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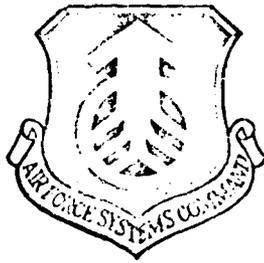
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MOLECULAR BEAM EPITAXY

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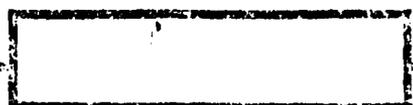
Wu Cheng Hwei and Huang Beau Chung

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# EDITED TRANSLATION

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## MOLECULAR BEAM EPITAXY

Wu Cheng Hsueh and Huang Beau Chung  
(Chungshan University)

Molecular beam epitaxy is a new epitaxial technique developed in the early seventies based on vacuum evaporation epitaxy. It involves the placement of the evaporating epitaxial material in a jet furnace and the heating inside the jet chamber in ultra high vacuum at  $10^{-10}$  torr or below to vaporize the material. Gas phase molecules are ejected from a small hole on the bottom of the jet furnace to form a molecular beam which directly deposits on a substrate maintained at a certain temperature (see Figure 1).

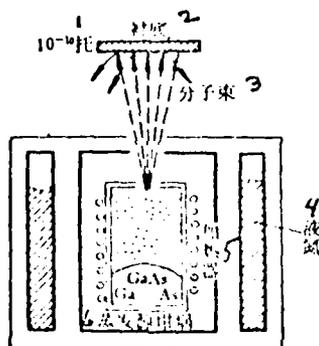


Figure 1. The principle of molecular beam epitaxy [1].

1.  $10^{-10}$  torr
2. substrate
3. molecular beam
4. liquid nitrogen
5. heater
6. evaporation source vessel

Since epitaxial deposition is formed by the adhesion of each molecule to the substrate, molecular beam epitaxy and vacuum evaporation epitaxy are basically the same in nature. But the vacuum used in conventional vacuum evaporation systems is approximately  $10^{-6}$  torr. A certain amount of

residual gas molecules can be introduced into the epitaxial layer. Therefore, it is required to have a higher deposition rate to prevent serious contamination by the residual gas. Molecular beam epitaxy is carried out under ultra high vacuum at  $10^{-10}$  torr, and very little residual gas exists in the system. The molecules ejected from the furnace have a negligible probability of colliding with any residual gas molecules before reaching the substrate. Therefore, the chances of impurity contamination in the epitaxial layer are small. Henceforth, the rate of epitaxial growth can be controlled to a very low level without serious contamination problems. In the meantime, the thickness of molecular beam epitaxy can be precisely controlled. Therefore, single molecular layer epitaxy can be realized for more uniform and flat surfaces than the ones obtained using gas or liquid phase epitaxy techniques.

Furthermore, because of the fact that the substrate and the molecular source are independent in molecular beam epitaxy, the substrate temperature in general is lower than that used in gas or liquid phase epitaxy. Therefore, all unfavorable thermal agitation processes (e.g., the diffusion of impurities in the substrate) and the effect of thermal defects due to lattice misplacement are also becoming less significant.

The third advantage of molecular beam epitaxy method is that it is possible to place several jet furnaces in the jet chamber based on special needs to individually adjust the molecular beam flow rate for each component. This allows the variation of chemical composition as well as dopant type and content in the epitaxial layer along the direction of growth which is impossible to accomplish using other epitaxial techniques.

