesting, discussion of the impact on materials that could be fabricated "one atom at a time". It struck me that for more than thirty years, some of us have been doing this, in one dimension at least, by the process known as molecular beam epitaxy (MBE). And in fact, the resulting materials have indeed opened new doors in physics, chemistry, material science and electronics.

MBE, as the name suggests, uses localized beams of atoms or molecules in an ultra-high vacuum (UHV) environment to provide a source of the constituents to the growing surface of a substrate crystal. The beams impinge on the crystal kept at a moderately elevated temperature that provides sufficient thermal energy to the arriving atoms for them to migrate over the surface to lattice sites. The UHV environment minimizes contamination of the growing surface. In the UHV environment, the beam atoms and molecules travel in nearly collision-free paths until arriving either at the substrate or else at chilled walls of the chamber where they condense and are thus effectively removed from the system. When a shutter is interposed in a beam, that beam is effectively turned off almost instantly. These features make it possible to grow the films very slowly without contamination, and, most importantly, to change the composition of the arriving atom stream very abruptly; in fact, the composition of the flux can be changed in times much shorter than that needed to grow a

single atom layer of the film. Very simplistically, MBE growth might be likened to "spray painting" the substrate crystal with layers of atoms, changing the composition or impurity level in each layer until a desired structure is obtained. In this sense MBE is nearly the ideal approach to material preparation since the composition can be tailored, layer-by-layer. We shall see, however, that much more is involved, and that unraveling the details of growth has added much to our understanding of surface processes. In fact, it may be argued that the greatest value of MBE is the insight into crystal growth that it continues to provide.

2. Historical background

The growth of semiconductor thin films from the vapor has a long history; however prior to the 1970s these films were not structurally equivalent to bulk material and thus were of little use from a device standpoint. One particular problem for compound semiconductor films had to do with the very different vapor pressures of the pure constituents, as much as two orders of magnitude for Ga and As at temperatures useful for film growth. Thermal evaporation of separate As and Ga sources would require impossibly precise temperature control to produce equal vapor pressures, and thus equal arrival rates of the constituent atoms at the substrate. Collins et al. [1] used two crucibles containing Ga and Sb to evaporate films of GaSb onto a glass substrate; their method was based on the concept that due to the angular decrease in the flux of each element away from the centerline of its crucible, there would be a location somewhere between the two crucibles where the flux ratio would produce a stoichiometric film. The resulting films were unfortunately highly polycrystalline, so that little could be determined about actual composition. Earlier, Günther attempted to provide the proper vapor ratio by separate control of the temperatures of nonmetal, metal and substrate [2]. Again, the resulting films were not well ordered and so were of small interest to the device engineers.

The reader today may find it difficult to realize how difficult it was to obtain information about the condition of the substrate, the composition of the vacuum, and the crystallinity of films grown in those early days (1950s–1960s). Usually it was necessary to carry out post-growth electron diffraction studies to determine whether the films were crystalline or not, and often the results took several days to obtain—long after the growth procedure had been all but forgotten! However a revolution in surface analysis took place in the late 60s with the introduction of small mass spectrometers, Auger electron spectroscopy and compact electron diffraction equipment. In fact, the discovery of the MBE process came about not with the intent of finding a new method of crystal growth, but rather as a study of surface–vapor interactions with a new, compact mass spectrometer [3]. In 1968, John LePore and I were studying the reflection of pulsed molecular beams of Ga and As_2 from GaAs surfaces in UHV in order to measure the energy of adsorption. It became clear that the presence of a layer of Ga greatly increased the bond strength of As adsorbed on the Ga compared to the energy of As on GaAs. This suggested that the vapor pressure/arrival rate of different species might not be controlling the composition, since excess As appeared to be quickly desorbed from the clean surface at temperatures above 300 °C. In fact, simply by maintaining a slight overpressure of As and/or P to insure complete reaction of Ga, we were able to obtain epitaxial growth of GaAs and GaP at around 500 °C [4]. This temperature was significantly lower than was needed for VPE, and thus MBE seemed to hold some promise as a low temperature alternative to the current epitaxial techniques.

In 1969 A.Y. Cho published landmark results reporting the first in situ observations of the MBE growth process using high energy electron diffraction [5]. This structural analysis capability proved to be crucial for characterizing MBE epitaxy because it provided an instantaneous feedback on the influence of growth conditions on film structure. Cho demonstrated that MBE growth could produce atomically flat, ordered layers; thus these studies marked the beginning of the use of MBE for practical device fabrication. Cho went on to publish a number of key papers during this

period among which he demonstrated how to incorporate doping impurities [6], and ultimately, how to fabricate GaAs–$Al_xGa_{1-x}As$ laser structures, which at the time was considered the crucial test for a III–V materials process [7].

There were other important advances that quickly followed. In 1973 Chang et al. [8] reported on the growth of a superlattice structure consisting of alternating layers of GaAs and AlGaAs. Later, they were able to observe evidence in the transverse conductance of these structures that indicated the resonant tunneling between the GaAs layers predicted by their theory [9]. At the same time, Dingle et al. observed structure in the optical absorption spectrum of superlattice structures associated with quantized energy levels due to carrier confinement in one dimension [10]. Thus in the short period of about five years, MBE moved from being a novel but very uncertain film growth method to becoming an established research tool in which the general directions for future work were well established. Since then MBE research has escalated rapidly, with the publication of numerous books, monographs and conference proceedings that summarize the extensive body of work [11–16].

3. Experimental methods

MBE is an experimental approach to epitaxial film growth, which has emphasized including the modern tools of surface analysis to obtain a real time analysis of the surface and its environment. It has also been a very demanding art in which the economic stakes have been high. As a result there has been a great deal of experimental innovation that frequently has been of high value in other disciplines. In this discussion of the experimental aspects of MBE we will discuss the working components of MBE systems and indicate their evolution as the details of the growth process have become clearer from the happy union of surface analysis with crystal growth.

Fig. 1 shows a schematic front view of a basic MBE growth chamber. A thin, crystalline substrate wafer is mounted on a heater block such that it can be brought to face the source ovens used to evaporate the constituent atoms or molecules. Mechanical shutters driven from outside the vacuum chamber are used to switch the beams on and off. Because of the extensive use of chilled walls surrounding the source ovens and the substrate, the beams make essentially a single pass through the chamber before condensing on the cold walls, and the background pressure in the system remains very low. This preserves the purity of the growing film and at the same time allows the reflection high energy electron diffraction (RHEED) gun to operate without damage from corrosive reaction with residual vapors. The RHEED system provides a diffraction pattern on a phosphor-coated window that is indicative of the ordering of the substrate surface. Thus the observer can immediately see the effect on film crystallinity due to changes in the growth conditions, e.g., exposing the surface to the source beams or changing beam intensity or substrate temperature. This is the essential MBE system, very similar to the ones in use in the 70s. For many research applications this type of system is completely adequate, for example, where relatively small substrates are used and where sample throughput is not a big issue. However, for modern semiconductor device fabrication, throughput is very important and large substrate wafers are used so that modifications must be made to improve deposition uniformity and to minimize the downtime.

3.1. Vacuum considerations

The essence of the MBE concept is that the growth surface is kept clean by the UHV; thus the vacuum environment surrounding the growing crystal must be kept as low as possible to avoid contamination that might affect electrical properties, film morphology and even whether or not epitaxial growth takes place. To put this into perspective, consider that the number n of gas atoms impinging on unit area of surface in unit time is

$$\frac{dn}{dt} = \frac{P}{\sqrt{2\pi mkT}} \ \mathrm{cm^{-2}\,s^{-1}} \qquad (1)$$

P is the gas pressure, m is the atomic mass, k is the Boltzmann constant and T is the absolute

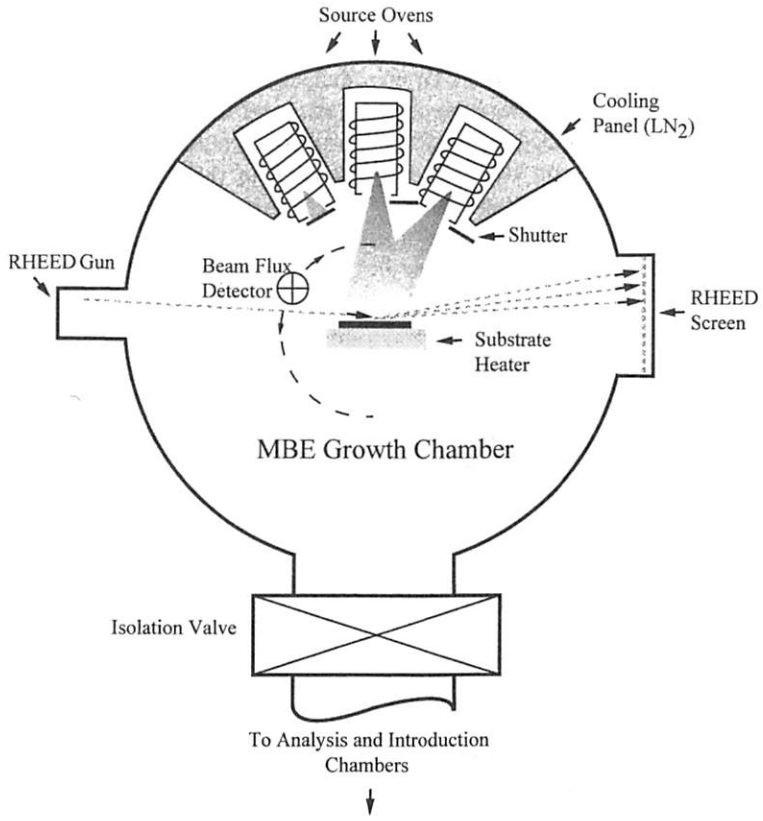

Fig. 1. Top view of a simple MBE chamber showing the essential growth sources, shutters, beam flux detector and the RHEED system for monitoring structure during growth.

temperature. For example, if the vacuum pressure P is measured in Torr and if the atomic mass m is converted to molecular weight M in g, then Eq. (1) becomes

$$\frac{dn}{dt} = 3.5 \times 10^{22} \frac{P}{\sqrt{MT}} \text{ cm}^{-2}\text{s}^{-1} \quad (1a)$$

For a typical residual gas molecular weight of about 40 g and a temperature of 25 °C, the rate of gas arrival is $3.2 \times 10^{20} P$ (Torr), and for a pressure of 10^{-6} Torr the arrival rate is 3.2×10^{14} cm^{-2} s^{-1}. The number of atoms in a cm^2 of the cube face of Si is also about 3.2×10^{14}, thus the arrival rate in a second at 10^{-6} Torr is nearly equal to the number of atoms in a cm^2 of surface. Hence in one second a complete monolayer of residual gas arrives at the surface, (although all the arriving atoms may not react or "stick" on the surface). The sobering implication of Eq. (1) is that even at a good UHV of 10^{-10} Torr, a clean surface will become badly contaminated with *reactive* background gas in just a few hours. We emphasize "reactive" because, fortunately, many semiconductor surfaces are relatively unreactive with common background gases, and thus can be preserved in the clean state significantly longer.

