CHAPTER-II

REACTIVE EVAPORATION METHODS

Reactive evaporation is a variant of Günther's Three Temperature Method (TTM) /1/ and is based on the fact that continuous condensation of a given vapour at a given deposition rate takes place only if the substrate temperature drops below a critical value. Differences in magnitude of these critical values, which are functions of the interfacial energies, make it possible to condense a given vapour type or a combination (i.e. a compound) preferentially on the substrate surface.

The condensation flux $N_K$ of a given vapour on a given substrate, exceeds zero only if the ratio $p/p_e$ of the actual vapour pressure $p$ and the equilibrium pressure $p_e$ exceeds a critical value $q_c$.

\[ N_K > 0 \text{ if } (p/p_e) > q_c \quad (2.1.1) \]

since this pressure may be related to the substrate temperature, it can be shown that the condition for progressive condensation at a given substrate temperature involves exceeding a critical incident flux, i.e.,

\[ N_K = 0 \text{ if } N_+ \leq N_{+c}(T) \quad (2.1.2) \]

\[ N_K > 0 \text{ if } N_+ > N_{+c}(T) \quad (2.1.3) \]
where $N_+$ is the incident flux and $N_{+c}$ is the critical value of incident flux. If the flux exceeds $N_{+c}$, the condensation flux rises rapidly and approaches a maximum value given by

$$N_K \text{ max} = \mathcal{L} (N_+ - N_e)$$  \hspace{1cm} (2.1.4)

where $\mathcal{L}$ is the condensation coefficient and $N_e$ the number of reevaporated atoms.

The state of affairs described above and illustrated in figure 1 may be represented in terms of a critical temperature $T_c$ assuming a constant incident flux $N_+$.

$$N_K = 0 \text{ if } T > T_c(N_+)$$  \hspace{1cm} (2.1.5)

$$N_K > 0 \text{ if } T < T_c(N_+)$$  \hspace{1cm} (2.1.6)

Thus by analogy with figure 1, the condensation can be represented schematically as a function of substrate temperature as in figure 2, i.e., after dropping below the critical temperature $T_c$, condensation sets in spontaneously and quickly approaches a maximum.

Suppose the vapour phase consists of two components A and B and both being incident on the substrate under consideration. If the vapour density is low enough, we may neglect collisions between particles.
Figure 1: Variation of condensation flux $N_K$ with flux $N_+$ of incident particles.
of the components A and B in the vapour phase. However
interactions can take place between such particles with­
in the adsorbed stage on the substrate surface. These
interactions may lead to the formation of molecules

$$A + B \rightarrow AB$$ (2.1.7)

where AB stands for all possible compounds $A_n B_m$. A
rough estimate of the interaction probability on the
surface gives a density

$$n_{AB} = \text{const.} \frac{n_A n_B \bar{D}}{}$$ (2.1.8)

where $n_A$ and $n_B$ are the number of adsorbed atoms A and B
and $\bar{D}$ the mean diffusion coefficient. This estimate is
rough because we are not considering the energies of the
particles and we know that only if the particles collide
with sufficient translational energy they will react to
form the compound molecule. Since the number of adsorbed
atoms is proportional to actual vapour pressure $p$, or the
incident flux $N_+$ of the particular vapour, the density
$n_{AB}$ should also be proportional to the product of incident
fluxes ($N_{+A} N_{+B}$) or vapour pressures ($p_{eA} p_{eB}$).

In order to estimate the critical values which
now apply, the equilibrium pressures $p_{eA}$, $p_{eB}$ of the
components and $p_{eAB}$ of the compound must be considered.
$p_{eAB}$ usually corresponds to the dissociation pressure of
Figure 2: Variation of condensation flux $N_K$ with substrate temperature $T$. 
the compound and is equivalent to the pressure of the more volatile component (say, A) in equilibrium with the compound. In most cases, this value is much lower than the equilibrium pressure $p_{eA}$ of the pure component A. Thus the critical values of one component A in the presence of the other component B should vary as follows:

$$N_{+cA}(B) \ll N_{+cA}$$

(2.1.9)

$$T_{cA}(B) > T_{cA}$$

(2.1.10)

This means that it will be possible to condense A (in combination with B, of course) at a lower critical flux in the presence of B for a given substrate temperature. Or in terms of substrate temperature it means that a higher substrate temperature may be used to deposit A in combination with B for a given flux of A.

