PART I

Metal/Semiconductor Heterostructures I

THERMODYNAMICS, KINETICS AND INTERFACE MORPHOLOGY OF REACTIONS BETWEEN METALS AND GaAs

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ABSTRACT

The chemical stability of interfaces between metals and GaAs was discussed in terms of reaction sequence and diffusion path concepts. The factors which determine interface morphology were also given. These general ideas can be applied to any interfacial reactions between two dissimilar materials.

1.0 Introduction

Essential to the designing of microelectronic devices is the need for connections between active elements and therefore the need for active contacts. The need for reliable, low-resistance, reproducible, and stable ohmic contacts and Schottky barriers is particularly great for III-V compound semiconductors such as GaAs and for solid solutions of III-V compound semiconductors. In addition to exhibiting the appropriate electrical properties, a successful contact needs to be chemically stable. However, the chemical stability and hence the electrical properties of a contact are governed by the thermodynamics, kinetics and interface morphology of phase formation between the metallizing elements and the compound semiconductors.

During the past few years, a large number of experimental results have been reported in the literature concerning the metallization of III-V compound semiconductors, primarily GaAs. These studies have included the identification of the phases formed and to some extent the resulting morphologies when M/GaAs contacts were exposed to specific environments. Frequently, due to the paucity of relevant phase equilibria, thermodynamic, and kinetic data for ternary Ga-M-As systems, a rationalization of these results (some of which appear to be contradictory) has been difficult, if not impossible. The recent studies by us[1-15], Williams and co-workers[16-20], Beyers, Kim and Sinclair[21], and Sands[22,23] have demonstrated the importance of phase diagrams in the understanding of interfacial reactions between thin-film metals and GaAs. In addition, the concept of diffusion path in ternaries has been introduced by us[1,5-7,9,10,13,15] to rationalize the phase formation in M/GaAs contacts. The factors which determine phase formation sequences and phase morphologies in terms of thermodynamic and kinetic view points have also been discussed by us.[5] These ideas have been applied to M/GaAs diffusion couples in both the bulk and thin-film forms. We have found that the reaction sequences and diffusion paths for all M/GaAs couples investigated to-date are similar for the bulk and thin-film cases.

2.0 Interfacial Stability

2.1 Thermodynamic Considerations

It is well-known by now that most metals are not chemically compatible with GaAs.[1,3,10,21,22,24] Figure 1 shows three typical phase diagrams of Ga-M-As when M is not in thermodynamic equilibrium with GaAs and when the only stable binary phases are Ga_3M, GaM, GaM_3, MAs, M_2As_3 and GaAs. The diagram in Fig. 1(a) depicts the case when the binary phases exhibits limited solubilities of the third component elements. The diagram in Fig. 1(b) depicts the case when the binary phase MAs dissolves a considerable amount of the counter phase "GaM". The symbol "GaM" denotes the unstable

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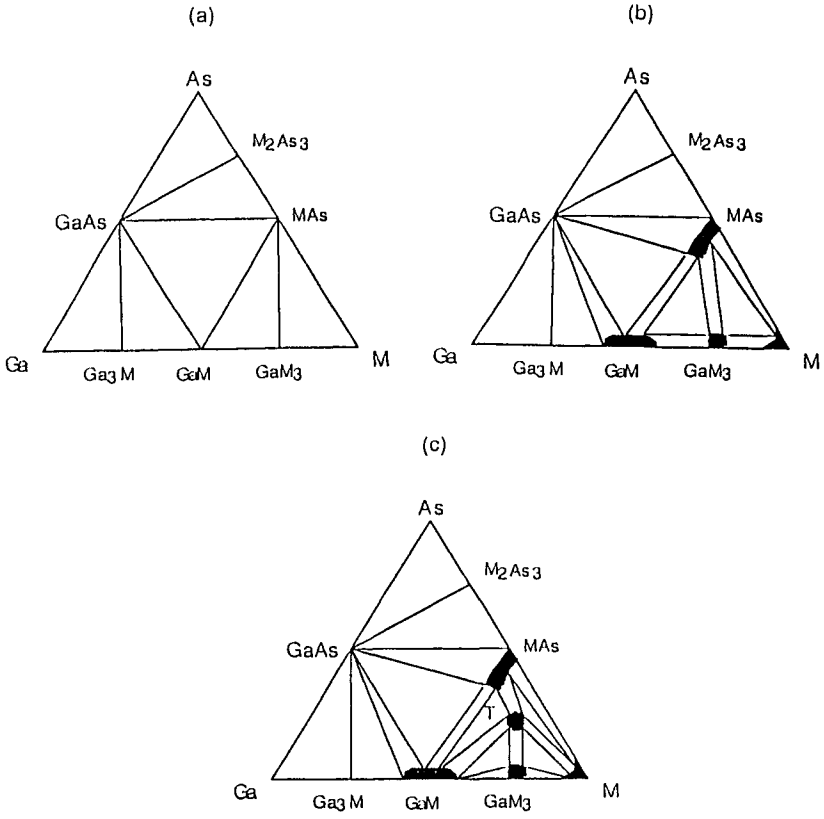