However, the purity constraint for MBE growth is even more severe. If it is desirable to maintain the background impurity level at, say, one part per million, then clearly the contamination of each surface layer must be kept at that level. MBE growth is relatively slow, typically about 1 ML/s, thus to keep the arrival rate of background species at one part per million would require a pressure of 10^{-12} Torr! For many specialized semiconductor devices, the impurity level must be much less than 10^{-6}, thus it is perhaps surprising that such low levels can be obtained. While the slow reaction of

many residual gases with the semiconductor plays a part, it is also true that great attention must be given to the design of all components used in an MBE system to avoid outgassing at elevated temperatures, and that careful vacuum processing is critical.

The system shown in Fig. 1 is sometimes described as a "batch" system, where substrates are loaded one at a time on the heater block after opening the system to air, and then the entire growth chamber is evacuated, baked, etc., all of which requires many hours of pumping before a suitable vacuum level is finally obtained. The need for greater throughput of material led to the idea of introducing substrates through a "load-lock" chamber in which one or more substrates are loaded while the growth chamber remains under vacuum. Only the small loading chamber need then be evacuated, and this greatly reduces the contamination of the vacuum in the growth chamber as well as increasing the output of processed wafers. Typically, the growth chamber in a load-locked system can operate for months without exposure to atmosphere, and the source ovens, shutters, etc. all become thoroughly outgassed; the predominant background gases in such a system are simply the high vapor pressure constituents, e.g. the group V elements in the case of III–V MBE.

Modern MBE systems will normally consist of several vacuum chambers, each with a suitable pumping system. A fairly typical system as shown in Fig. 2 will usually consist of at least three

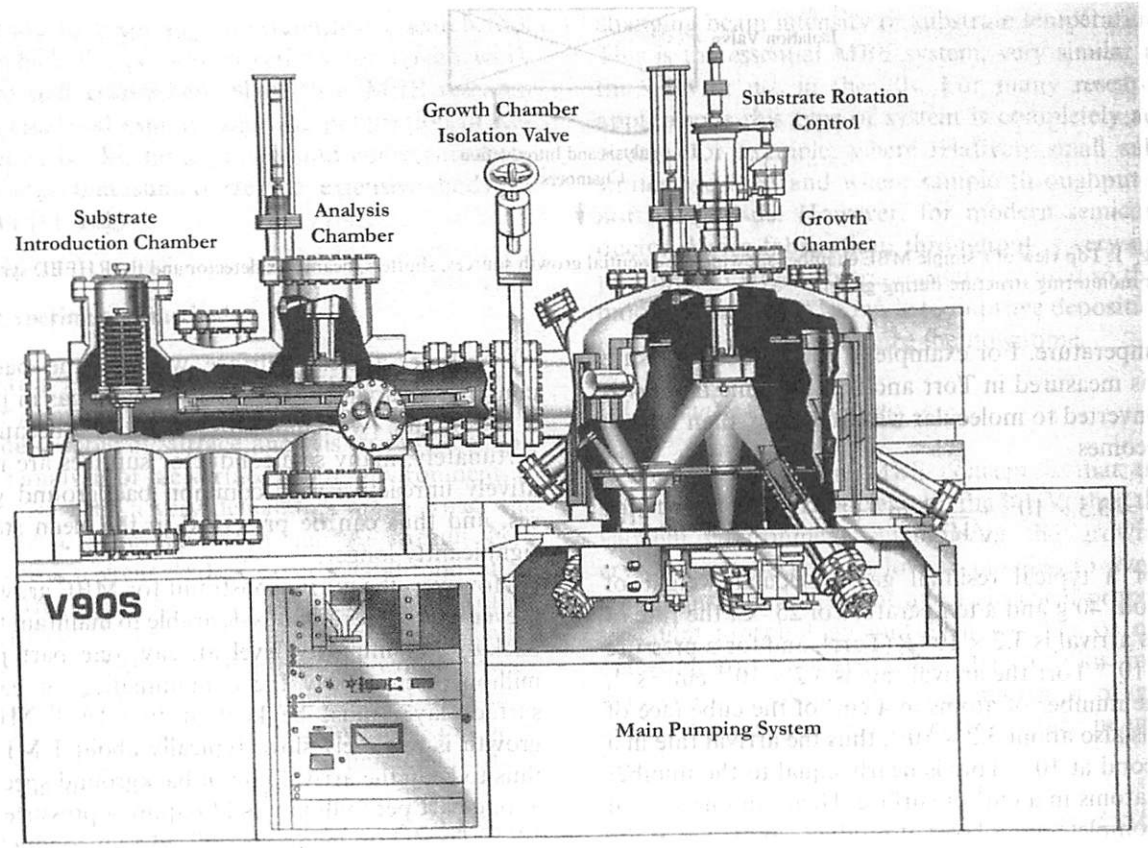

Fig. 2. Side cutaway view of a commercial MBE system with a substrate introduction chamber on the left, analysis chamber, and growth chamber on the right. Substrate transport occurs on trolley connecting the chambers (courtesy of Vacuum Generators, Ltd.).

independently pumped chambers, although there can be many variations on the general theme. A vacuum interlock or introduction chamber is used to allow substrates to be installed on a transport device in a small volume which is pumped down prior to opening the valve to the rest of the system to reduce the amount of air load introduced into the main vacuum. The introduction chamber often will have provision for heating the substrates prior to introduction into the main vacuum system in order to outgas the substrates and their holders. A second chamber is often used for additional substrate preparation and surface characterization, using tools such as AES and/or XPS. An essential feature of MBE from the very beginning has been the presence of surface analysis tools in the systems. The UHV environment and the limited spatial extent of the atom beams make it possible to include some tools, typically electron diffraction and mass spectroscopy, in the immediate growth area to provide a real-time measure of the nature of the growing surface and its environment. In the earlier batch systems an Auger spectrometer was frequently included, but current systems typically include a separate analysis chamber in which to examine the condition of the surface before and after growth. The third chamber is used for the actual growth and usually can be isolated from the rest of the system during both growth and substrate introduction in order to (1) avoid the contamination of the analysis chamber and the surface probes with vapors produced during growth and (2) minimize vacuum contamination of the growth chamber during pressure bursts when the intro chamber is opened to the main vacuum. Additional growth chambers are sometimes included in order to carry out the epitaxy of additional layers where the constituents of the different layers may be incompatible. For example, it is not a good idea to grow II–VI and III–V semiconductors in a single chamber since the components of one are dopants in the other, and there are usually significant residual pressures from the more volatile species remaining after growth.

Load-locked systems require a means for transporting substrates from the loading chamber to the growth chamber, and the development of simple and reliable means for moving substrates and coupling them to holders in UHV has been very useful both to MBE technology and to surface science in general. Sample transport from chamber to chamber has been accomplished in a variety of innovative ways. The requirements are to have means for selecting a wafer from a multiple wafer stack in the introduction chamber, then to move that wafer into another chamber and to dock it securely onto a heater/manipulator, all without mishap or contamination of the wafer by dust particles in the system. The bearings providing smooth transport or rotation must not seize in the UHV environment, and there must be positive control over the sample position, particularly when docking and undocking from the chamber manipulators. These are difficult requirements, and have been met by using magnetically coupled transport rods, by trolley systems with rotary linkage to the external world (as in Fig. 2), or by bellows sealed rods providing extended linear motion. There has been a great deal of reliability testing by MBE researchers, to an extent that present day systems work remarkably well, regardless of the particular method used. The success of these techniques have made it possible to construct large systems with many growth and analysis chambers which can even be used by multiple operators simultaneously. Of course, these techniques have added to the cost and complexity of MBE systems, but the economic consequences of MBE research have been sufficient justification.

Modern production MBE systems are designed to maximize throughput for commercial fabrication of MBE devices. High production rates are achieved by using industry standard, large area substrates, and by growing on multiple wafers simultaneously. This is achieved by mounting the large substrate wafers on a rotating platen that can move under multiple source ovens. This increases the size of the system and the growth chamber in particular, and the larger dimensions then demand increased output from the sources to maintain the flux at the substrates. Obviously there are many additional considerations in the scaling up of such a system, which are beyond the scope of the present discussion.

3.2. Growth chamber details

The growth chamber is where the critical part of the process occurs and it typically contains the following essential components for MBE growth:

1. source ovens,
2. beam shutters and actuating mechanism,
3. substrate heater and sample docking mechanism,
4. in situ growth characterization tools,
5. mass spectrometer and/or separate beam flux monitor,
6. cryopanels to act as cryopumps and to condense unused beam flux.

Normally, an isolation valve is used to close off the growth chamber except when substrates are loaded or removed. All of these components must be designed to minimize the outgassing of impurities, particularly those components that become heated by either the source ovens or by radiation from the substrate. For example, molybdenum metal typically contains a small amount of sulfur impurity, which can evaporate at elevated temperatures; furthermore S is a donor dopant in III–V materials. Thus Mo is undesirable for use where there is a possibility of it getting too hot. Ta sheet or foil is much less prone to produce volatile impurities and is preferred.

The source ovens typically are mounted so that each is surrounded by a chilled panel (usually filled with liquid N_2), which acts to reduce radiative heating of the chamber. A large variety of source oven designs have been used depending on the temperature needed to evaporate the source material and on whether the material is a major or a minor constituent. Fig. 3 shows a fairly standard type of source oven. The crucible containing the source is normally a high grade of pyrolytic boron nitride (PBN) since much experimentation has shown this material to be least reactive with a wide range of source materials, including highly reactive elements such as Al and Ga. The conical shape has been shown to reduce the focused "beaming" of the evaporating flux as well as maintaining a more constant angular dependence as the contents of the crucible is depleted, i.e. a lengthy tubular region

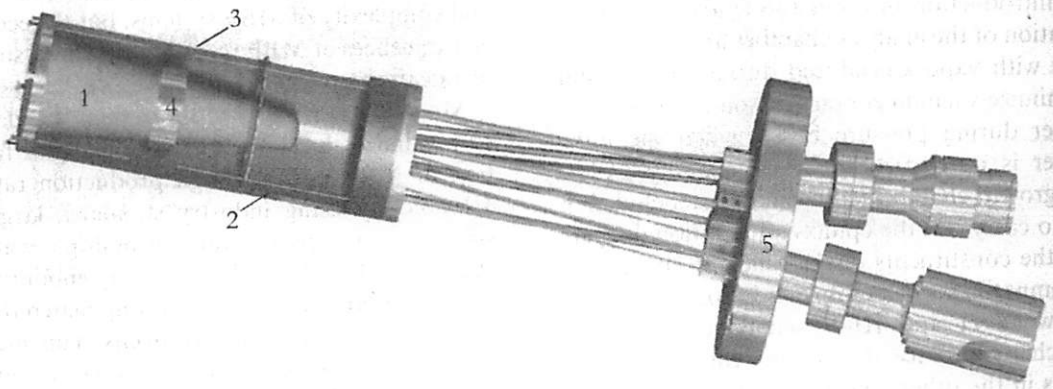

Fig. 3. Cutaway view of an MBE thermal effusion furnace: (1) pyrolytic BN crucible (2) resistive heater filament, (3) metal foil radiation shields, (4) wrap-around thermocouple and (5) mounting flange (courtesy of EPI, Inc.).

above the charge increases the beaming of the flux along the tube axis, leading to poorer uniformity in the deposited layer. The crucible itself is surrounded by several layers of Ta foil that serve as a radiation shield to improve the power efficiency of the source and to reduce the heating of the surrounding cryopanel and loss of LN_2. The temperature of the crucible is measured with a thermocouple attached to a Ta belt wrapped around the crucible. The thermocouple is normally a Type C (W/Re 5/26%) since those alloys are refractory, relatively clean, and resistant to reaction with vapors from the crucible.