At a given substrate temperature $T$ and for incident fluxes $N_{+B} < N_{+cB}$, no condensation of any kind is possible while the incident rate $N_{+A}$ is low. However, at a critical value $N_{+cA}(B)$, sufficient molecules AB are formed on the substrate, and nucleation and progressive condensation of AB starts. This critical value $N_{+cA}(B)$ itself depends on the incident flux of the component B. With further increase of $N_{+A}$, no increase of condensation flux $N_K$ is possible until, with $N_{+A} > N_{+cA}$,
Figure 3: Condensation diagram for two incident components A and B.
condensation of unreacted A takes place. Figure 3 shows the condensation diagram for two incident components A and B for a given substrate temperature.

The plus points of reactive evaporation include the following.

(1) Elimination of the synthesis of the compound prior to deposition. This is advantageous because the tedious and sometimes expensive metallurgical process which needs high temperature rocking furnaces and facilities to seal the ampoule containing the reactants at high vacuum ($10^{-5}$Torr), is eliminated.

(2) High temperatures ($>2000^\circ$C) are frequently needed to evaporate high melting point carbides, nitrides, and oxides. If resistive heaters are used, the film will get contaminated because of the evaporation of the heater itself. And also it may not be possible to get high evaporation rates which are essential in industrial processes. Reactive evaporation overcomes this defect, because almost all the metals evaporate below $1500^\circ$C with sufficient vapour pressure, so that high deposition rates of the compounds are possible.

(3) The decomposition of the compound on heating in vacuum and consequent loss of the original composition in the films are inherently not present. It must be mentioned that TTM and reactive evaporation
were originally developed to overcome this disadvantage in ordinary evaporation technique.

(4) The lowest substrate temperature possible is dictated by the condensation temperature of the more volatile component and is usually low (e.g. O₂, S₂, and Se₂) and consequently this method can be used as an efficient technique for the preparation of amorphous films.

(5) Dopants can be evaporated simultaneously at a suitable rate and thus a uniform dispersal of the dopant can be easily achieved.

(6) Film growth can be started and stopped abruptly and hence abrupt interfaces are possible.

(7) In general, different compounds in a binary or ternary system may be prepared by adjusting the evaporation rate of the individual components and substrate temperature.

The technique has now been so perfected that it is possible to deposit epitaxial films of certain compounds (InAs and InSb) at rates approaching that of vapour phase epitaxy (0.5 - 1 micron min⁻¹) with excellent carrier mobilities /2/. If this high rate of deposition can be extended to other III-V compounds like GaAs and InP, it will be possible to dispense with UHV conditions, where it is solely used for preventing the incorporation of
impurities in the growing film. This will certainly give a boost to semiconductor heterojunction laser technology which now requires costly and time consuming MBE.

This technique which has been so successfully used in the case of many technologically important compounds suffers from the following drawbacks which arise from the low chemical reactivity of the particles used for film formation as discussed in chapter XI.

(1) The use of large volatile flux and consequent wastage of the volatile element.

(2) When high deposition rates are needed, large volatile flux leads to the use of high volatile partial pressure ($10^{-4}$ to $10^{-2}$Torr) which reduces the mean free path and also scatters the non-volatile beam away from the substrate surface. Also the high pressure in the vacuum system reduces the evaporation rate of the non-volatile component.

(3) Because of the high volatile elemental pressure, some unreacted volatile flux may get entrapped in the growing film which will have drastic effects in the film properties. It has been reported that refractive index, hardness etc. of TiO$_2$ films prepared by this technique decreases as the oxygen partial pressure is increased to
get high deposition rates /3/. Though this has been explained as due to the large number of collisions TiO molecules suffer in the gas phase and consequent lack of energy of the particles, it seems that this is due to the entrapment of unreacted volatile element (here oxygen) in the growing film. And that explains why the films have a lower hardness and refractive index.