## 1. Deposition Process

The growth of molecular beam epitaxy is progressing based on kinetics. The molecules ejected from the furnace to the surface of the substrate are first adhered to the surface. However, they must undergo several kinetic processes before becoming the epitaxial deposit. Molecules deposited may be re-evaporated from the surface of the substrate. This re-evaporation process is a function of substrate temperature. In the epitaxy of a single component material, there is only one type of molecular beam involved which makes the deposition process relatively simple. When the molecule arrival rate  $R_M$  (number/cm<sup>2</sup> . sec) of the molecular beam at the surface of the substrate is less than the re-evaporation rate  $R_M^E(T)$  at the temperature of the substrate, all the molecules deposited are simultaneously re-evaporated. No epitaxial deposition is obtained on the substrate. Only when  $R_M > R_M^E$ , deposition on the substrate will appear. The deposition rate increases with increasing  $R_M$ . In Figure 2 the dotted lines a and b show the situations of homogenous epitaxy and heterogeneous epitaxy, respectively. Some difference exists between the two types. In the former case, molecules can grow directly either at positions of low potential energy on the surface of substrate of identical composition or at already existing growth centers on the surface of the substrate. In the latter case, the formation of some stable nucleation centers must take place first. Therefore, it requires a molecular arrival rate far in excess of  $R_M^E$ . Thus the  $R_M$  at which deposition begins to appear is different from that of homogenous epitaxy. Since the surface of the substrate cannot be completely flat and some micro-defects usually exist, they offer some favorable sites for the formation of nucleation centers. Therefore, the actual required molecule arrival rate is less than  $R_M^S$  for an ideal smooth surface which corresponds to the solid curve in Figure 2.

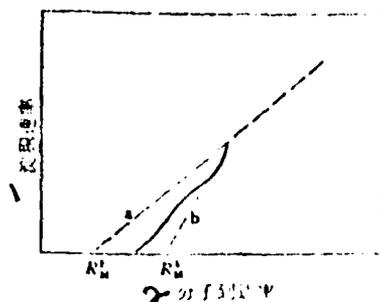


Figure 2. Deposition rate vs. arrival rate curves [2].

1. Deposition rate
2. Molecule arrival rate

The epitaxial deposition process of a compound formed by two components is shown in Figure 3. Let us assume that the molecule arrival rate for the x component  $R_X$  is a constant and vary the molecule arrival rate  $R_M$  of component M. If every M molecule reaches the surface of the substrate can immediately combine with an X molecule on the substrate to form the  $M_X$  binary compound then no deposition occurs on the substrate when  $R_M$  is less than the re-evaporation rate  $R_{MX}^E$  for  $M_X$ . Only when  $R_M \geq R_{MX}^E$ , deposition appears (for heterogeneous epitaxy,  $R_M \geq R_{MX}^S$  is required. Since it is also limited by the constant value  $R_X$ , when  $R_M$  increases to  $R_M = R_X$  and beyond, the deposition rate becomes a constant. The excess M molecules are re-evaporated from the surface and carried away by the vacuum system. Within the range between the onset of deposition and the constant rate deposition, the epitaxial deposition obtained on the substrate will be made of the compound which obeys the stoichiometry rigorously. Beyond that, if  $R_M$  keeps on increasing to above the re-evaporation rate of the M component at the substrate temperature, there will be excess M molecules unevaporated in the deposition layer besides the binary compound. The deposition thus goes up with increasing  $R_M$ . However, the deposition obtained is no longer a chemical compound obeying certain stoichiometry. Instead, it becomes a M-rich binary compound. The choice of the value of  $R_M$  should also be limited. It not only must be

larger than the re-evaporation rate of the compound but also smaller than the re-evaporation rate of itself. Otherwise, excess X component would exist in the deposit when  $R_M < R_X$ . When  $R_M < R_M^E$ , the deposition of component X on the substrate would also exist. From the above discussion, it is apparent that by properly controlling the molecule arrival rates of various components it is possible to obtain an epitaxial compound which obeys the stoichiometry.

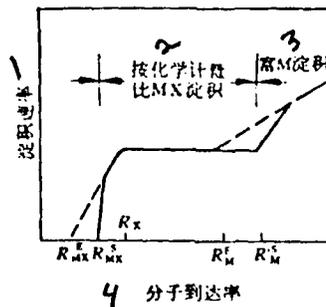


Figure 3 [2].