The angular distribution of flux from a crucible is an important issue in terms of the thickness uniformity of an MBE film. A simple calculation provides a first order approximation. The intensity of the flux radiating out from a point source clearly is proportional to $1/r$, the distance of the source from the substrate. For a substrate perpendicular to the axis of the crucible a distance r_0 away, the distance r at any point off the axis of the crucible is equal to $r_0 \cos\theta$, where θ is the angle between the crucible axis and the line to the point. However a unit area of the substrate intersects a solid angle which is also proportional to $\cos\theta$; and finally, if the substrate is not perpendicular to the source, the area of the source viewed by the substrate is again proportional to $\cos\theta$. Thus the flux should vary approximately as $\cos^3\theta$. It is clear that there is a fairly rapid decrease in flux with angle away from the centerline of the source. One can minimize the variation either by using small substrates or by moving the substrate far from the source, but this reduces the overall intensity, i.e., the deposition rate. Fortunately there is another solution that we will discuss below.

The oven shown in Fig. 3 is useful for a wide range of elements, e.g. In, Ga, Al, etc., but high vapor pressure materials require modifications. For example, growth of III–V films requires that an excess pressure of Group V element be used, thus a large volume of source material is needed to minimize refills (and consequent contamination of the growth chamber). Furthermore, it has been found that fewer defects in the film occur when the V element vapor, normally composed of tetramers, e.g. As_4, are thermally cracked to dimers. This can be accomplished in a tube containing a heated filament on which the As_4 molecules impinge en route to the substrate. Fig. 4 shows a source oven for high vapor pressure materials equipped with a cracking filament. The container for the source material has a large volume that is located on the exterior of the growth chamber while the heated source tube (containing the cracker section) extends through a flange into the high vacuum. A valve separates the source container from the source tube to allow precise regulation of the beam flux, and also to allow the source container to be closed off from the growth chamber during bakeout and when the growth chamber is opened to air. This prevents excessive deposits of high vapor pressure material in the growth chamber. P_4 deposits, in particular, can ignite when exposed to air. It is also very important to prevent oxidation of the source material, since the presence of oxides in the beam flux can lead to structural defects in the film.

This extended, but certainly incomplete, explanation for the oven design is intended to convey the idea that a very large amount of both analysis and trial and error have been expended on designing the ovens to produce clean, reproducible sources of atoms or molecules. Fortunately for the experimenter, a large assortment of source ovens and other components are now available from commercial sources [17], and these have been thoroughly tested and specifically optimized for a wide range of elements and compound sources.

The beam shutters are simply plates that can be interposed across a beam to prevent the flux from reaching the substrate. However, even with these simple components, some important design features have been implemented after lengthy experience. Originally, the shutters were Ta plates positioned to pass rather closely in front of a source crucible to cut off the beam as effectively as possible. Experiments have shown that this configuration is not optimum because the Ta sheet will reflect radiation back into the source crucible, causing its temperature distribution to increase. Then when the shutter is opened, there will be an initially higher flux transient due to the hotter average temperature in the source. By positioning the shutters farther from the source ovens, angling

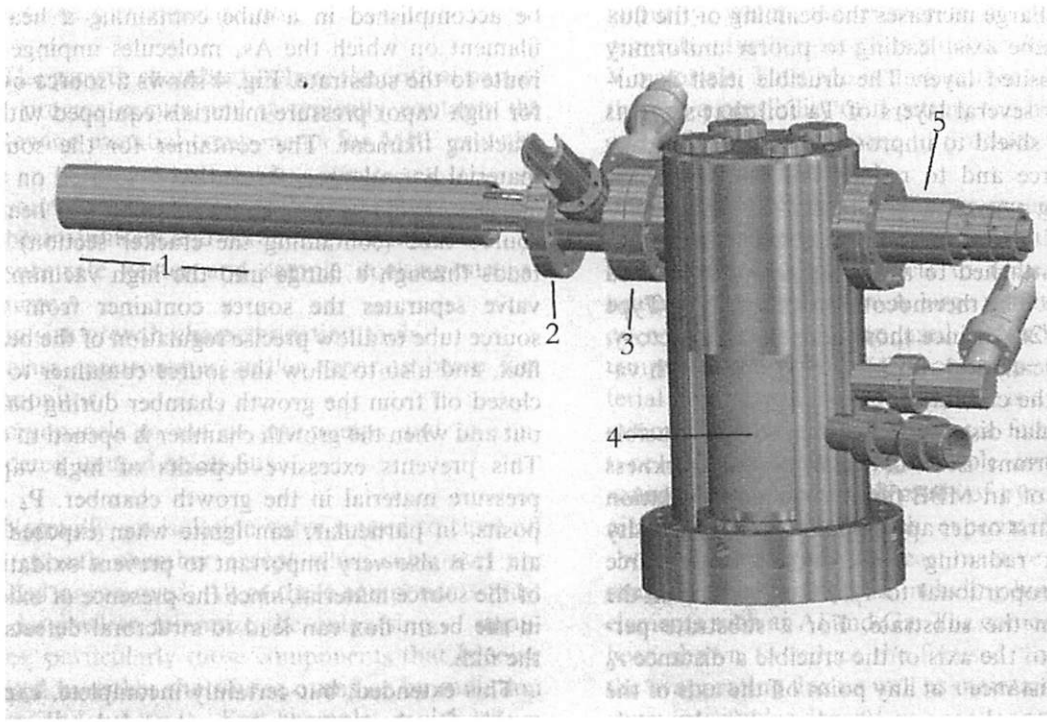

Fig. 4. Cutaway view of valved oven for high-vapor-pressure elements (e.g., As_4, P_4, etc.): (1) internal hot zone for molecular cracking of tetramers to dimers, (2) mounting flange, (3) valve seat for isolating charge, (4) externally heated large volume PBN insert crucible and (5) controlled leak valve stem (courtesy of EPI, Inc.).

them, and constructing them from PBN, there is less radiation reflected and consequently the shutter transient is greatly reduced. In the original configuration with closely mounted metal shutters, my students have observed transients in the metal beam flux of as much as 20% or more with a decay time of 30 s or so. Thus the effect is non-trivial, at least when very thin layers are grown. Again, the point to be made is that the strength of MBE is the control over growth conditions, and yet some very subtle effects must be taken into account in order to achieve that control.

Substrate mounting for epitaxy is important because quite often the precise control of temperature during growth can be critical. It is surprisingly difficult to make good thermal contact between a semiconductor wafer and an underlying metal heater. One successful approach that has been used since the early work on MBE is to bond the semiconductor wafer to a metal heater plate using a low melting metal such as In which provides a liquid thermal contact at the growth temperature. Indium is particularly useful because it is usually relatively insoluble in either the substrate or the metal heater plate, and because the vapor pressure is fairly low up to about 600 °C. Another advantage of the liquid metal bonding is that the surface tension of the liquid provides fairly strain free adhesion of the substrate to the heater so that clamping can be kept to a minimum; as a result, the epitaxial layers after growth do not show the thermal strain-induced slip lines that appear near the points of attachment on substrates which are firmly clamped to the heater unit. Finally, the metal bonding approach is very useful for odd shaped substrates, where no special provision need be taken for the geometry. There are problems with metal bonding, however. For higher growth temperatures the In will vaporize and may contaminate the growth surface; In induced defects can frequently be observed near the edges of In-mounted wafers. Also, if the wafers are

subsequently to be processed in a semiconductor fabrication facility, the In metal must be thoroughly removed from the back of the wafer before further processing steps to avoid contamination of the process line.

To avoid the use of In backing, the use of sample holders with radiative coupling between substrate and heater has become quite popular in recent years. The substrates, which must be of exact dimensions to fit a particular holder, are placed in an open ring, which then is locked into position in close proximity to a ribbon or wire heater wound so as to closely fill the area behind the wafer. Radiation from the heater that is more energetic than the band gap of the semiconductor wafer is absorbed by the wafer, and heats it rapidly because of the low thermal mass. To avoid temperature gradients due to hot spots directly over the radiant elements, a thermal diffusing plate made from sapphire or BN is often placed between the heater and the substrate to even out the radiation pattern. Aside from the advantage of not needing to clean the back of the substrate after growth, another advantage of this method of substrate heating is that the smaller thermal mass of heater and substrate allows faster changes in temperature.

Measurement of the substrate temperature is surprisingly difficult to do. Accurate temperature measurement with a thermocouple requires a good thermal contact between the thermocouple and the substrate material. Most semiconductor MBE systems are arranged so as to allow rotation of the substrate during growth (see next section); thus it is not feasible to bond a thermocouple directly to either the substrate or the heater. A non-contacting stationary thermocouple can be mounted directly behind the substrate to measure the radiant flux from the substrate, but this arrangement provides only a relative measure of temperature changes so accurate temperature calibration is necessary. To calibrate substrate temperatures, many investigators use an infrared optical pyrometer in order to be able to measure temperatures in the range 400–600 °C. If semiconducting substrates are used, the bandpass of the pyrometer must be chosen to be an energy window centered above the bandgap of the semiconductor; otherwise the pyrometer simply observes the radiation from the substrate heater element that is transmitted by the substrate. Further complicating matters are the changes in total emissivity that are produced by the growth of an epitaxial layer. Coating of the optical window through which the pyrometer observes the substrate can also cause problems [18,19]. Single temperature point calibration is possible using the melting of In or Sn or other metal eutectic structures attached to the surface of the substrate, or by RHEED observations of surface phase transitions, however these methods are obviously not as accurate as is possible with a plot of thermocouple reading vs. substrate temperature covering the entire temperature range of interest.

We mentioned above the problem of obtaining a uniform beam flux across a large substrate wafer. There is an additional aspect to consider, which is that in most instances more than one beam source is involved in the growth. For example, in Fig. 5, a Ga source is directed at a large substrate from one side of the substrate and an In source is directed at the other, with the purpose of depositing a binary alloy film of, say, $In_{0.5}Ga_{0.5}As$. It is clear from the figure that the angular distributions from the two sources change the ratio of In to Ga across the wafer. To avoid having a concentration gradient, the wafer can be rotated continuously throughout the growth. Since typical growth rates are ~1 ML/s the rotation rate should be fairly rapid to avoid the formation of a periodic or "superlattice" structure (see below). Needless to say, rotation of the substrate creates some design problems because the heater structure under the substrate generally needs to remain stationary (slip ring electrical contacts are not practical for the amount of power needed), and because of the tendency for hot bearings to freeze up in UHV. However, commercial MBE systems have solved these difficulties and are generally reliable.