Chemical reaction rate may be increased in two ways. The first method is by increasing the translational energy of the particles so that they can overcome the potential barrier and the second method is by lowering the potential barrier itself so that particles with very low energies can react.

It may not be easily possible to enhance reaction rate by increasing the substrate temperature so as to increase translational energy, as this will lead to increased dissociation of the compound formed and also increase chemical reactions with the underlying substrate. Stability of the substrate at high temperature is another problem which has to be taken into consideration. One way to increase the translational energy of the particles is by increasing the source temperature. But the associated increase in rate of evaporation must be prevented and this can be achieved by using flash
evaporation like techniques. But the practical kinetic energies attainable by this technique is limited to 0.2 to 0.3 eV. The most versatile way of increasing the kinetic energy of the particles is by ionizing the particles with electron beams or suitable radiations and accelerating them in electric fields.

Historically the first method which used some of these techniques to increase chemical reaction rate is the activated reactive evaporation /4/ of Bunshah and Raghuram. Their original set up is shown in figure 4. The secondary electrons from the molten pool of the metal is attracted by a low voltage probe (biased positively around 100 V) and these electrons ionize the reactive gas atoms generating a thick plasma. Because of the presence of the plasma, chemical reaction rate is very much increased and Bunshah and Raghuram could deposit TiC at a rate of 12 µm min⁻¹ at a source substrate distance of 15 cm using this technique. It may be mentioned that using ordinary reactive evaporation, titanium and the reactive gas used, acetylene, do not react to form the compound.

Let us analyze this process in some detail. It will be shown in Chapter XI that the reacting species must possess a certain amount of translational energy to overcome the potential energy barrier for reaction. It is also shown there that the reaction rate should increase if we increase particle energies. In ARE the ions are
Figure 4: Set-up for ARE used by Bunshah and Raghuram.
not accelerated to the substrate as may be seen from Figure 4. This is because usually ions are positively charged and will be attracted only to the negatively charged pool of the metal and this is in a direction opposite to that of the substrate. Moreover, the applied electric field is confined to a small region above the source of secondary electrons and ionization of the atoms predominantly take place beyond this field. Hence the only increase in translational energy of the atoms is from collisions with electrons. Consider, for simplicity, an electron colliding head-on with a gas atom at rest. From the principle of conservation of momentum,

\[ mv + MV = mv_1 + MV_1 \]  \hspace{1cm} (2.1.11)

where \( m \) and \( M \) are the electronic and ionic mass and \( v, v_1 \) and \( V, V_1 \) are the initial and final electron and ion velocities respectively.

From the principle of conservation of energy,

\[ \frac{1}{2} mv^2 = \frac{1}{2} mv_1^2 + \frac{1}{2} MV_1^2 + W_p \]  \hspace{1cm} (2.1.12)

where \( W_p \) is the ionization energy of the atom. Solving these equations for \( V_1 \), we get,

\[ V_1 = \frac{Mv + \sqrt{2Mv^2 - 2M(1 + \frac{M}{m})W_p}}{\frac{M}{2} \left( 1 + \frac{M}{m} \right)} \]  \hspace{1cm} (2.1.13)
Since \( \frac{M}{m} \) is a large quantity, \( V_1 \) can be approximated to

\[
V_1 = 2m \left[ v \sqrt{v^2 + 2W_p/m} - \frac{2W_p}{m} \right] / M \tag{2.1.14}
\]

Substituting typical values, it may be seen that, the increase in kinetic energy of the particle is approximately equal to 0.1 eV which is less than the thermal energy of the particle.