Figure 1.

Three possible phase diagrams of Ga-M-As at constant T and P.

a. There are no mutual solubilities in any of the binary phases.
b. There is extensive solubility of Ga in MAs.
c. There is a ternary phase T along the GaAs-M join.

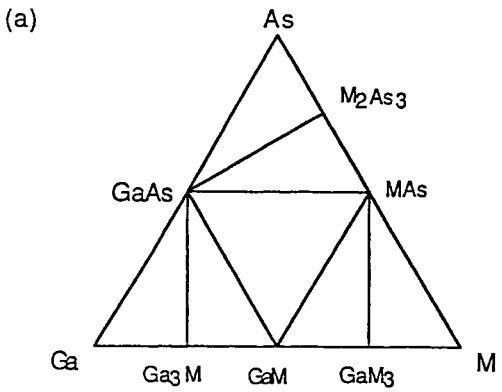
phase GaM which exhibits the MAs structure. The diagram in Fig. 1(c) depicts a case where, in addition to extensive solubilities of MAs, GaM, GaM_3 and (M), there exists a ternary phase T with a composition lying along the GaAs-M join. The appearances of the three types of phase diagrams depend upon the relative stabilities of the competitive phases, i.e. Ga_3M, GaM, GaM_3, MAs, M_2As_3, GaAs and T, the lattice stabilities of the component elements and the intermediate phases, and the thermodynamic solution behaviors of the solution phases. In order to be able to accurately calculate the phase diagrams of Ga-As-M, it is necessary to know the Gibbs free energies of the phases and the solution behaviors of the phases with extensive solubilities. Since most of the data are not available, accurate phase diagram determination is necessary. Several ternary Ga-M-As systems in the composition range of relevance to the metallization of GaAs have been determined by us. It is evident from Fig. 1 that in all three cases, the M/GaAs contacts will undergo chemical reactions when subjected to sufficiently high temperatures. In some cases, a sufficiently high temperature may be only 100°C or even lower. However, in view of the many types of phase equilibria exhibited by Ga-M-As, the kinetics of the reactions for the M/GaAs couples are quite different, as will be discussed in the next section.

2.2 Kinetic Considerations

2.2.1 Diffusion Paths

Thermodynamics tells us what will happen when equilibrium conditions are achieved but does not tell us what combinations of phases may form under actual conditions. For instance, we cannot tell what phases will form when M is in contact with GaAs from the phase diagram given in Fig. 1(a). While only one path is possible in a binary couple, this is not true for a ternary couple. When M is in contact with Ga for a binary Ga-M shown in Fig. 1, the three intermediate phases Ga_3M, GaM and GaM_3 will form, the only possible diffusion path. On the other hand, when M is in contact with GaAs, there is more than one possible path. Figure 1(a) is reproduced as Fig. 2(a) with two possible paths given in Fig. 2(b,c). When M is in contact with GaAs, several phases may form, such as GaM, GaM_3 and MAs. According to Kirkaldy and Brown[37], given a specific ternary diffusion couple there is only one diffusion path. Recent experimental studies by van Loo and co-workers[43-46] on oxide/metal systems, Leute[47] on pseudo-ternary compound semiconductor/compound semiconductor systems, and by us[1,5-8,10,15] on GaAs/M systems yield results in accordance with this statement. Although it is possible in principle to calculate the diffusion path, it is practically impossible given the current state of our understanding of ternaries such as Ga-M-As. We must depend upon experiments to determine the diffusion paths of GaAs/M couples. If the diffusion path is that given as path I (Fig. 2(b)), MAs would be in contact with GaAs; on the other hand, if path II (Fig. 2(c)) is the diffusion path, GaM would be in contact with GaAs. From a device point of view, it is important to know which of these phases is in contact with GaAs under equilibrium conditions.