3.3. Growth characterization and rate monitors

From the very beginning, MBE has benefited enormously by the inclusion of analytic tools that provide real time information on the topography of the surface, the condition of the vacuum and the

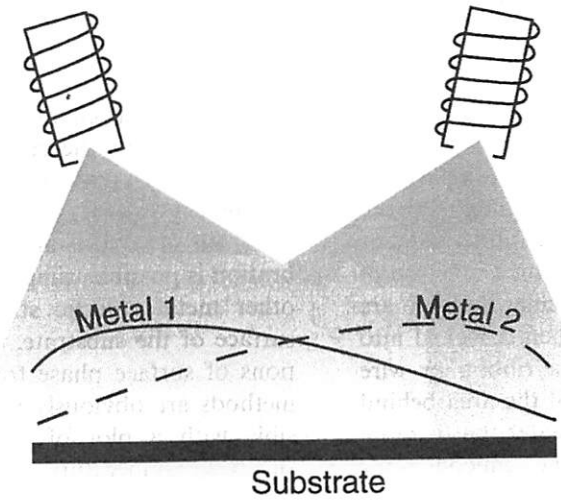

Fig. 5. Diagram showing the coverage distribution on a non-rotating substrate for dual opposing metal source crucibles.

precise growth rate. While the earliest MBE systems used a single chamber for both analysis and growth, the modern systems limit the analysis in the growth chamber to only those probes which provide real time information about the growth process, such as RHEED [5,20]. It is also useful to have some means for measuring the flux of atoms from the source ovens, since the growth rate may not be a good indication of the flux. The simplest way of determining beam flux is with an ionizing detector such as an ion gauge or mass spectrometer that can be placed directly in the molecular beam. While an ion gauge is compact and can easily be positioned in the beam, a mass spectrometer has the big advantage of distinguishing between various vapor species, and, in addition, can be used to detect problems with the vacuum. For beams that condense on cooled surfaces, such as Si, accurate flux measurements can be made with a quartz crystal microbalance; however uncertainties in the condensation coefficient as a function of the elevated temperature of the substrate make some other calibration methods essential [21]. Both types of equipment are commercially available with valves and shutters to minimize unwanted deposits. Atomic absorption by the beams provides a direct measure of the beam flux but requires some more complicated hardware [22]. Various other optical techniques have been used to observe or infer the growth rate of films, including infrared reflectometry [23,24] and ellipsometry [25,26]. However, growth rate measurements are most easily obtained from RHEED observations, which we describe below.

Undoubtedly the single most important analytical tool for the film grower has been the RHEED system for real time observation of the crystal structure of the growing film. Most MBE systems today either include an electron gun and phosphor screen for displaying RHEED patterns while the film is growing, or a low energy electron diffraction (LEED) system for viewing the structure before and after growth. The great advantage of RHEED is that the geometry allows the system to operate while the substrate is exposed to the molecular beams, and thus one can obtain real-time structural information. The appearance of a RHEED pattern not only shows when the surface oxide is removed (since the oxide is amorphous and gives rise to a diffuse diffraction pattern) but also shows the improvement in the surface ordering that occurs with the subsequent annealing. Clean semi-

conductor surfaces are reconstructed into a geometric configuration that minimizes the energy of electrons in localized bonds at the surface; this reconstruction is evident in the RHEED patterns as diffraction features positioned between the bulk, or "integral order" diffraction spots. The fractional order beams indicate that the surface unit cell is a multiple of the bulk spacing, e.g., the well-known Si(1 1 1) 7×7 structure. The presence of these "fractional order features" provides a qualitative measure of the long range ordering of the surface.

The most remarkable application of RHEED information, however, has come from the inference of the mechanism of film growth obtained from the time dependence of the intensity of the diffraction features. I have a vivid memory of a dark, stormy night in Minnesota (it was indeed during a blizzard) when L. Curtis Shannon and I were trying out our new MBE machine. We turned off the room lights to improve the view of the RHEED screen; because of the storm the room was almost completely dark. When Shannon opened the shutter controlling the Ga oven to begin the growth sequence, we observed with amazement that the diffraction spots were pulsing in brightness. As we continued the growth, the diffraction beams became steady, but after turning off the Ga beam for a period of time, then restarting the growth, the same behavior occurred. We were stunned, with no idea of an explanation. In the days that followed a steady stream of visitors came in to view our strange phenomenon, but no one could explain it. Unknown to us at the time, two other groups, one in England [27], the other a few miles away from us at the University of Minnesota [28], had come up with a very interesting explanation for this amazing behavior. On a properly cleaned and annealed surface that has been smoothed by the growth of a few tens of monolayers of material and annealed to improve the ordering, growth occurred mainly by the addition of new atoms/molecules to the edges of monolayer steps. (A monolayer on the (1 0 0) face of a crystal of GaAs is taken to be a bilayer of Ga plus As.) This is a mechanism in which the growth of each atom layer is largely completed before the next begins, i.e. a layer-by-layer growth mechanism [29]. Fig. 6 shows a sketch of the intensity of the specular RHEED beam as a function of time,

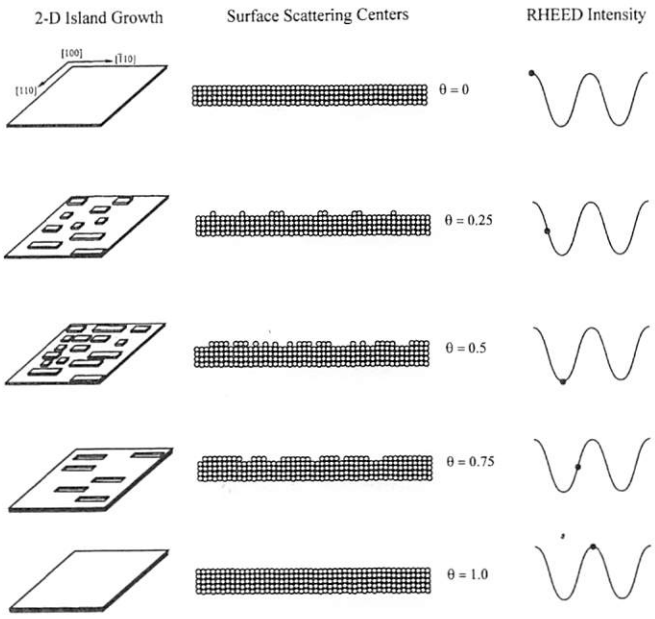

Fig. 6. Schematic diagram of the correlation of surface coverage of 2-D clusters with idealized RHEED oscillations.

beside two views of the condition of the surface. The arriving atoms first nucleate in 2-D islands if steps are not present on the smooth surface. Subsequently, arriving atoms can migrate to the existing step edges to complete the monolayer and return the surface to a smooth condition. Thus the surface cycles between smooth and atomically rough, with a period corresponding to the time to complete a monolayer of growth. The rougher surface causes more diffuse scattering of the RHEED beam, leading to a lower intensity of the diffracted beams. The correspondence between the RHEED oscillation period and the monolayer growth rate was clearly established by empirical measurements of film thickness after growth [27,28]. Thus the RHEED oscillations provide a precise method of measuring growth rates in real time. While RHEED oscillations were first observed in the growth of GaAs layers by MBE, a large body of literature now exists demonstrating the same effect in other materials including metals [30,31], and by a variety of growth processes including various types of chemical beam epitaxy (CBE), atomic layer epitaxy (ALE), and chemical vapor deposition (CVD). The general growth mechanism that produces oscillations is clearly widespread for a large variety of materials.

Besides providing a measure of the growth rate of a film, the RHEED pattern also gives useful information about the geometry of the surface, including the roughness. Soon after Cho introduced RHEED into GaAs MBE systems [5], he also demonstrated that the etched GaAs surface is relatively rough, but becomes much smoother with growth [11]. RHEED patterns clearly show the improvement of surface geometry, since the smoother surface has diffraction features that are streaked normal to the surface due to the more 2-D character of an atomically flat surface. The improvement of the surface is a direct result of the fact that the arriving atoms/molecules are mobile on the heated substrate and predominantly find bonding sites at step edges. Thus there is a strong tendency for terraces to enlarge by the accumulation of material at the edges [13,32].

RHEED also serves (somewhat indirectly) to identify the chemical nature of the surface. Semiconductor surfaces typically reconstruct in order to minimize dangling bond densities at the surface. In the case of compound semiconductors, where the crystals are often composed of alternating layers of metal and nonmetal atoms, the low index planes can either be predominantly metallic or nonmetallic. This is evident in the diffraction pattern since the reconstruction changes as the surface composition changes. A well known example is the GaAs(1 0 0) surface, where the As-rich reconstruction, which is observed during the growth of GaAs under an excess of As, is described as the 2×4 structure, while the Ga-rich structure which forms at a lower As to Ga flux ratio is described as a 4×2 structure. There are a number of other structures which have been observed on this particular surface, which depend on the growth temperature and the ratio of As to Ga in the arriving flux [33]; however the transition from one structure to another, such as from the principal 2×4 As-rich structure to the Ga-rich structure, can be observed (from the RHEED pattern) to occur very rapidly (<1 s) when the As beam is interrupted during MBE growth (at rates of ~ 1 ML/s), indicating that the transition is the result of submonolayer changes in surface concentrations. The point we wish to make is that the surface structure is quite sensitive to the stoichiometry of the top layer, and this can be an important parameter in determining growth conditions.

Thus the RHEED system provides a tool for monitoring growth rate, for a qualitative measure of surface topography and for monitoring the surface structure that, in certain instances, can provide a measure of the surface composition. Also important to the user is that the RHEED system is relatively insensitive to the ambient in the growth chamber, that is, RHEED images can be obtained with equal clarity either while beams are incident on the substrate or when growth has been terminated and the substrate is cooled; furthermore the geometry is such that there is no part of the RHEED system positioned in front of the sample to block access to the surface since the RHEED beam arrives at a glancing angle. RHEED analysis of crystal growth dynamics has, in fact, become a separate field of study, and a definitive summary of recent work has been published by Braun [34].

There are a few potential problems with the use of RHEED in a deposition system. The phosphor screen used to display the diffraction pattern can gradually become coated with the deposited material, but it is not too difficult to clean the glass window and replace the phosphor. Glass windows are presently available commercially which can be kept at an elevated temperature to reduce the condensation of film material. For film growth where film purity and crystalline perfection must be optimized, it is undesirable to flood the growing surface with energetic electrons because beam-induced cracking of residual gases can take place, thus it is generally preferable not to use the RHEED for an extended time on the actual surface of the growing film. Many crystal growers will have a small auxiliary substrate that can be used to establish the beam flux and growth rate prior to actually growing on the large substrate intended for device fabrication.

