Growth kinetics of III-V compound semiconductors

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In the present communication, the recent developments in the growth kinetics of vapour phase epitaxy, liquid phase epitaxy and liquid phase electroepitaxy of III-V compound semiconductors have been reviewed. Investigations on the nucleation and growth mechanism of III-V binary, ternary and quaternary compounds grown from VPE are presented, compared with the available experimental results and there is a good agreement between them. Computer simulation technique has been used to construct the concentration profiles of the solute atoms present in front of the crystal-solution interface during the Liquid Phase Epitaxy and Liquid Phase Electroepitaxy of III-V binary, ternary and quaternary compound semiconductors. The growth rate of the materials and hence the thickness of the grown films have also been determined.

In recent years, there has been tremendous development in the fabrication of optoelectronic/photovoltaic devices and infrared detectors. This development in the fabrication is attributed to growth of high quality and compositionally uniform epitaxial layers of III-V semiconducting materials from various epitaxial growth techniques. Mastering epitaxial growth is an essential requirement for fully realizing the potential of the III-V technology for the construction of novel devices for microwave and optoelectronic applications. Because of the variety and complexity of the material systems involved, several approaches towards epitaxial growth have been developed during the past three decades.

Vapour Phase Epitaxy (VPE) processes are widely used to deposit thin, highly uniform solid films from gaseous precursors. VPE is very versatile and offers good control of film structure and composition, excellent uniformity and sufficiently high growth rates. Perhaps the most important advantage of VPE over other deposition techniques is its capability of conformal deposition, i.e., depositing films of uniform thickness on highly irregular surfaces. VPE films are used as mechanical or optical coatings and in microelectronics manufacturing. VPE is one of the techniques to deposit films of 0.1-10 μm thickness of carefully controlled composition onto monocrystalline silicon wafers.

Chemical Vapour Deposition processes use chemically reacting gases to deposit thin solid films. In general, a reactive gas mixture flows continuously through the controlled environment of a reactor process chamber that contains the substrates on which deposition takes place. Chemical reactions in the gas phase and at the surface, which are activated thermally, by light, or by glow discharge plasma, lead to the deposition of the bulk materials.

Diffusion Limited/Kinetically Limited Growth

In all growth processes, the change from one state, i.e., the initial reactant gases, to another, i.e., the final state with some solid deposits and some gaseous reaction products is dealt with. In practice, this change must be completed within a reasonable time and so the rate of change from initial to final state is important. This rate is determined by the chemical kinetics of the process and by the gas flow and transport phenomena (heat transfer, species diffusion) in the reactor. As a result, CVD process and film qualities are highly determined by transport phenomena in the gas mixture and by chemical reactions in the gas mixture and at the wafer/substrate surfaces. In particular, the growth rate and the growth uniformity strongly depend on these phenomena. The studies on fundamental aspects of CVD, therefore, involve both chemical kinetics and transport phenomena.

However, depending on the specific process characteristics, it is sometimes possible to make useful studies of CVD process aspects neglecting either the influence of chemical kinetics or the influence of transport phenomena. For this purpose, it is useful to distinguish between two extreme operating conditions. In the first extreme, the rate of incorporation of reactive species into the solid film is extremely slow compared to the maximum rate in
which these species can be transported from the bulk gas flow to the wafer surface by convection and/or diffusion. In this case, the film growth rate is determined by the chemical reaction rates at the substrate surface. This kind of CVD operations are often referred to as kinetically-limited CVD growth. Clearly, the gas flow and transport phenomena have little influence on the film growth rate in this kind of CVD operation. In the other extreme, the rate of incorporation of reactive species into the solid film of the wafer surface is extremely fast compared to the maximum rate at which these species can be transported to the wafer surface. Now, any molecule of the reactive species that makes it to the surface will react instantaneously and the concentration of reactive species just above the wafer surface will be close to zero, i.e., the surface concentration will be much smaller than the concentration in the bulk. In this case, the growth rate is determined by the rate in which the reactive species can be transported to the substrate surface and fully depends on the gas flow and transport phenomena in the reactor, whereas the precise mechanisms and kinetics of the chemical reactions have less influence on the growth rate. This is often referred as mass transport limited or diffusion limited growth.

Mechanism of VPE Growth of III-VI Compound Semiconductors

Various fundamental aspects of growth of III-V, II-VI and I-III-VI₂ binary, ternary and quaternary compound semiconductors from the vapour phase on the diffusion limited growth region and reaction kinetics regions have been investigated at Crystal Growth Centre, Anna University.

Vapour Growth/Vapour Phase Epitaxy/Chemical Vapour Deposition/Chemical Vapour Transport have become the major techniques for the production of device quality semiconductor materials of many types. The complexity of these methods arises from: (i) Multi-component species are generally involved in the chemical reactions, (ii) The chemical reactions may produce certain intermediate products, (iii) The growth process has numerous independent variables, and (iv) The deposition process includes many consecutive steps.

VPE/CVD process involves the transport of chemical species from the gas phase onto the substrate surface. The atoms are transported to the growing solid-vapour interface through the vapour phase. The theory of Vapour Phase Epitaxy/CVD involves various aspects, viz., (i) Mass transport, (ii) Kinetics, (iii) Nucleation, and (iv) Reactor modeling/dynamics.