Because microelectronic devices are made in the form of thin-films, it is equally important to study the kinetics of thin-film phase formation on GaAs. Let us now refer to Fig. 1(a) or 2(a) for discussion. When a thin-film metal M is deposited on GaAs, the final equilibrium mixture will be GaAs, GaM and MAs. If the diffusion path is that of path I, we will have the final configuration of GaAs|MAs|GaM. On the other hand, if path II is the diffusion path, the final configuration of thin-metal film deposited on GaAs would be GaAs|GaM|MAs. Although there are indications that the results obtained from some bulk and thin-film M/Si binary couples may not be the same[25-30], the results of our studies on GaAs/M couples are similar for both the bulk and thin-film cases.[1,5-8,10,15] If discrepancies between the bulk and thin-film studies do occur, additional investigation will be carried out



(b) Path I

GaAs	MAs	GaM	GaM_3	M

(c) Path II

GaAs	GaM	MAs	M

Figure 2. a. A hypothetical Ga-M-As ternary isothermal section.
b. A possible diffusion path for a couple of GaAs/M.
c. Another possible diffusion path for a couple of GaAs/M.

to ascertain whether they are intrinsic in nature.

2.2.2 Interface Morphology

Up to this point, we have not discussed the interface morphology, which is determined by the growth kinetics of the phases in a couple. Wagner[31] has considered the morphological and kinetic aspect of displacement reactions in the solid state. In a later paper, Wagner[32] established the criteria for the stability of a flat growth interface. Rapp and co-workers[33-35] have utilized this concept to study reactions in M/oxide and M/sulfide couples. Let us now apply these criteria to a GaAs/M diffusion couple under two specific conditions as discussed by Lin et al.[5] In Fig. 3(a), assuming that the initially predominant moving species is Ga and that As diffuses the slowest, the growth of GaM_3 and MAs would necessarily occur at the GaM_3/M and GaAs/MAs interfaces, respectively. A moving interface is referred to as a growth front. The growth of GaM_3 and MAs is controlled by the diffusion of Ga and M respectively. The flux of Ga arriving at position I exceeds that at position II, resulting in the formation of a planar GaM_3/M interface. Similarly, the flux of M arriving at position III exceeds that at position IV, again resulting in the formation of a planar GaAs/MAs interface. On the other hand in the second case, as is shown in Fig. 3(b), the species M is the predominant moving element for the growth of GaM_3 and MAs. In this case, the growth fronts of GaM_3 and MAs are at the MAs/GaM_3 and GaAs/MAs interfaces, respectively. If the rate-controlling step for the growth of GaM_3 is the diffusion of Ga, then the growth rate at position I is higher than that at position II. Under these circumstances, a planar MAs/GaM_3 interface would be unstable. The situation for the GaAs/MAs interface is the same as that in Fig. 3(a) and therefore the interface remains planar. From the above discussion, it may readily be seen that a knowledge of the predominant moving element and the rate controlling steps to phase growth are the key points to understanding and predicting interface morphology. In fact, we have successfully applied the above concept to the preliminary results obtained for GaAs/Pt[10,11], GaAs/Ir[10,15], GaAs/Co[6], GaAs/Ni[8], and GaAs/Nb.[10]

2.2.3 Phase Formation Sequence

The diffusion path of a ternary diffusion couple such as GaAs/M represents the stable phase arrangement between the end phases, i.e. GaAs and M for the GaAs/M couples. However, depending upon the types of phase equilibria and the relative mobilities of the component elements, the phases formed initially and even the phases formed subsequently may not correspond to the stable phase arrangements. Although it is difficult to know in advance precisely the phase formation sequence, we may follow the ideas suggested by Lin et al.[5] to forecast possible phase formation sequences. The three phase diagrams given in Fig. 1 are reproduced in Fig. 4. Let us assume that the diffusion path corresponds to GaAs|MAs|GaM_3|M for the case shown in Fig. 4(a) and to GaAs|MAs|GaM|GaM_3|M for the cases shown in Figs. 4(b,c). Three possible reaction sequences are given in Fig. 4. Let us now discuss the rationale for forecasting the reaction sequences for the phase diagram in Fig. 4(c).