An alternative to RHEED for growth rate analysis is the use of a thickness measurement that is not dependent on the angular position of the substrate, and which will not cause degradation of the film. Optical methods that do not depend on the angular position of the substrate are becoming more popular for the measurement of deposition rates. One of these techniques relies on the interference in IR reflectivity when a film is deposited on a substrate with different dielectric constant. In the simplest version, the IR pyrometer observing the substrate at constant temperature measures the change in emission as the film grows [23,35]. This method requires that the film be relatively transparent to the optical band detected by the pyrometer. It also requires that the pyrometer window be kept free from deposits that would reduce the optical intensity. A clever way to avoid deposits on the window is to use a Si surface as a mirror to reflect the optical emission from the substrate and yet avoid a direct path to the window for atoms/molecules desorbing from the substrate [18]. The reflectivity of the Si seems to be little affected by a thin film of deposited material from the growth, and the longer indirect path to the window prevents coatings from forming. Heating the optical windows is also an effective way in which to keep them free of coatings [22].

Other workers have used spectral ellipsometry to obtain real time information about surface composition, optical properties and growth rate of films in an MBE system [36,37]. Spectral ellipsometry measures the reflectivity of the perpendicular and parallel polarized components of a light beam over a range of wavelengths in order to determine the complex index of refraction and layer thickness of a transparent film on a reflective substrate. The index of refraction can be related to the composition using the effective medium approximation; thus spectral emissivity provides significantly different information than does RHEED. Furthermore, provided a substrate holder which can rotate precisely in the plane parallel to the substrate surface is used, it is possible to obtain this information while the substrate rotates to maintain uniform growth over a large area. One limitation of this method is again the need to prevent condensation on the optical windows.

Maracas et al. [37] used spectral ellipsometry to monitor beam flux ratios. The RHEED oscillation technique for measuring growth rate (described above) is primarily an indication of the metal flux, since the non-metal, As in the case of GaAs, is provided in excess. Thus the growth rate is limited by the metal flux. The As flux can be measured only approximately using the mass spectrometer. However, after depositing a known amount of Ga on GaAs (determined by the growth rate), these investigators then determined the length of time required for the As beam to convert the Ga into epitaxial GaAs based on measurements of the dielectric function as it returned to the values for GaAs. There were several experimental challenges that were overcome, a principal problem being the design of a substrate manipulator with sufficient mechanical stability to allow measurements during growth when the substrate was heated.

Even though the vapors in the chamber used for epitaxial growth can produce deposits of the film constituents which may form insulating films on the electron optics of analytical tools such as AES, there is always a need for additional tools in the growth chamber to obtain more real time information about growth. Chambers et al. [38] describe a system that uses the RHEED beam to

excite Auger electrons from the growing film. The electrons are analyzed in a small, high throughput spectrometer which does not block the substrate from the molecular beams. The system described by Chambers et al. is used to grow epitaxial oxide films and contains electron beam heated sources to provide metal beams (Mo and Cr) and an electron cyclotron resonance (ECR) source to provide O atoms. The system is also provided with quartz crystal oscillator monitors to measure beam fluxes; however the in situ AES capability showed clearly that the CRO monitors gave an incorrect measure of film composition because not all of the incident flux was incorporated into the growing film on the 750 °C substrate. The AES analysis has also been crucial in determining the composition of mixed metal oxides during growth. The system contains a separate analysis chamber with both XPS and X-ray diffraction capability. The message from these experimenters is quite clear: as the material systems become more complex, more in situ analytic capability becomes essential. Because of the UHV environment, many of the new tools of surface physics are easily accommodated within the growth chamber for this purpose.

4. General mechanism of molecular beam epitaxy growth

The information provided by these techniques has been absolutely essential in understanding how to optimize the growth process and has given surface scientists some remarkable insight into the nature of the dynamics of the surface of a growing crystal. The in situ studies of surface structure by electron diffraction have led to an understanding of the dynamic motion of steps on a growing surface, while the use of tools that unveil the details of the atomic structure of the surface, i.e., the scanning electron microprobe, has shown that MBE growth produces extremely well ordered surfaces on many materials. This makes it possible to study the detailed structure of such surfaces without the complications resulting from contamination or the loss of constituents due to the preparation process. Furthermore the experimenter has great control over the precise conditions of the surface, i.e., the surface chemical composition can be altered at will and the effect on the arrangement of surface atoms can be studied. In this section we will describe in rather general terms the prevailing wisdom about growth mechanism of MBE films. Tsao has reviewed the theory of this basic growth model in considerable detail [33]. A number of elegant STM studies on Si surfaces exposed to Si vapor have corroborated most of the elements of this general scheme [39,40].

The etched substrate surface after the thermal removal of surface oxide is typically rough on an atomic scale as shown by a spotty RHEED pattern and by TEM observations that indicate rough features as much as 10 nm above the surrounding flat areas. The degree of roughness is very much a function of the polishing treatment and the subsequent annealing in UHV. Once epitaxial growth begins, however, the surface rapidly becomes much smoother and the RHEED pattern shows this smoothing by developing streaked diffracted features [20]. This smoothing of the surface was predicted by Frank and van der Merwe [41] based on a model that involved the migration of arriving atoms/molecules over flat terraces on a rough surface with incorporation into the lattice at step edges. Wider terraces have a larger collection area for vapor species and thus have bounding step edges that advance more rapidly than those bounding narrow terraces. The consequence of this step growth is that terraces tend to become similar in size, the smaller terraces disappear and the surface becomes smoother. Eventually the surface evolves to a nearly uniform array of terraces, as can be seen in the STM image of a Si(1 0 0) surface in Fig. 7 [42]. An interesting feature of the Si(1 0 0) step edges is the way in which the edges alternate between relatively smooth and relatively ragged. This has to do with the manner in which the Si surface atoms reconstruct by forming dimer chains to minimize the number of unpaired electrons at the surface; the smoothness of the step edges depends on whether the reconstructed surface has the Si dimer chains lying parallel to or perpendicular to the step [43]. However, the main feature of the surface to consider is the nearly perfect flatness of the terraces.

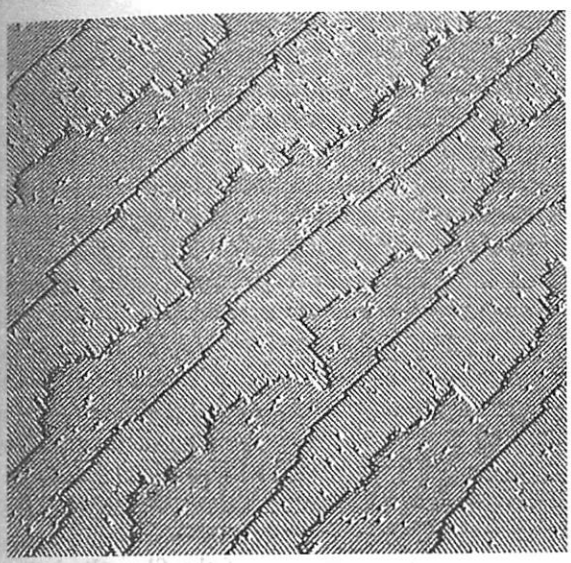

Fig. 7. Scanning tunneling microscope image of a Si surface, ~0.3° off (1 0 0) orientation showing the type A steps (Si dimers parallel to steps) and type B steps (Si dimers perpendicular to steps). Uppermost part of the surface is at lower right, with downward tilt to upper left. Scale is ~110 nm square (courtesy of Prof. Max Lagally).

Once the surface becomes atomically smooth, with only an array of monolayer steps as shown in the figure, further growth can proceed in either of two modes, depending on the nature of the surface and the mean free path of atoms/molecules on the surface. If the terrace width is comparable to or less than the diffusion length of atoms, then under normal growth conditions it is possible for the atoms arriving on the surface to diffuse to step edges, and growth occurs by the steady growth of steps, which advance across the surface, described as the "step flow" regime. Step flow will occur on surfaces similar to that shown in Fig. 7 that are slightly off the principal plane axis, i.e., vicinal surfaces on which the terraces are not too wide, at temperatures, which are high enough to provide good surface mobility. Aoki and coworkers have shown that the difficult problem of producing flat interfaces in the strained growth of $In_xGa_{1-x}As/In_yAl_{1-y}As$ grown on InP can be solved by using "step flow" growth on the (4 1 1) surface [44]. On the low index (1 0 0) surface, these authors observed that the wider terrace width does not permit step flow growth and the interfaces are much rougher, as indicated by broadening of the photoluminescence peak.

The other growth mode occurs when the terraces are wider than the diffusion length. In this instance 2-D nucleation occurs on the terraces, which leads to periodic roughening and smoothing of the surface as each monolayer fills in again. This is the situation that produces the dramatic oscillations in the RHEED intensities, discussed above. It is not surprising that increasing the surface mobility (by, for example, increasing the temperature) can lead to a transition from the 2-D nucleation mode to the step flow mode, which is indicated by a disappearance of the RHEED oscillations as the temperature increases. Neave et al. have used measurements of this type to infer the kinetic parameters and diffusion length of Ga atoms on vicinal surfaces whose terrace length can be calculated from the crystal orientation [45]. Alternatively, lowering the temperature can cause the onset of RHEED oscillations, at least until the surface mobility decreases so much that atoms are no longer able to form large islands. Clearly, surface mobility is a key element in determining growth mode.

5. Beam flux and stoichiometry

An important consideration is the control of the composition of the deposited film. The material properties of semiconductors are particularly sensitive to deviations from stoichiometry, where vacancies of one or the other of the components may form electrically active centers. Clearly this would be undesirable, and yet we have previously indicated that precise control of the temperature of the ovens providing the constituent vapor flux is difficult to achieve.

(A) Elemental growth: The simplest growth system is one with only a single component, and Si, because of its technological importance, has been studied more than any other material system. In the case of the growth of a single element, compositional control is not an issue. What is necessary is a source of Si vapor sufficiently intense to provide a growth rate much larger than the

contamination rate from residual impurities. While solid Si has been occasionally used as a Si vapor source, the vapor pressure is so low at the melting point, $\sim 4 \times 10^{-4}$ Torr, that the deposition rate is too low to deposit more than a few monolayers. Therefore typically in Si MBE the Si vapor is derived from an electron beam heated source crucible, to obtain a large enough flux at the substrate. Thus the term "beam" is used very loosely, since the Si atoms simply evaporate radially outward from the hot zone of the evaporator. Because of the low vapor pressure of Si at the typical growth temperature of ~600 °C, the condensation rate of the Si vapor is near unity with very little reevaporation.

The vapor pressure of Ge is approximately two orders of magnitude greater than that of Si, but is too low at the melting point to use a subliming source. It is possible to derive a sufficient flux of Ge from a molten charge in a heated crucible to grow an elemental film at very slow growth rates, but it is much better to use an electron beam heater for the source to avoid contamination due to slow deposition. Again, the condensation on the substrate is essentially unity. In any event, stoichiometry is not an issue for a single component material.

(B) Compound growth: When the films have more than one constituent, the problem of compositional control becomes an issue. We can consider three possible scenarios, depending on the vapor pressure of the constituents.