The growth requires heterogeneous nucleation and includes surface reactions in which the incoming gas species and the intermediate products due to the chemical reactions are adsorbed on the surface and subsequently diffuse to energetically favorable sites for the incorporation of atoms into the crystal lattice. Therefore, the deposition process can be divided into two main steps, viz. (i) Gas diffusion through the boundary layer, followed by (ii) surface reaction. The deposition rate equations are derived based on the rate-limiting step. The different elements of the growth process can be described by: (i) Mass transport in the bulk gas flow region from the reactor inlet to the deposition zone, (ii) Gas phase reactions leading to the formation of film precursors and byproducts, (iii) Mass transport of film precursors to the growth surface, (iv) Adsorption of film precursors on the growth surface, (v) Surface diffusion of film precursors to the growth sites, (vi) Incorporation of film constituents into the growing film (island), (vii) Desorption of byproducts of the surface adsorbed species, and (viii) Mass transport of byproducts in the bulk gas flow region away from the deposition zone towards the reactor exit.

Mass transport

Mass transport in the vapour growth is an extremely complex problem involving fluid flow and diffusion processes. Driving force for mass transport is a function of both concentration and temperature. Modeling of mass transport in the gas phase is an important problem described by:

\[ MX + G \leftrightarrow M(s) + GX \]

where MX, G and GX are gaseous reagents and M(s) denotes deposited solid phase. The net diffusion flux of the species MX, G, GX may be described as a superposition of two fluxes, one towards the substrate surface and one away from the substrate towards the bulk of the gas.

Kinetics

The kinetics of vapour growth may be rather complex. Typically, the growth process consists of many sequential steps. The first step is the adsorption of gas species on the substrate surface. The amount of adsorbed gas depends on its equilibrium partial pressure and temperature. For a given temperature, the mass of adsorbed gas can be calculated according to the theory of Langmuir isotherm, from which the
fraction of occupied surface sites (θ) can be calculated.

In surface reactions, if the formation of the adsorbed atoms is the rate-limiting step, the mass transfer flux can be calculated using:

\[ J_s = (K_d/RT) (p_s - p_{eq}) \]

where \( J_s \) is the mass transfer flux by surface adsorption, \( K_d \) the mass transfer coefficient, and \( p_{eq} \) the equilibrium partial pressure. Efforts are going on to enhance the modeling procedures of VPE/CVD of III-V and II-VI compound semiconductors.

**Nucleation and growth processes**

The older theory of nucleation is based on thermodynamical approach. The nucleus of the new phase is formed from the supersaturated vapour. Below a certain size, the nucleus is subcritical because it has a better chance of disappearing than of growing. Above, a certain size, the surface becomes a relatively small portion of the total nucleus, and the bulk free energy, which is now the dominant factor, favours the growth.

The newer theory is based on the atomistic nucleation concept. It deals with the statistical mechanics and chemical bonding characteristics of solid surfaces. Not all surface sites have equal bonding characteristics. Those with strong bonds are particularly favourable nucleation sites. Again, after nuclei reach a certain size, it becomes energetically more favourable for them to grow than to reevaporate. The growing nuclei come into contact and finally coalesce, thus forming a continuous film.

In three-dimensional island growth, referred to as Volmer-Weber growth, small clusters are nucleated directly on the substrate surface. The clusters grow into islands of the film material that eventually coalesce to form a continuous film. This growth mode takes place when the film atoms are more strongly bound to each other than to the substrate. In the other growth mechanism called Franck-Vander Merwe growth, two-dimensional layer-by-layer growth occurs when the film atoms are equally or less strongly bonded to each other than to the substrate. This growth mode applies to homoepitaxy on clean substrates. Often, slightly off-axis oriented substrates are used to suppress island nucleation and to promote layer growth. The layer-plus-island growth mode, also called Stranski-Krastanov growth, is a combination of the other growth modes. After the growth of one or few monolayers, subsequent layer growth becomes unfavourable, and island forms on top of the initial layers.

**Comparison with Experimental Data**

Extensive theoretical and experimental activities on the growth of III-V compound semi-conductors have been carried out.

Reaction kinetics limited growth models have been developed for number of systems grown from the vapour phase. The number of growth parameters corresponding to the growth of compound semiconductors using VPE have been calculated and compared with the available experimental results. Fig. 1 shows the comparison between our theoretical work and the reported experimental values of the dependence of the composition of the GaAsP layers on the deposition temperature. Similarly, the extensive works on the growth of the quaternary compound GaInAsP from the VPE have been carried out. Comparison of our theoretical findings with the experimental results of Sugiyama et al. is made in Fig. 2 where \( M_5 \) is defined as the group V hydride mole ratio (\( p_{PH_3} + p_{AsH_3} \)).

For the case of the diffusion or the transport limited growth of the compound semi-conductors, computer simulation technique has been followed to construct the concentration profiles in front of the growing interface and hence the growth rate and thickness of the grown film have been calculated and compared with the theoretical findings. The results for one such system (InGaAs) are shown in Fig. 3.

![Fig. 1 — Comparison of the theoretical predictions and reported experimental values on the dependence of composition of GaAs\(_1-x\)P\(_x\) layers on deposition temperature](image-url)
Conclusions

A systematic work on the growth and growth kinetics of III-V compound binary, ternary and quaternary compound semi-conductors from the vapour phase and liquid phase has been carried out for almost all the systems\(^5\) - \(^8\). Different parameters influencing the growth of these systems have been investigated in detail.

References