1. deposition rate
2. stoichiometric deposition of  $M_X$
3. M-rich deposition
4. molecule arrival rate

#### 1. Adhesion Coefficient

In reality not all the molecules ejected to the substrate become the deposited epitaxial layer. It was discussed previously that before a molecule becomes combined with the epitaxial layer certain kinetic processes must take place. The adhesion on the surface of the substrate is unstable before becoming part of the epitaxial layer. It is possible to stay on the surface for a short time period and then flies away from the substrate. Molecules have an average staying time  $\tau$ . If there are  $N$  molecules already adhered to the surface then the

probability for them to leave the surface is  $\frac{1}{\tau}$ . Now let us define that the number of molecules reaching the surface of the substrate in unit time period is  $N$ . It can roughly be assumed that only  $N \cdot \frac{\tau}{\tau}$  molecules will combine and become the epitaxial layer. We then define

$$N = \frac{n}{\tau} N \tau$$

as the adhesion coefficient of molecules to the surface of the substrate.

Since  $n$  itself is practically related to the kinetic processes, therefore the adhesion coefficient reflects the reaction kinetics of the surface. The length of average staying time reflects the magnitude of the adhesion coefficient. Therefore, through the measurement of the average staying time the adhesion coefficient  $S$  can be obtained.

The factors affecting the growth rate and composition in molecular beam epitaxy are the molecule arrival rate  $R_M$ , the substrate temperature  $T$ , and the adhesion coefficient of molecules to the surface of the substrate  $S$ .

Single component epitaxy is relatively simple to describe. In the epitaxy of compounds, since it involves the mutual influence between two or more components, practical and individual considerations are necessary. For certain compounds, epitaxial growth is accomplished by subliming the compound from heating and it is then carried out as the molecules of the compound in vapor phase. Therefore, their deposition is very similar to that of single component epitaxy. However, many compounds decompose into vapors in element forms after heating. In this case, there exists the problem of mutual interaction and variation of the adhesion coefficient for each element.

Take Ga As as an example. Arthur et al. used a pulsed Ga molecular beam and an As molecular beam to study the growth kinetics of GaAs on the GaAs substrate based on a reflection method and obtained the average staying time of Ga and As molecules on the GaAs surface. When the substrate temperature is below 477°C, all the Ga atoms reaching the substrate are adhered to the surface. The adhesion coefficient is approaching 1. As molecules, however, are almost all reflected with its adhesion coefficient approaching zero. But if the surface of the substrate is covered by free Ga atoms, then As molecules may be adhered. The adhesion coefficient is proportional to the number of Ga atoms covering the surface. If the surface of the substrate is already covered with a layer of Ga atoms as a pretreatment, the adhesion coefficient of As molecules there can increase to close to 1. From the above, it can be concluded that the growth of stoichiometric GaAs epitaxy can be achieved by adjusting the rate of As molecule arrival  $R_{As}$  so that it exceeds the arrival rate of Ga atoms  $R_{Ga}$ . The results obtained are shown schematically in Figure 4.

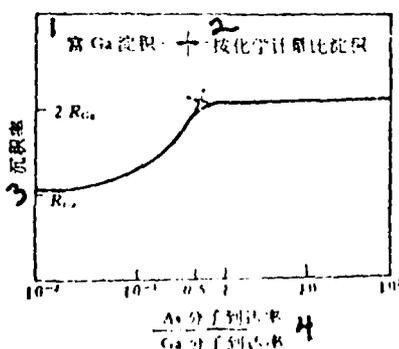


Figure 4 [2].  $R_{Ga}$  fixed unchanged.

1. Ga-rich deposit
2. Stoichiometric deposit
3. deposition rate
4.  $\frac{\text{As molecule arrival rate}}{\text{Ga molecule arrival rate}}$

Surface reaction kinetics and temperature are related. Therefore in order to reflect the result of this process the observed quantity - the adhesion coefficient is a function of substrate temperature. As the substrate temperature increases, the adhesion coefficient decreases and the epitaxial rate slows down. However, it is more favorable for the crystal growth. In the meantime, due to the increasing re-evaporation rates of all the components from the substrate it is possible to obtain stoichiometric compounds within a wider range of variations in molecule arrival rates. However, when the temperature is too high, the adhesion coefficient will drastically decrease to approach zero. On the other hand, at lower temperature, although faster growth rate can be reached yet it is unfavorable for crystal growth. It is easy to form polycrystalline or even amorphous deposits. Furthermore, the tolerable range of molecule arrival rate is too narrow to obtain stoichiometric epitaxy. Therefore, the proper substrate temperature must be selected.