Hence we have to look for other causes for a very large increase in chemical reaction rate. In ordinary reactive evaporation, the particles are not ionized and they have to collide with sufficient translational energy to overcome the potential barrier (see Chapter XI). But when one of the particles is ionized, the activation energy necessary for chemical reaction become very low or equal to zero. In other words for ion molecule reactions, the potential barrier is very low or does not exist at all. This is because of an inverse fifth power attractive force arising from point charge-induced dipole interaction between the ion and the molecule /5/. This long-range attraction, greatly increases the rate of collisions above what would usually obtain if both the particles were ground state neutrals, and is responsible for the very large cross sections (10^{-14}/cm²) of many ion-molecule reactions at thermal energies. So collision rate is increased and almost all collision leads to a
reaction and also the reaction rate is nearly independent of temperature. In the case of a plasma as used in ARE, the velocities of ionized and neutral particles obey the Maxwellian distribution of velocities (because due to collision with electrons, the velocities of the atoms or molecules are not changed much) and the rate constant is approximated by Gioumousis and Stevenson's formula /6/ 

\[ r = 2 \pi \varepsilon \left( \frac{\alpha_e}{\mu_r} \right)^{1/2} \]  

(2.1.15)

where \( \alpha_e \) is the polarizability of the molecule, \( \mu_r \) the reduced mass of the colliding pair and \( e \) the electronic charge. From this expression, a rate constant of about \( 10^{-9} \text{ cm}^3 \text{ sec}^{-1} \) can be predicted for most collisions of ion with non-polar molecules. In order to get an idea of the increase in reaction rate due to ionization, this rate constant must be compared with bimolecular reactions involving atoms and radicals which have rate constants of the order of only \( 10^{-11} - 10^{-14} \text{ cm}^3 \text{ sec}^{-1} \).

Though chemical reaction rate is tremendously increased, making it possible to get high deposition rates by the use of ARE, there is still the problem of amorphous areas and unreacted species getting entrapped in the growing film. This, as we know, will adversely affect film properties. It is well known that if the substrate temperature is so chosen that the reevaporation of amorphous
and unreacted areas are favourably increased, high quality films can be obtained. It is also found that if the ratio of substrate temperature $T$ to the normal boiling point of the compound $T_b$ is approximately 0.33, films with optimum properties are obtained /7,9/. This particular substrate temperature will also increase diffusion into the reevaporated areas and microhole free films with good carrier mobility etc. can be obtained. If too high a substrate temperature is chosen, the crystalline areas of the film itself will reevaporate and film quality will be poor.

If high substrate temperature is not practicable for any reason, another way to obtain almost all the beneficial effects of high substrate temperature is by giving additional kinetic energy to the ionized and neutral particles by accelerating the ionized particles to the substrate and making it collide with neutral particles before they reach the substrate surface. Such a method is known by various names like Biased Activated Reactive Evaporation (BARE) /10/ or Reactive Ion Plating (RIP) /11/. In this method, the substrate is kept at a high negative potential (around 3KV) and the ions are accelerated to the substrate. An analysis by Teer /12/ showed that for a typical system with an applied voltage of 3KV and a gas pressure of $10^{-2}$ Torr, the ions lose almost 90% of the energy by transferring their energy to
neutral atoms in traversing the cathode dark space. If the mean free path $\lambda_0$ and the length $Z_c$ of cathode dark space are assumed to be 0.5 cm and 10 cm respectively under the conditions given above, a total number 

$$(Z_c/\lambda_0)N_o = 20 N_o$$

of energetic neutrals are produced, where $N_o$ is the number of ions leaving the edge of the cathode dark space towards the cathode in unit time. The average energy of the ions arriving at the cathode is approximately $(V_c/Z_c) 2 \lambda_0 = 300$ eV and of the neutral particles is $V_c(Z_c - 2 \lambda_0) (\lambda_0/Z_c)/Z_c = 135$ eV, for the same conditions, assuming they suffer no collisions after gaining their energy. From this it can be seen that energetic neutral atoms (less than 135 eV) are in the majority and ions with moderately high energy (about 300 eV) are in the minority for film formation.

The most important physical process which occur during ion-plating and allied techniques are

(1) ion induced (and energetic atom induced) desorption of adsorbed impurities from substrate surface. This cleaning effect gives excellent adhesion of the film to the substrate.

(2) ion penetration and entrapment in the substrate and coating.
(3) Ion induced sputtering of substrate and coating. If the energy of the ions are properly adjusted, this backspattering effect can be used to sputter away amorphous and disordered regions leaving the crystalline region intact. This process may be used to get films with optimal properties.

(4) Recoil displacement of substrate and coating atoms. This leads to good intermixing and improvement in adhesion and microhardness results.
References:


