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MBE growth of GaAs and III-V alloys

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The growth of GaAs and III-V alloys by MBE is now a well-established method used to prepare a whole range of devices. One of the advantages of MBE is that the same technology can be used to study the processes controlling growth. This article will discuss the present state of knowledge concerning the growth of binary compounds such as GaAs and of alloys with mixed group III and mixed group V elements. It will also discuss the relation between growth conditions and resulting film properties for binary compounds, alloys, and interfaces.

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I. INTRODUCTION

The mechanisms controlling the growth of GaAs and related alloys by MBE have been studied extensively both by modulated molecular beam techniques and by reflection high energy electron diffraction, RHEED. The modulated beam technique gives detailed information on the kinetic factors controlling the growth process while RHEED is used to determine the surface structures present during growth. More recently angle-resolved photoemission studies of MBE grown surfaces have provided detailed information on the atomic configuration of the surface.

This article will discuss the present state of our knowledge concerning the processes controlling growth and the relation between these and the resulting properties of the films. The discussion will concentrate first on GaAs and other binary compounds, then upon alloys with mixed group III and V elements, and finally on the relation between the growth conditions and film properties.

II. GROWTH OF III-V COMPOUNDS

The growth of (100) GaAs by MBE has been studied extensively and sufficient work has been carried out on other binary compounds such as InAs,¹ InP,² AlAs,³ to show that similar behavior is observed for most combinations of Al, Ga, and In with P, As, and Sb. The discussion throughout this section will concentrate on GaAs but qualitatively similar effects will also be observed for the other binary compounds at somewhat different temperatures.

The Ga and As populations present on the surface during growth will depend on both the substrate temperature and the relative fluxes of Ga and As atoms reaching the surface. Ga is always supplied as the monomer by evaporation from the liquid and has a unity sticking coefficient on the GaAs surface over the whole range of temperatures used for growth. At high temperatures Ga will re-evaporate, this effect becomes important when the rate of re-evaporation becomes significant compared with the arrival rate. This effect will be discussed further below in relation to the growth of alloy films. The growth rate of the layers is simply determined by the net supply rate of Ga atoms.

As can be supplied in several ways, as the tetramer As₄, by sublimation from the solid, or as the dimer As₂, by dissociating the As₄ molecules using a special two-zone furnace.⁴ As₂

can be produced by evaporating GaAs. It can also be supplied by thermally dissociating arsine to give As₂ and possibly As (Ref. 5). At the substrate temperatures used to grow GaAs, < 750 °C, As atoms would rapidly reassociate on the GaAs surface to give As₂ molecules and therefore the choice is effectively between As dimers or tetramers. If As is supplied from arsine it is, however, worth noting that significant amounts of atomic and molecular hydrogen will also arrive at the GaAs surface during growth and this may have a beneficial effect on the properties of the resulting films.

When GaAs is grown from Ga and As₂ the reaction is a first-order dissociative chemisorption of As₂ molecules on single Ga atoms.⁶ This process is illustrated schematically in Fig. 1. The sticking coefficient of As₂ is simply proportional to the gallium flux and tends to unity on a Ga-rich surface. Excess As₂ is lost by re-evaporation, in general therefore stoichiometric GaAs will be grown. For GaAs grown from Ga and As₄ a more complex process is involved.⁷ This is illustrated schematically in Fig. 2. Pairs of As₄ molecules react on adjacent Ga sites resulting in second-order dependence of the As₄ desorption rate on adsorption rate at low As coverages. The maximum sticking coefficient for As₄ molecules is 0.5 and the requirement for a pairwise interaction could result in a higher concentration of point defects for films grown with As₄. The different growth processes involved with As₂ and As₄ may be expected to influence the properties of films grown under otherwise identical conditions.

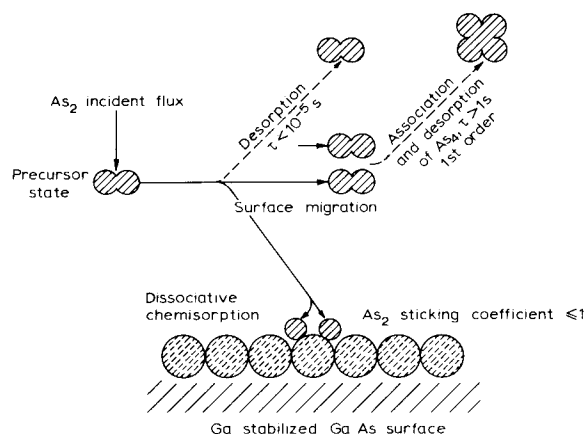
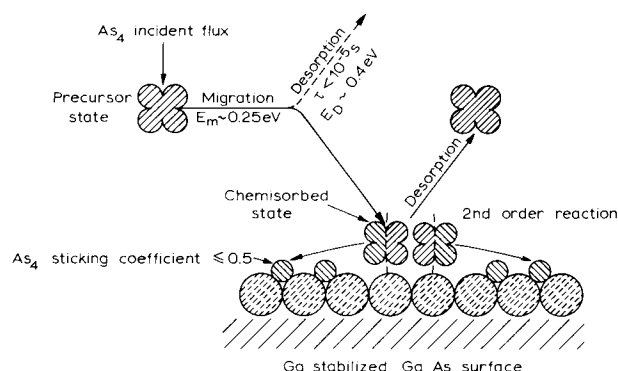


FIG. 1. GaAs growth from Ga and As₂.

FIG. 2. GaAs growth from Ga and As_4 .

As the substrate temperature is increased during growth As_2 is lost by desorption resulting in an increased Ga surface population.⁸ This behavior can be seen in RHEED studies of the effect of substrate temperature on the surface structures present during growth.⁹⁻¹² At low temperatures and high As to Ga flux ratios an "As-stable" (2×4) structure is observed while at high temperatures and low As to Ga ratios a (4×2) "Ga-stable" RHEED pattern can be observed. In-between various transition structures can be seen. There is no fixed concentration of Ga and As atoms corresponding to a particular surface structure but reasonable estimates have been given for the likely values.¹¹

Recent angle-resolved photoemission studies of GaAs (2×4) surfaces prepared by MBE¹³ have shown that the surface As atoms are dimerized with the bridge bond tilted. This overall model is similar to the one proposed for Si(100) surfaces,¹⁴ and the tilted dimer must result in a lower energy configuration for the surface As atoms. The twofold periodicity observed in the RHEED pattern arises directly as a result of the As atoms being dimerized. The reconstruction orthogonal to the dimerization is probably of less fundamental significance and may merely reflect the sequencing of the dimer tilt from row to row. It is much less obvious what gives rise to the reconstruction observed on Ga-rich surfaces and as yet no detailed picture has emerged for such structures.

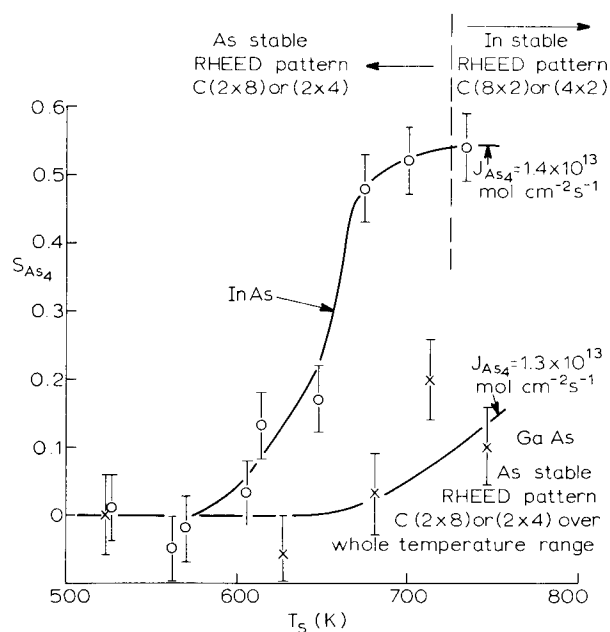
Above about 660°C the GaAs surface evaporates noncongruently,¹⁵ that is, the rate of evaporation of As as As_2 exceeds that of Ga. To grow films above this temperature it is necessary to supply excess As to compensate for this loss. What is not clear, however, is whether the models evolved for films grown at lower temperatures apply to films grown in this high-temperature regime, or whether other mechanisms are involved. Growth certainly takes place under more Ga-rich conditions and both the majority and minority carrier properties are influenced significantly by substrate temperature. This is one area where more detailed work is required before a complete picture of the GaAs growth process is obtained. Problems associated with growth above the congruent evaporation region are also of importance in discussing the growth of alloy films since the limiting temperatures for the binary end members can be significantly different. This point will be discussed in more detail below.

III. GROWTH OF ALLOY FILMS WITH MIXED GROUP III ELEMENTS

Alloy films with mixed group III elements can be grown at low temperatures with few problems. The sticking coefficients of the group III elements are unity and therefore the alloy composition is simply determined by the relative fluxes reaching the surface. Three alloy systems InGaAs, InGaP, and AlGaAs have been studied in some depth since all have potential device applications. The electrical and optical properties of such films are, however, strongly influenced by substrate temperature and in practice therefore it may not be possible to obtain suitable alloy films by growth at low temperature. Three problems arise as the substrate temperature is increased.

The first effect which is observed as the substrate temperature is increased arises because of the different rates of loss of group V dimers from the binary end members of the alloy. This can be seen, for example, for InGaAs where measurements of the sticking coefficients of As_4 on GaAs and InAs as a function of temperature¹⁶ show that at high temperatures the rate of loss of As from InAs is much higher than from GaAs. This is illustrated in Fig. 3. Below about 300°C the rate of loss of As_2 is negligible for both compounds but in order to grow at higher substrate temperatures the As flux must be increased to compensate for the increased loss from In atoms in the surface of an InGaAs alloy.¹⁷

A second more serious problem can arise which is illustrated in Fig. 4. This shows Auger spectra for InGaP films grown on a GaAs substrate.¹⁶ At higher substrate temperatures the surface becomes enriched with In. Similar effects have been reported recently for InGaAs films grown at about 500°C ,¹⁸ where the surface becomes In rich and for AlGaAs,¹⁹ and where it is suggested that the surface is depleted in Al. In each case the group III element with the higher vapor pressure is present as an enriched surface

FIG. 3. The effect of temperature on the sticking coefficient of As_4 on GaAs and InAs.

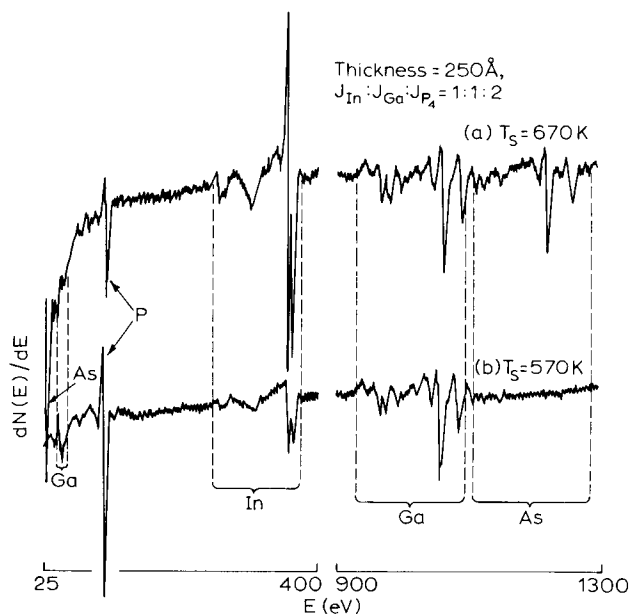


FIG. 4. Auger spectra for InGaP films grown on GaAs at different temperatures.

phase. It is also suggested^{17,18} that films grown under such conditions are inhomogeneous with an In deficiency at the substrate layer interface.¹⁸ All these effects will limit the sharpness of interfaces between alloys of different composition grown under such conditions.

The third effect which occurs during growth at high temperatures is due directly to the different vapor pressures of the group III elements over the alloy. We can estimate the rate of loss of the group III elements from the vapor pressure data.²⁰ This is a reasonable approximation because the vapor pressure of the element over the compound, e.g., Ga/GaAs is similar to the vapor pressure of the element over itself Ga/Ga¹⁵ and for alloys grown at high temperatures the surface will be enriched in the more volatile group III element. The results of this calculation are shown in Table I. Typical growth rates used in MBE are about a monolayer per second or a micron per hour and therefore we expect to observe a significant loss of In for InGaAs films grown above 550 °C and a loss of Ga for AlGaAs films grown above 650 °C. Variations in substrate temperature during growth will result in changes in alloy composition unless the fluxes reaching the surface are changed accordingly.

TABLE I. Approximate rate of loss of group III elements at monolayers per second.

Temperature (°C)	In	Ga	Al
550	0.03
600	0.3
650	1.4	0.06	...
700	8	0.4	...
750	30	2	0.05

IV. GROWTH OF ALLOYS WITH MIXED GROUP V ELEMENTS

For alloys such as GaAsP,²¹ InAsP,²¹ or GaSbAs²² the lower vapor pressure group V element is incorporated preferentially at low temperatures. For GaAsP and InAsP the sticking coefficient of As, either As₂ or As₄, is much greater than that of P, P₂, or P₄ and for GaSbAs alloys Sb has a higher sticking coefficient than As. This provides a simple method of controlling the composition of such alloys. For example, if the As flux, J_{As} , reaching the GaAsP surface is small compared to the Ga flux, J_{Ga} , and excess P is supplied, the As fraction Y will be given by

$$Y = 2 \times J_{As} / J_{Ga},$$

where the As flux is supplied as the dimer or the tetramer.

The reason for the very different sticking probabilities of the various group V elements is not at present understood. It was suggested that the sticking probability might be influenced by the surface lifetime of the various species,^{21,22} but this cannot be correct because, even though the lifetime of As₂ molecules is much shorter than P₄ molecules, they are incorporated preferentially.²³ The surface lifetime cannot therefore be the factor controlling the incorporation rate and at present the mechanism is unknown.

At higher substrate temperatures,^{22,23} when the rate of loss of the dimers becomes significant compared with the growth rate, composition control becomes more difficult. For GaAsP the As fraction decreases with increasing substrate temperature as shown in Fig. 5. This arises because the partial pressure of As over GaAsP is higher than that of P at any given temperature and therefore the re-evaporation rate is higher, leading to an effective reduction in the amount of As incorporated in the film. The temperature dependence of the Sb fraction in GaSbAs films²² can be understood on the same basis.

An interesting situation arises when growing quaternary

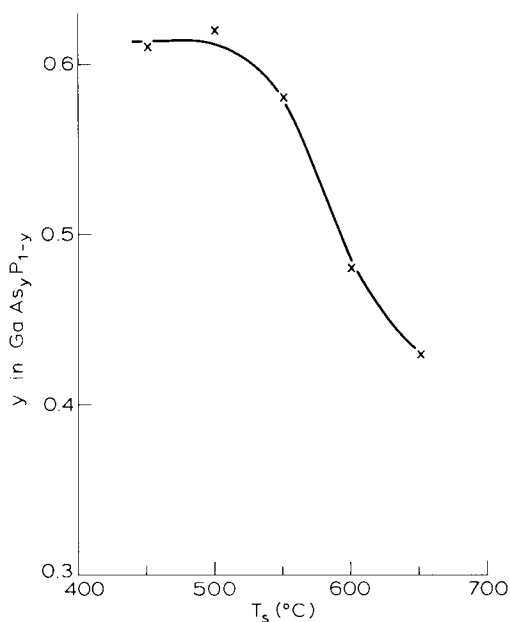


FIG. 5. Effect of substrate temperature on the composition of GaAsP films.

alloys of InGaAsP because for InAsP the vapor pressure of P is higher than As at any given temperature, but for GaAsP the opposite situation holds. Depending on the In to Ga ratio increasing the substrate temperature could increase or decrease the As content of the resulting layers.