In the first case, if both constituents have low vapor pressure, so that the adsorbed species have a long surface lifetime before reevaporation, then the problem for the crystal grower is simply to control the flux of both kinds of atoms/molecules to produce the desired ratio in the film. In other words, the film composition is determined by the arrival rate of atoms at the surface. An example of this is the alloy Si_xGe_{1-x} where there is complete miscibility in the solid phase and reevaporation of either element is minimal. The challenge then lies in precise temperature control of the sources. As indicated above, one-degree temperature change produces on the order of 2% variation in beam flux in sources using the evaporated elements. However, a small deviation from the desired ratio of Si to Ge is unimportant, since Si and Ge are incorporated on equivalent lattice sites. A variation of the ratio of Si to Ga does not lead to vacancy formation and thus does not have a major effect on the electrical properties.

The second possibility is one in which one of the constituents has a higher vapor pressure as an element than in the compound. For example, elemental As has a vapor pressure at the typical GaAs growth temperature of 550 °C that is roughly seven orders of magnitude larger than the vapor pressure of As in equilibrium with GaAs. As we have indicated above, a (nearly) stoichiometric film can be obtained by supplying an excess flux of As (typically as As_2 molecules) to react with all of the arriving Ga; the unreacted As will be reevaporated from the surface. (We are so far ignoring the defect structure of the film; the beam flux ratio of As to Ga can have a significant influence on the concentration of vacancies of either species.)

The third possibility is that both of the constituents have higher vapor pressures as elements than in the compound. This is true for most of the II–VI compounds. For these materials, the first monolayer of either component can adsorb on the substrate, but subsequent layers will be less strongly bound due to the weaker elemental bond, and at elevated temperatures will simply desorb. By exposing the substrate alternately to each beam long enough to deposit successive monolayers of each component, stoichiometry is achieved because only a monolayer will stick on each exposure, and each monolayer reacts with the preceding one. This process has been termed ALE [46,47]. ALE is useful in producing a film consisting of alternating layers of the constituents, e.g., the ideal configuration of the zincblende and wurtzite structures in the $\langle 100 \rangle$ direction consisting of alternating layers of each species. ALE has the advantage that uniform coverage is not as dependent on surface migration as is MBE, since the components arrive at adsorption sites from the vapor or by rapid migration from a physisorbed layer. As a result, ALE is particularly useful in providing uniform coverage over non-planar surfaces (although in this case it is often true that the substrate is not a single crystal and so the film may not be epitaxial).

The ALE approach can also be used to grow materials of the second type described above. For example, GaAs can be grown by exposing the substrate alternatively to first Ga and then As beams separately. Since the shutters on a standard MBE system can usually be programmed to operate automatically, the timing can be adjusted to any desired cycling of beams. It has been observed that the surface mobility of adsorbed Ga atoms is significantly greater when As is not incident; thus if the shutter timing is such that Ga begins arriving in the absence of an As flux, there is greater smoothing of the surface. This type of growth has been termed migration-enhanced epitaxy (MEE) [48], and is reported to improve epitaxial growth at low temperatures, where the reduced mobility of the metal atoms normally leads to roughening of the surface. It may be particularly useful when growing a heterostructure where the different metal species may have widely differing surface mobilities at a fixed growth temperature. This would normally lead to a roughening of the interface as soon as the lower mobility metal is deposited.

A clever variant of this approach is to phase-lock the shutter operation to the RHEED oscillation period to begin a heterointerface only at the time when the maximum in the RHEED intensity indicates that optimum smoothness of the growing surface has been achieved. For example, in very narrow quantum wells, the variation in well width produced by disorder in a single layer of atoms can produce noticeable degradation in the optical properties such as increasing the width and reducing the intensity of the main recombination peak in the photoluminescent spectrum. In Fig. 8 we show schematically the structure of a quantum well device with interfaces formed when the surfaces are relatively rough and when the surfaces are maximally smooth. Superlattices grown by phase-locked epitaxy (PLE) have shown significant improvement in optical and structural properties over superlattices grown with shutter operation at a random phase of the surface molecular coverage [12,49].

6. Surfactant assisted growth

We have emphasized the role of surface migration in improving the crystalline quality of

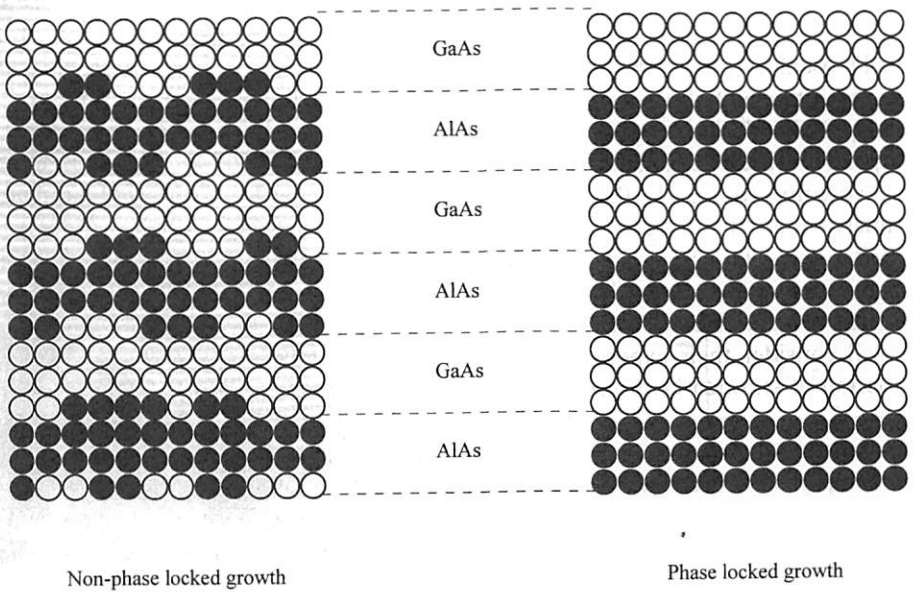

Fig. 8. Cross-sectional diagram of superlattices grown with random shutter timing and with shutters timed to change at completion of monolayer growth, i.e., PLE.

epitaxial films. If the surface species are able to migrate to step edges, a planar growth interface is maintained. However, if the temperature is too low, mobility may not be great enough to achieve a thermodynamically stable structure, and smooth growth may not result. Recently several authors have explored the use of impurities described as "surfactants" to improve surface mobility; these are materials that act to weaken the bonding of the arriving constituent atoms to the substrate, thus enhancing their surface mobility. The impurities themselves are almost entirely rejected from the growing film. For example, Okada and Harris have found that irradiating the surface of GaAs during growth with atomic H permits the growth temperature to be lowered from 580–600 °C to as low as 330 °C with no loss of structural quality of the epitaxial film [50]. There is much that is not clear about the process, e.g., how much H is adsorbed and how does it leave the growing film? Presumably the H film is segregated to the surface as the film grows with little incorporation into the film. Nevertheless the H (derived from a tungsten filament heated in H_2 gas) clearly makes a significant difference in the growth kinetics. Hydrogen is also used as a surfactant in the homoepitaxial growth of Si [51]; however these authors believe that H on Si *reduces* the surface mobility of the Si. The evidence for reduced mobility was the much longer persistence of RHEED oscillations on the H-covered surface, which was interpreted as indicating a shorter mean free path for the arriving Si. However Pillai et al. [52]; have observed similar RHEED behavior and have come to exactly the opposite conclusion, namely, that the longer oscillation persistence indicates a *greater* surface mobility because the surface layers are more likely to be completed without 2-D nucleation of the next layer occurring. We will consider their experiment further in the discussion of strained layer growth.

7. Heteroepitaxy, superlattices and quantum wells

One of the most amazing and important consequences of the 2-D growth by MBE is the ability to produce structures consisting of alternating thin layers of two different semiconductor materials with similar crystal lattice constants. If this stack of layers is grown in such a way that there is a periodicity to the structure, it is described as a "superlattice" since the period of the structure is larger than the lattice spacing in the crystal. The fact that such structures can be grown routinely with individual layers as thin as a few monolayers, and with the total number of layers essentially limited only by the grower's patience says a great deal about the growth process. Cross-section transmission electron micrographs clearly show that the perfection of the superlattice is as good at the end of the growth as it is at the beginning, if not better! Fig. 9 shows a repeated stack of four monolayers of GaAs on four layers of AlAs, with the growth continuing from the bottom to the top. In order for the interfaces to improve, the starting surface must have been almost atomically smooth, with only a regular array of monatomic steps, as in Fig. 7. Furthermore, this nearly ideal surface must have been preserved after the completion of each layer, otherwise the surface irregularities would quickly become magnified to an extent that the interfaces would lose their definition as the layers

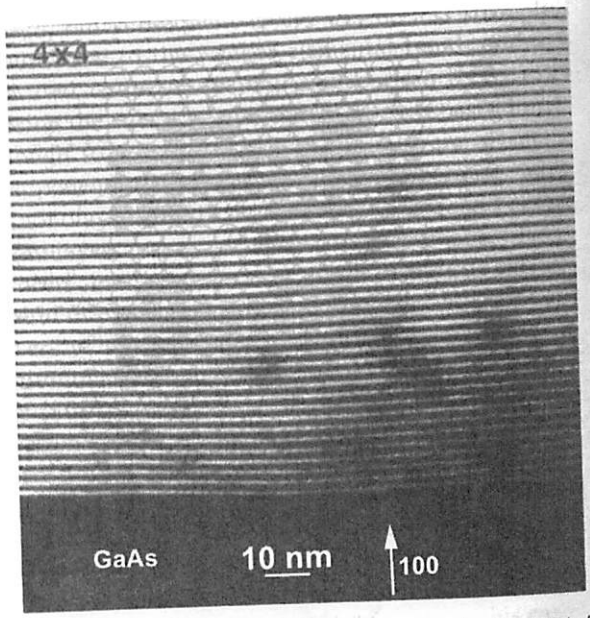

Fig. 9. Cross-sectional transmission micrograph of a GaAs/AlAs superlattice with four layers of each material in a period (courtesy of Lucent Technologies, Inc.).

accumulate. While GaAs and AlAs are an important example of materials with nearly the same lattice constant, this is, of course, only rarely true. For other III–V compounds it is more likely that the superlattice structure will be strained, unless efforts are made to use ternary or quaternary alloys, e.g., $In_xGa_{1-x}As$, that are lattice-matched to each other and/or to the substrate. We discuss strained layers in the next section.