## 2. Molecule Arrival Rate and Evaporation Source

In the jet furnace shown in Figure 1 the nozzle dimension is smaller than the mean free path of molecules in the furnace under the pressure conditions. Only those molecules which never collided with the furnace wall may be ejected from the nozzle into the vacuum chamber. It is different from free evaporation. Inside the furnace a quasi-thermal equilibrium exists. Based on the theory of gas molecular kinetics, for an ideal jet furnace with nozzle area  $S$  at temperature  $T$  the molecular beam flow intensity is

$$N = 3.51 \times 10^{19} p_s / \sqrt{MT} \quad (\text{number/sec}), \quad (1)$$

where  $M$  is the molecular weight of the source and  $p$  is the vapor pressure in the furnace. As shown in Figure 5, let us assume that there is an arbitrary unit area  $ds'$  which is at an angle with respect to the normal direction of the furnace nozzle, then the number of molecules reaching  $ds'$  per second is

$$n(\theta) = \frac{N}{\pi} \cdot \frac{\cos \theta \cos \phi}{r^2} ds' \quad (2)$$

If we let  $\phi = 0$  and  $\theta = 0$  which is the case that the ejection surface is parallel to the substrate surface, then the incoming number of molecules onto an unit area on the substrate is

$$\begin{aligned} n &= \frac{n(\theta)}{ds'} = \frac{N}{\pi r^2} \\ &= 1.12 \times 10^{11} \frac{pS}{r^2 \sqrt{MT}} \quad (\text{number/cm}^2 \times \text{sec}) \quad (3) \end{aligned}$$

This is the molecule arrival rate. It is obvious that the molecule arrival rate is dependent on the furnace temperature, the size of the nozzle, pressure in the furnace and the relative position between the nozzle and the substrate.

Evaporation sources of molecular beams can be either ultra pure elements or compounds. If the compound itself is used as the evaporation source, then it is necessary to use the pressure-temperature curves of all the components of the compound (i.e. p-T curves). Again take GaAs as an example; at high temperatures GaAs decomposes into Ga, As<sub>2</sub>, As<sub>4</sub> vapors. As shown in Figure 6, the vapor pressure of the Ga-rich GaAs is not the same as that of the As-rich GaAs at the same temperature. When GaAs is heated to above 637°C, As is first evaporated and very rapidly a Ga-rich state is reached inside the furnace. At this time, the evaporated gas contains Ga, As<sub>2</sub> and As<sub>4</sub> as obtained from a stable Ga-rich GaAs source. When the temperature in the furnace exceeds 900°C,

it is known that the vapor pressure of  $As_2$  has already exceeded that of Ga by comparing the vapor pressures of  $As_2$ ,  $As_4$  and Ga. However, the vapor pressure of  $As_4$  is still far less than those of  $As_2$  and Ga. Therefore, it can be considered as negligible. Henceforth, it is possible to obtain a Ga and  $As_2$  molecular beam source from GaAs by the proper control of furnace temperature. As discussed previously, the deposition rate of Ga is determined by the arrival rate of the Ga atom. In order to increase the growth rate of GaAs, it is possible to install an auxiliary jet furnace to increase the intensity of injection of the Ga atoms.