In summary no simple method exists for predicting the fluxes required to grow alloy films of a specific composition at high substrate temperatures. The best empirical approach is to limit the supply rate of the preferred group V element keeping an excess of the other group V species to maintain stoichiometric growth. For such alloys control of substrate temperature during growth is of critical importance because this will influence the alloy composition.

V. GROWTH PROCESSES AND FILM PROPERTIES

Several recent studies have shown a clear correlation between the growth conditions used and the resulting film properties for binary compounds, alloy films, and interfaces between layers of different composition. The electron traps characteristic of MBE growth,²⁴ M_1 , M_3 , and M_4 , decrease with increasing substrate temperature²⁵ and over the same temperature range the optical quality (internal efficiency) of p -type GaAs improves dramatically.²⁶ For films grown under otherwise identical conditions it is also known that the use of As_2 as opposed to As_4 reduces the density of the same electron traps^{27,28} and improves the photoluminescence efficiency of GaAs layers.²⁹ The presence of either of Pb^{25} or H_2^{25} can also reduce the concentration of electron traps present and in addition H_2 can improve the majority carrier properties of GaAs.³⁰

For alloy films similar improvements have been observed, both As_2^{31} and H_2^{32} can improve the optical properties of AlGaAs and for GaInP the presence of Pb on the surface during growth reduces the concentration of deep centers.³³

For AlGaAs–GaAs heterostructures it has also been proposed that increasing the substrate temperature reduces the interface recombination velocity³⁴ and that the use of As_2 can also have a beneficial effect.³¹

In all of the examples quoted above it is far from clear whether the improvement in properties results from a reduction in the concentration of impurities or from a reduction in concentration of native point defects. Secondary-ion mass spectrometry studies³⁵ have shown that the concentration of heavy-metal impurities in GaAs decreases monotonically with increasing substrate temperature but it is difficult to imagine that changing from As_4 to As_2 can reduce the concentration of extrinsic impurities by an amount equivalent to the reduction in the deep-level concentration observed in GaAs films. It is tempting therefore to conclude that the changes in As species has reduced the concentration of native defects such as As vacancies. The observed reduction of deep levels with increasing substrate temperature,²⁵ and hence decreased As surface population, seems at variance with this suggestion and with the observation that increasing the As to Ga ratio also produced a reduction in deep-level concentration.²⁵ It has therefore been suggested that the deep levels are complexes between impurities and native defects (As vacancies). On this basis as the substrate tempera-

ture is increased the sticking coefficient of the impurities is reduced and at fixed substrate temperatures increasing the As to Ga ratio or changing from As_4 to As_2 reduces the As vacancy concentration.

A second set of puzzling observations³⁶ also require comment in this context. It is known that the properties of AlGaAs–GaAs modulation-doped structures depend upon the order in which the layers are grown, for the so-called normal structure where AlGaAs is grown on top of GaAs the enhanced mobilities are much better and less sensitive to substrate temperature than the equivalent inverted structures where GaAs is grown on top of AlGaAs.³⁶ It has been suggested³⁶ that this relates to the influence of substrate temperature on the morphology of AlGaAs.³⁷

It is possible therefore that the incorporation of impurities is influenced by the morphology of growth and that it is the density of steps on the surface which is strongly influenced both by the growth conditions or the presence of heavy metals. If so, the reduction in deep levels and the improvement in photoluminescence efficiency, etc. might be related fundamentally to changes in the morphology of the growth process.

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