"Quantum wells" are produced by depositing a narrower band gap semiconductor between layers of a different material, with a wider bandgap than the well material. If the thickness of the narrow bandgap center well is much less than the wavelength of electrons in the material, in the range from a few to tens of atom layers, the electron energy levels are discrete in the well, i.e., "quantized" and the structure is described as a quantum well. A structure comprised of a periodic sequence of quantum wells is a superlattice. Quantum wells and superlattices are of great interest because the electronic and optical properties are quite different from bulk semiconductor material. Many of the early theoretical predictions of solid state physics have been precisely confirmed in these devices that so closely approximate the ideal models used in the theory. For example, the energy levels of electrons in a quantum well no longer form a continuum of states as they do in the conduction band of a bulk semiconductor, but rather they are "quantized" into discrete levels by the fact that the quantum well has one dimension, perpendicular to the surface, which is of the order of the wavelength of electrons in the film. This can lead to a number of strange and sometimes useful properties. Instead of transmitting light of energy less than the band gap and absorbing all wavelengths above the band gap, as in a bulk semiconductor, a quantum well absorbs light only at energies corresponding to the energy difference between the valence band and the discrete levels in the quantum well. This leads to an absorption spectrum with a series of peaks at the edge just below the continuum. Of course, it would be difficult to measure the minute optical absorption of a single quantum well, so the experiment is carried out on a stack of many wells, which are so reproducible to make that all are the same width and hence show the same spectrum. This, in fact, was the historic experiment carried out by Dingle et al. that was mentioned in the discussion of the history of MBE [10].

Another technologically significant phenomenon observed with quantum wells is the greatly increased electron mobility that occurs, particularly at low temperatures. When the surrounding wide bandgap barrier layers are doped with donor impurities while the quantum well itself is undoped, the electrons produced from the ionized donors drift into the quantum well, i.e. spill over into a region of lower energy, where transport parallel to the layer can occur without scattering from the ionized donors. In effect, the free carriers have been separated physically from the ionized donors by confining or "modulating" the doping to only the barrier regions. This produces a much higher electron mobility than would occur in bulk material doped to produce the same electron density. Field effect transistors, which utilize modulated doping, are known as high electron mobility transistors, or HEMTs; they are also described as modulated doped FETs, or MODFETs [53]. Fig. 10 shows a graphical representation of the conduction band in a MODFET. Because of the separation of positive and negative charges, an electric field is produced which shows up as curvature in the conduction band edge at the boundary between the barrier and well. In order to better separate the electrons from their parent ions, a small, undoped spacer layer of AlGaAs is normally included in the structure and is indicated in the diagram.

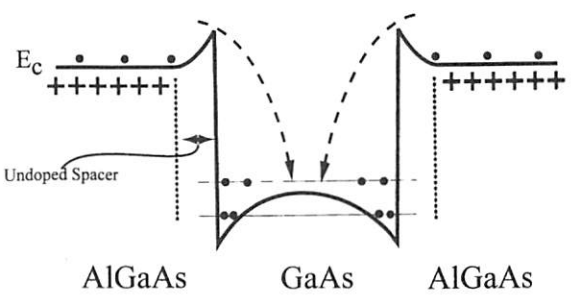

Fig. 10. Schematic diagram of the conduction band in a AlGaAs/GaAs MODFET. Ionized donors represented by (+), electrons represented by (•). Diagram includes an undoped spacer in the AlGaAs to improve the physical separation of charges to reduce scattering.

Much of the early work on superlattices and quantum wells was based on the material system GaAs–$Ga_xAl_{1-x}As$ because the Al content in the alloy increases the bandgap and yet the two binary compounds have nearly the same lattice constant. The MBE process, at least in principle, makes possible the growth of selected ternary and quaternary III–V alloys, since the composition of the film can be controlled by the relative beam fluxes. Fig. 11 shows the lattice constant vs. bandgap for III–V binary materials and their ternary alloys. It is evident that the lattice constant varies widely for the various alloys. If one is restricted to binary compound substrates, the mismatch between ternary film and binary substrate can be substantial. Thus the technology for growing strained layers is extremely important in order to have access to the full range of materials and properties offered by the III–V alloy family, as well as other families, notably, Si–Ge.

8. Strained layer epitaxy

The subject of strain in epitaxial layers is extremely important because of the obvious fact that most often heteroepitaxial layers are grown on a substrate with a different lattice constant. Clear evidence for the strongly ordering nature of a clean substrate is given by observations that the initial growth of a film mismatched to the substrate often occurs with the film adopting the two-dimensional spacing of the substrate, i.e., the film growth is "pseudomorphic" with the substrate. Fig. 12 illustrates the difference between commensurate, or lattice-matched growth, pseudomorphic growth with uniaxial distortion of the film, and relaxed, incommensurate growth. Depending on the amount of mismatch, the distortion of pseudomorphic growth causes increasing strain in the film to an extent that relaxation eventually occurs with the generation of misfit dislocations in the plane of the interface. Frequently the relaxation is catastrophic with extensive slip, and disruption of the planarity of the surface. A number of calculations have been made to determine the critical thickness of the epilayer at which the strain is sufficient to cause the generation of dislocations. The original theory of Matthews and Blakesley was a straightforward mechanical energy balance, and provides a reasonable fit to more recent experimental data [54]. Fig. 13 is a plot of the variation of critical thickness vs. percent mismatch for the system of Si_xGe_{1-x} on Si. The figure shows that there are definite limitations on the thickness of pseudomorphic growth. It should be noted that the exact value of critical thickness depends on the elastic constants for the film material; thus this is not a universal curve. People and Bean [55] have discussed the more detailed considerations for strained layer growth and have modified the curves somewhat, although in general, the simpler theory provides a good fit to the data.

There are various ways to get around the mismatch problem. As indicated in Fig. 13, as long as the film thickness is below the critical thickness, a planar film can be grown on a mismatched substrate. Strain effects will, however, alter the band structure of the film, which may be an important consideration for subsequent experiments. The traditional method of dealing with mismatch between film and substrate has been to grow a graded buffer layer, where varying the composition from that of the substrate to that of the film gradually alters the lattice constant of the film.

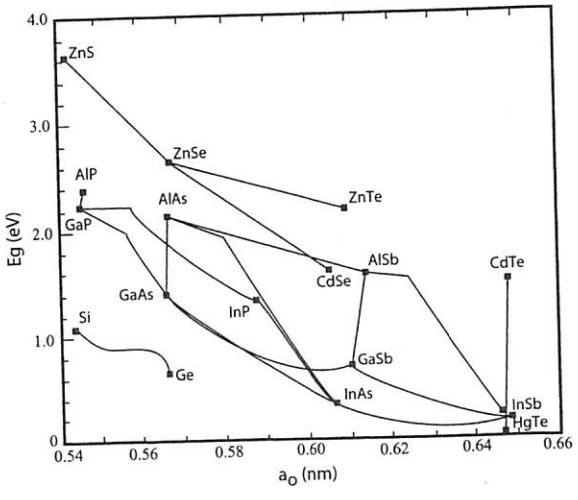

Fig. 11. Plot of band gap vs. lattice constant for elemental, III–V and II–VI semiconductors. The solid squares represent the values for the indicated binary compounds; the lines show the band-gap values for the intermediate ternary alloys.

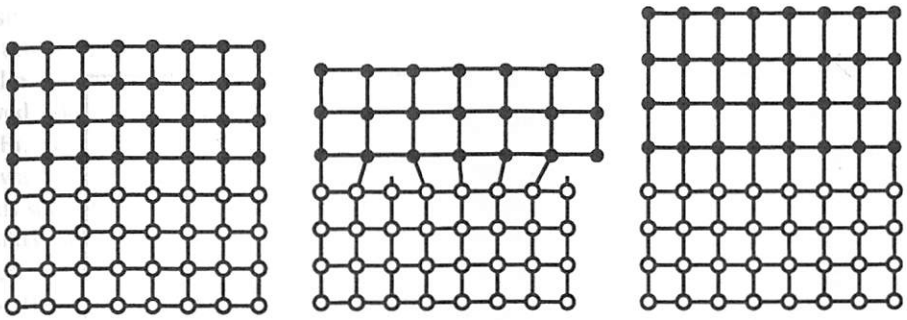

Fig. 12. Cross-section schematic of atomic arrangement in various modes of epitaxial growth: (a) lattice-matched, commensurate growth; (b) lattice-mismatched, relaxed growth; (c) lattice-mismatched, strained pseudomorphic growth.

MBE is a particularly effective method to do this because the relative beam fluxes of constituents can be varied in a very controlled fashion; thus it is easy to begin by growing e.g., GaAs and then to direct a gradually increasing In flux toward the substrate by a programmed temperature sequence of the In source to eventually deposit a film of $In_xGa_{1-x}As$ where x can be as large as 0.3 or greater for buffer thicknesses of the order of 0.5 μm. (InP is normally used as a substrate for larger values of x.) Graded buffers, however, do not eliminate stress; they merely distribute it over a larger volume of material, and threading dislocations are often observed in TEM studies of such structures.

Another approach is to introduce a strained superlattice buffer, where alternating layers are strained either in tension or compression. This has the advantage that dislocations are often constrained to lie parallel to the interface, and thus do not extend into the final layer of interest. The growth of strained superlattices with the alternate layers in compression and tension is an active research area that is much too broad for the scope of this chapter. Ref. [56] provides an excellent presentation of the current status of research in this field [56].

There is an additional problem with strained layers, which is that strain can be relieved by the rejection from the bulk of the species causing strain, i.e., there can be strain-enhanced diffusion to the surface with the accumulation on the surface of the atoms causing strain. For example, InGaAs quantum wells grown with GaAs barriers on a GaAs substrate show a skewing of the In spatial distribution toward the surface as a result of such strain-enhanced outdiffusion and excess evaporation of the In [57]. Not only can this occur with the layer constituents, but doping impurities can also be rejected or segregated to the surface if they introduce sufficient strain into the lattice. This effect can be useful in certain instances (see the discussion below on the use of surfactants to facilitate growth), as well as being a problem.