When a GaAs/M couple is exposed to a high enough temperature, interdiffusion will occur at the interface. Initially the overall composition near the interface should be close to the GaAs and M connection line. Once the amount of foreign elements reaches the sustainable limit of the crystalline solid, new phases nucleate at the interface. According to the phase diagram in Fig. 4(c), the T phase would most likely form first. This behavior is due to kinetics. The composition of the T phase is close to the initial composition at the interface, and therefore less time would be necessary to redistribute the elements in order to nucleate this phase.

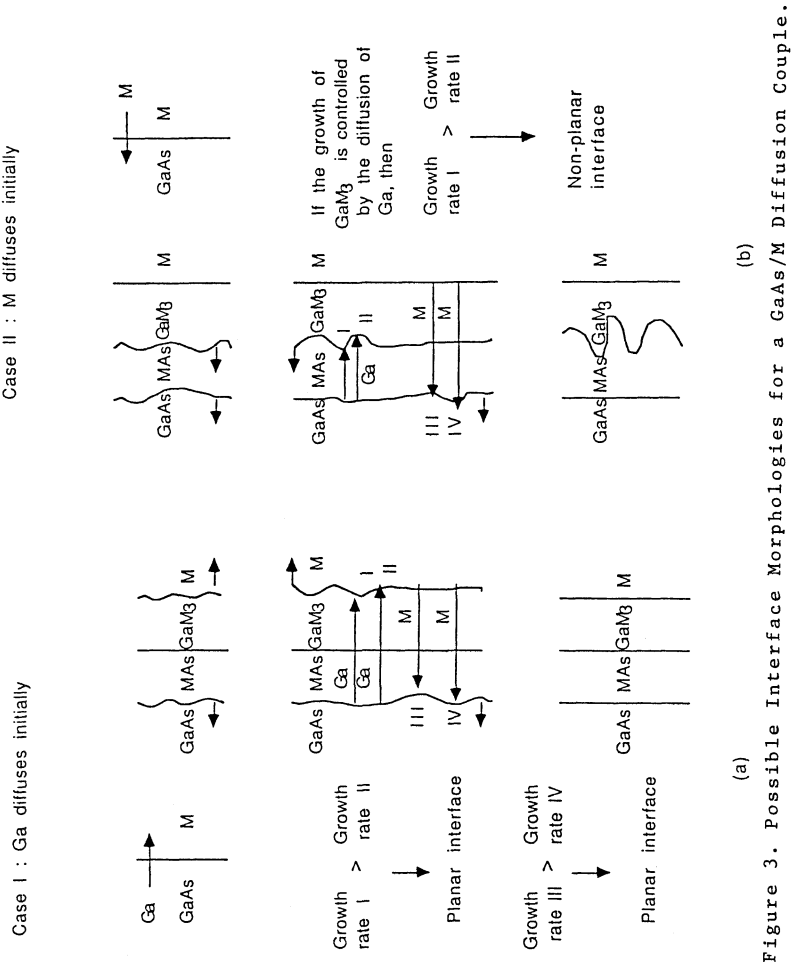


Figure 3. Possible Interface Morphologies for a GaAs/M Diffusion Couple.