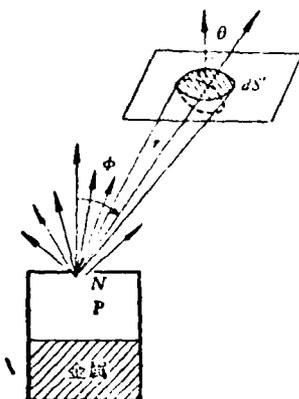


Figure 5. The distribution of molecular beam obeys the cosine law. [3]  
 1. metal

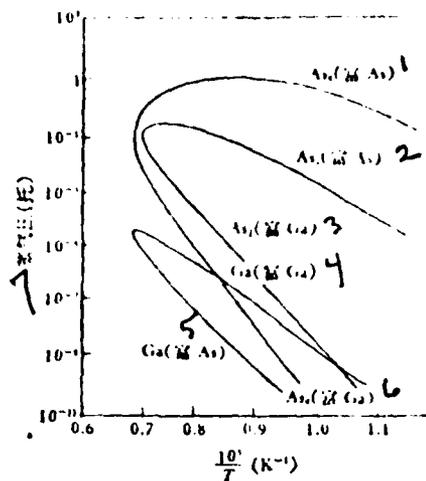


Figure 6 [4]

1.  $\text{As}_4$  (As-rich)
2.  $\text{As}_2$  (As-rich)
3.  $\text{As}_2$  (Ga-rich)
4.  $\text{Ga}_2$  (Ga-rich)
5. Ga (As-rich)
6.  $\text{As}_4$  (Ga-rich)
7. Vapor pressure (torr)

The doping of the epitaxial layer is carried out by placing the dopant material into another jet furnace to produce a dopant molecular beam. By controlling the furnace temperature and vapor pressure inside the furnace, it is possible to obtain the required extent of doping. However, the doping process includes the two steps which are the adhesion of the dopant molecule on the substrate and the subsequent combination into the epitaxial layer. The situation is therefore more complicated. The current understanding in this area is still very limited.

## II. Introduction to the Apparatus Used in Molecular Beam Epitaxy

Figure 7 is a schematic diagram of the molecular beam epitaxy apparatus. It in general consists of the ultra-high vacuum system, the molecular beam epitaxy system, the substrate installation system, and the growth process monitoring system.

### 1. Ultra-high Vacuum System

The ultra-high vacuum system is a vacuum chamber made of stainless steel with ultimate vacuum reaching better than  $10^{-10}$  torr.

When epitaxial growth is in progress, it should be able to maintain  $10^{-9}$  torr vacuum. The most recent molecular beam epitaxy set-up places the epitaxy and its subsequent monitoring systems into two vacuum chambers with sampling valve installed in between. This design can avoid the contamination of the testing system by the epitaxy. Simultaneously, it will not expose the entire system to the atmosphere during changing of samples.

### 2. Molecular Beam Originating System

Molecular beam is produced by the jet furnace. The structure of a jet furnace is shown in Figure 1. It is made of boron nitride (BN) or ultra pure graphite. To avoid contamination by impurities produced by the furnace and the heating element, liquid nitrogen shield is installed surrounding the jet furnace. In order to control the flux of the molecular beam, it is necessary to install slit and shield in front of the nozzle. Several jet furnaces can be installed in the chamber based on the need.

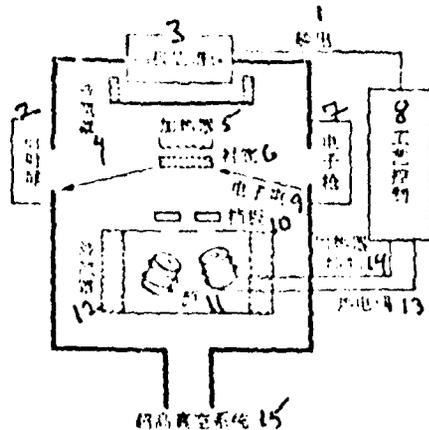


Figure 7. Schematic Diagram of a Molecular Beam Epitaxy Furnace [1]

1. output
2. diffraction shield
3. quadripole mass spectrometer
4. liquid nitrogen mask
5. heating element
6. substrate
7. electron gun
8. technological control
9. electron beam
10. shield
11. source
12. liquid nitrogen mask
13. thermocouple
14. heater control
15. ultra-high vacuum system

### 3. Substrate Installation System

At the present moment, the position of the substrate can be adjusted by the multi-degree-of-freedom mechanical device placed in the epitaxial furnace. The heater for the substrate is made of a molybdenum plate. The substrate can be fixed to the heater using a sample clamp or it is also possible to use In or Ga as the contact material between the substrate and the heating element. At epitaxial substrate temperatures, In (or Ga) becomes a liquid and the surface tension of the liquid is used to secure the substrate. Since the vapor pressure of In (or Ga) is very low, it will not seriously affect the vacuum in the system. Because In (or Ga) is used

as the medium, it allows the substrate to be heated evenly which cannot be easily accomplished by using the sample clamp.