While in some circumstances the structure of the substrate may force the epilayer into a metastable pseudomorphic configuration, at sufficiently high temperatures the surface layer is quite mobile, and as a result will attain a thermodynamically stable structure that depends on the energetics of surface and interface and also on the lattice strain. This may lead to the formation of islands of the epitaxial material, either on the clean substrate (which is described as Volmer–Weber growth [58]) or after the growth of a monolayer or so (Stranski–Krastanov growth [59]) instead of a smooth surface by the desired layer-by-layer (Frank–van der Merwe [40]) growth. Several investigators [60,61] have shown that the presence of an intermediate layer, a surfactant, can reduce the tendency for island formation and at the same time can reduce the temperature needed for surface mobility. In the growth of Si/Ge heterostructures, As and Sb have proven useful for this purpose. Arsenic in particular was

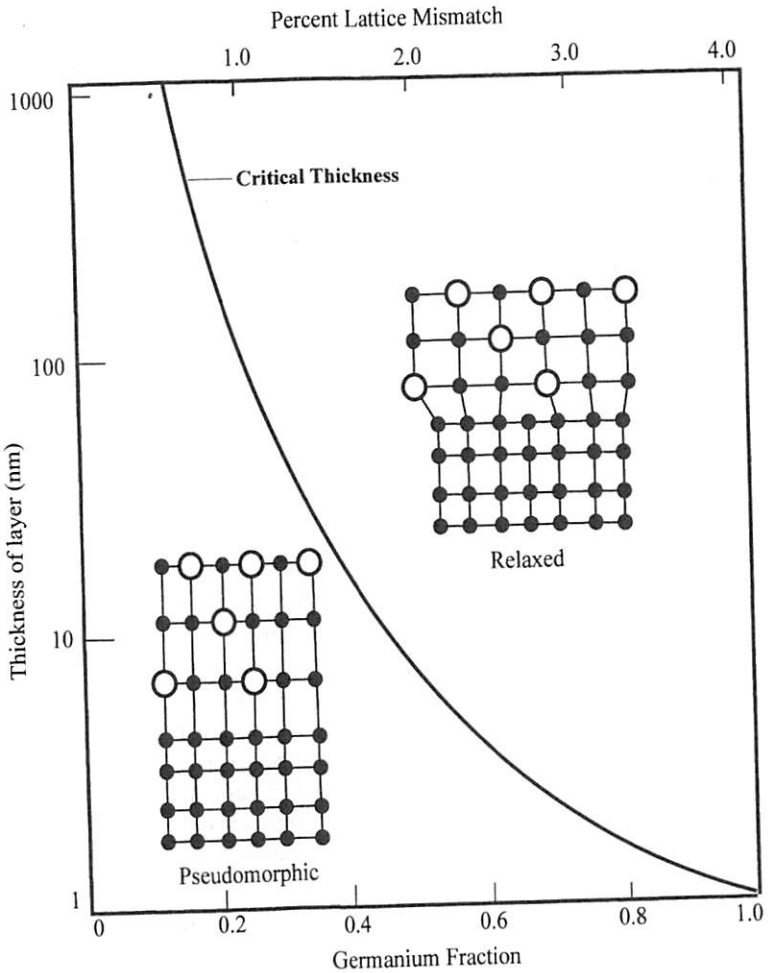

Fig. 13. Transition between pseudomorphic and relaxed growth modes for Si_xGe_{1-x} alloy films deposited on Si. The solid line is based on the calculations by Matthews and Blakesley [54].

shown to promote the growth of flat Ge layers on Si, and to prevent the incorporation of Ge into the growing Si layer. In both cases only monolayer amounts of the surfactant are required, since the As and Sb are strongly segregated to the growth surface. An As layer in particular permits the growth of very thick layers of Ge on Si, since strain is relieved not by misfit dislocations but by stacking fault arrays ("V defects") which do not destroy the planarity of the surface [60]. Unfortunately, both As and Sb are doping impurities in the Group IV elements, and sufficient amounts of the surfactants are incorporated into the growing films to alter the doping.

Sn does not act as a dopant in Si/Ge, since it is isoelectronic, i.e., has the same electronic configuration as Si and Ge, and it has also been found to facilitate the growth of Ge layers on Si and to minimize the segregation of Ge into the subsequent Si layer [62]. It is strongly segregated to the surface of the growing film so that only monolayer quantities are needed. There is a major difficulty with Sn-mediated Ge growth that is that the Ge layer thickness cannot exceed about 4 monolayers to avoid Ge island formation, i.e., the growth mode is clearly Stranski–Krastanov. Strained layers of $In_xGa_{1-x}As$ on GaAs with $x = 0.3$–0.4 have been grown using Bi as a surfactant [52]. The Bi

was co-deposited along with the constituents, yet was undetectable by X-ray diffraction on the completed film. Atomic force microscopy after growth showed island formation both with and without the Bi, yet the islands were much larger when the Bi was included, and, as was mentioned in the previous section, RHEED showed enhanced surface mobility when Bi was included. While these films were not the perfect planar structures to be wished for, there was certainly improvement in the film morphology with the use of a surfactant. Clearly, the use of surfactant-mediated growth is a very interesting research area that is relatively unexplored.

Recent reports of the use of compliant substrates have indicated another alternative to dealing with strained growth [63,64]. Rather than attempting growth on a rigid substrate that produces stress in the growing film, if growth occurs on a thin film substrate that is able to deform to match the growing layer, it should be much easier to grow thicker films that do not relax by dislocation generation. GaAs and AlAs have only a small mismatch (~0.15%) and have been favored for electronic devices because of the bandgap offset and because of the ease in growing thin layers of either material on the other. In addition, AlAs is chemically much more reactive than GaAs, which makes it possible to detach very thin films of GaAs from an AlAs substrate (or more likely, from a thin layer of AlAs on a GaAs substrate) by chemical etching. Thus it is possible to grow a very thin film of GaAs on a AlAs substrate or layer, bond the GaAs to a second substrate by a flexible adhesive such as liquid In and subsequently detach the thin GaAs from the original substrate by chemical etching in dilute HCl. The resulting structure consists of a very thin film of GaAs bonded by a compliant material to a supporting structure. The GaAs is thin enough and only weakly attached to the supporting structure so that it can deform to match the structure of an epitaxial film of different lattice constant deposited on it. This approach has proven very promising in the growth of InGaAs, where layers with a thickness as much as eight times the critical thickness have been grown without generating significant misfit dislocations. While the method is certainly novel and may be quite useful in certain instances where very small areas of substrate are needed, it does not seem to be the solution for mass production of electronic devices. The problems of handling large area compliant substrates appear formidable.

9. Quantum boxes

We have discussed quantum wells in one dimension. Why not extend the concept to three dimensions? The flippant response to that question is that it is considerably more difficult to do! MBE offers tremendous control over composition normal to the crystal surface, however control across the surface is not easily accomplished. The molecular beams used in MBE are very diffuse, and since they consist of neutral atoms, there is no way to focus and steer them electrically. Some 3-D control has been demonstrated using in situ shadow masks; however, because the beams originate from large area sources, and because multiple sources are required, it is difficult to use shadow masks for the definition of small features. Standard lithography following the growth of quantum wells has been used, as has the growth of wells on a lithographically patterned substrate. Both approaches are limited by the size of features that can be defined by optical lithography—at present typically one or two orders of magnitude larger than the width of quantum well structures.

Another new approach to quantum boxes takes advantage of the clustering of metal clusters on the surface of a III–V substrate. Whenever excess Group III metal is present on the surface of a III–V substrate at temperatures above the melting point of the metal, the metal film forms a very uniform array of small droplets, with the droplet size proportional to the amount of metal present. This has often been a problem in attempting to grow III–V materials under metal-rich conditions, where it is easy to get metal droplets on the surface and thus destroy the planarity. Now, however, a number of authors are using this general scheme to great advantage in producing quantum dots. Stinz et al. were able to produce InAs quantum dots surrounded by strained InGaAs by inserting a metal-rich step in the growth sequence, which

caused the growth mode to shift from Frank–van der Merwe to Stranski–Krastanov long enough to produce the dots [65]. This was followed by encapsulation with first InGaAs and subsequently GaAs. The resulting dots were approximately 80 Å in diameter. From a device standpoint, the results were promising because the photoluminescense produced by the dots was close to the technologically important 1.3 μm wavelength; the material is therefore a good candidate to produce 1.3 μm laser diodes. After annealing at high temperatures above 600 °C, there was a blue shift in the luminescence and a large reduction in intensity, suggesting that the quantum wells were gradually merging with the surrounding matrix, due to bulk diffusion. Understanding the processes leading to the formation and dissolution of quantum dots will clearly be a useful and active research topic.

10. Summary and conclusions

The discussion above has barely scratched the surface of the very active research currently in progress in MBE. We have attempted to give just a bit of the flavor of the wide diversity of research that is based on MBE growth. Of course, since its initial use in the growth of compound semiconductors, one of the principal driving forces behind MBE research has been the industrial need for specialized semiconductor devices, such as optoelectronic devices and high-speed transistors. These devices take advantage of the almost atomically abrupt interfaces between different materials comprising the crystal that are produced by the low growth temperatures and the ability to switch the growth beams rapidly. The ability to grow layers of different compositions with differing bandgaps and with precisely controllable thicknesses has made possible many novel devices such as HEMTS and multiple quantum well (MQW) devices which had previously not been attempted because the necessary control over the device structure was not available. Now that the fabrication of these devices has been demonstrated using MBE, there are other growth techniques, particularly the method known as organo-metallic chemical vapor deposition (OMCVD or MOCVD), which have matured and which are more suitable for mass production than is the relatively slow method of MBE. Many of the new devices are now also fabricated using these faster techniques; however it was the demonstration of the properties of these structures from MBE that provided the incentive to improve the other techniques.

MBE has also aided in understanding fundamental solid-state physics. Thin films comprised of layers of differing semiconductors with precise boundaries and geometries approach the ideal models long used by theorists. As a result, some dramatic demonstrations of quantum effects in solids have been observed using MBE structures. The MQW structures have shown the effect of spatial confinement in one (or more) dimensions on the electronic properties, where a continuous band of states is split into discrete quantum states, with remarkable agreement with previous theory. Resonant quantum tunneling devices in which carriers are transported across potential barriers at specific resonant energies have been studied and have been used as extremely high frequency oscillators. Thus the ability to produce prototypical film structures that are close to the idealized models amenable to theory has added significantly to our understanding of semiconductor crystals.

These new materials and devices have opened a significant window on the nature of thin films, their surfaces, and the dynamics of their growth. Studies of thin films in the past suffered from the non-reproducible nature of the films and surfaces. The new methods for growth and characterization have allowed the widely reproducible creation of large area, single crystal films with customized characteristics. This has certainly had much to do with the present excitement and interest in the field of surface science. While it is certainly true that other growth techniques have been modified and improved to facilitate the production of many of the structures and devices described above, MBE has been the research tool that has lead the way in demonstrating how to make novel film structures. This has occurred because of the unique combination of (a) ultra-clean vacuum conditions, (b) low growth temperatures, (c) precisely controllable sources of the film constituents and (d) in situ

surface analysis tools that are all characteristic of the MBE approach.

In the future, MBE should continue as an important research tool for materials preparation. It seems likely that there will be an ever-stronger marriage of the MBE technique with more sophisticated analysis tools. The combination of MBE with the various scanning probe microscopies has been a union of great productivity, since MBE is able to supply the highly ordered surfaces that are most informative. There is an increasing movement toward combining MBE as the surface conditioning tool in surface experiments, e.g., those involving synchrotron radiation studies, where MBE equipment is incorporated directly into the beam line. More complex films, such as oxide superconductors, are being prepared by MBE. It is evident that more complex material systems will require new sources for the constituents and dopants, such as focused ion sources to allow selected area doping, and a variety of chemical vapor sources to allow the growth of novel materials. Industrial use of MBE will involve more automated systems with capability for handling larger wafers in keeping with industry standards.

Finally, from a personal perspective, MBE has come a very long way from the first films grown in a glass tabletop UHV system on sub cm-sized substrates, to today's massive production systems, capable of growth on multiple six-inch (and larger!) wafers. Even research systems have become significantly more complex, as more analysis capability has been incorporated. It has been awe inspiring to see the huge increase in research interest and in sophistication of equipment and experiment over the years. But I still feel a profound excitement when I come upon a working MBE system in a darkened lab and view the RHEED monitor as it cycles up and down, indicating the atomic layers adding to a newborn crystal.

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