#### 4. Monitoring System

The monitoring devices can be added or taken away upon actual need. At least a quadripole mass spectrometer must be used to monitor the residual gas composition in the vacuum system and to determine the intensity of the molecular beam. It is also possible to transmit data from the mass spectrophotometer to a computer to control the epitaxial process. For the understanding of the surface structure, composition and growth process, low energy electron diffraction, high energy electro diffraction and Auger spectrometers should be installed as surface analysis instruments. The present molecular beam epitaxy apparatus is not only an epitaxy set-up but also becomes the combined equipment for surface research after the addition of various analysis devices.

### III. The Applications of Molecular Beam Epitaxy

Molecular beam epitaxy was only introduced for about ten years. Its application is still in the initial stage. The following is an introduction in three areas:

#### 1. The Fabrication of Devices

Due to the characteristics of molecular beam epitaxy, it is possible to grow an epitaxial layer of atomic thickness and smoothness which coincides with the requirement for photoelectric devices. At the present moment it is already used in the production of heterogeneous binary lasers, high

efficiency light emitters, and solar cells of various structure. In addition, because of low substrate temperature, the effect of diffusion of dopant is insignificant. Thus the composition of the epitaxial layer can be controlled. It is easy to fabricate a cross-section with an arbitrary dopant level to realize the equi-plane technology. This will aid to fabricate certain special microwave devices.

Another area which is considered to be of promising application is in optics. Originally, molecular beam epitaxy was used to produce a thin layer of high index of refraction material on the substrate as the optical waveguide. Although it can attain relatively low loss, yet the energy transmitted by light is still dissipated by some extent due to the drastic change in index of refraction at the boundary. If the molecular beam epitaxy method can produce a transition layer at the boundary of the waveguide with continuously varying index of refraction, then light will be gradually refracted to the waveguide at near the boundary with decreasing loss in optical energy. It is also possible to produce a multi-layer epitaxial film with two different materials in an alternate fashion on the outside of the waveguide to form the so called "Bragg's" reflection. By doing so, even if the index of refraction of the material of the waveguide is lower than that of the surrounding medium, light is still constrained inside the waveguide. The results are extremely low energy loss in light transmission and extension of wavelength of light transmission to the x-ray region. In the other devices used in integrated optics, some new applications are found for the molecular beam epitaxy technique.

## 2. The Research of New Materials

Molecular beam epitaxy has become an important means to obtain new types of material. For example, the use of two different materials or dopants in an alternate fashion can produce a multilayer crystal with artificial periodicity which is the so called "super crystal lattice" new material structure. Periodic single molecule layered GaAs-AlAs super crystal lattice material has already been made up to a  $10^4$  layer thick structure. In addition, since the energy level of the top of the valance band of GaSb is higher than that of the bottom of the conduction band of InAs, if they can be made as super crystal lattice material, then the conduction band of InAs and the valance band of GaSb will overlap and create a mutual interaction effect. Theoretically, it is predicated that this type of material will show an energy gap which varies monotonically with the distance of the periodicity. It will become a new type of super crystal lattice.

## 3. Surface Research

The surface of crystal is contaminated due to exposure to the atmosphere which alters the original surface condition. Therefore, information on the intrinsic surface cannot be obtained. Furthermore, due to surface oxidation there is an oxide layer on the connecting surface of the material which hinders the understanding of the structure of the boundary. In order to obtain a clean ideal surface, it is mandatory to study the crystal in ultra-high vacuum using ion bombardment or heating techniques



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