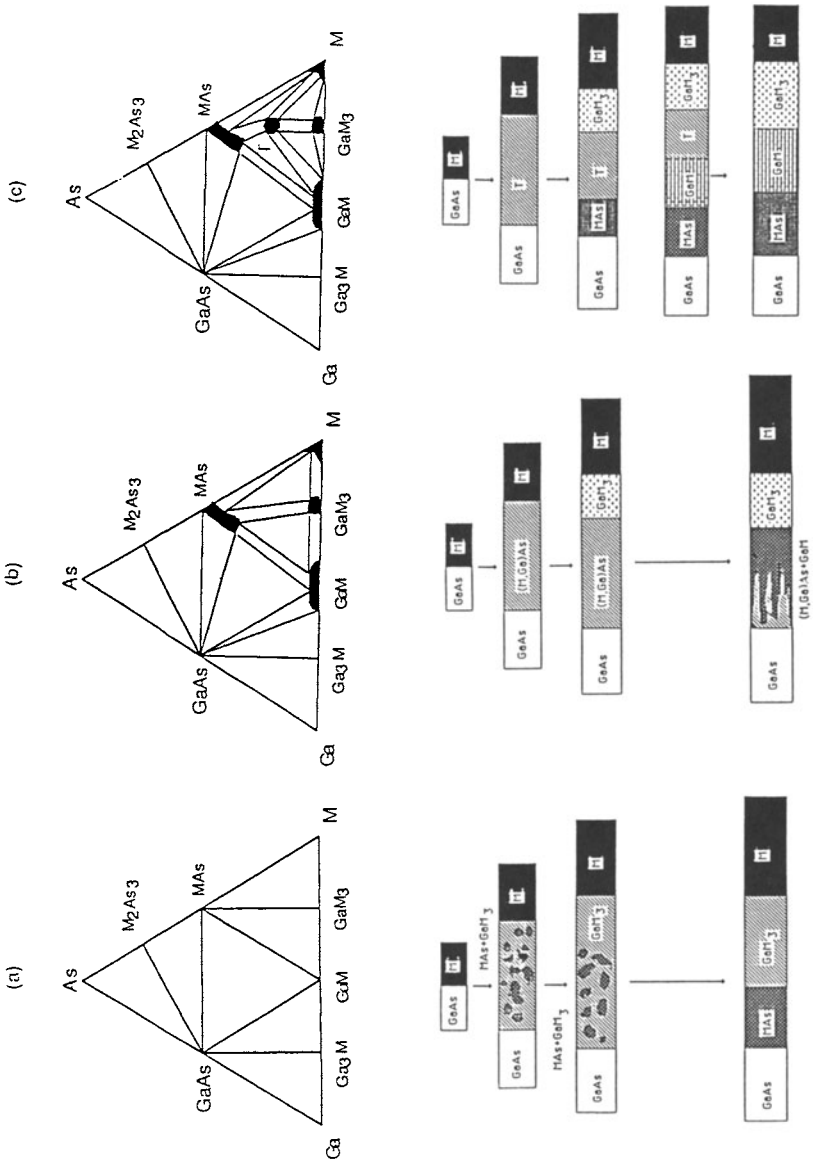


Figure 4. Possible phase formation sequences for three types of Ga-M-As phase diagrams.

We would then have an initial configuration of GaAs|T|M, but none of the interfaces would be at thermodynamic equilibrium. Consequently, more reaction evolution would take place. Although several phases may nucleate and form at the GaAs|T and T|M interfaces, we believe MAs would be the first one to nucleate and grow at the GaAs|T interface. Again, it would take less time to redistribute the elements from T to nucleate and form MAs than would be required to form GaM. At the same time, the phase GaM_3 would probably form at the T|M interface since it is in equilibrium with T and M. The configuration would then be GaAs|MAs|T|GaM_3|M with all of the interfaces at thermodynamic equilibrium.

Although the phases between GaAs and M are now thermodynamically stable, some of these phases may be kinetically unstable. The kinetic stabilities of the phases depend upon the relative fluxes at the various interfaces. Let us suppose that T is kinetically unstable. This is a reasonable assumption since the growth of a ternary phase or a solution phase in the ternary region requires specific elemental flux ratios. Then MAs and GaM_3 would grow at the expense of T with subsequent formation of GaM. The most likely evolution of the reaction sequence would be GaAs|MAs|GaM|T|GaM_3|M with the final stable configuration of GaAs|MAs|GaM|GaM_3|M, the diffusion path.

The preliminary results we have obtained concerning the reaction sequences for GaAs/Co[2,4,6,9], GaAs/Ni[8], GaAs/Pd[1,10] and GaAs/Pt[10,11] are consistent with the arguments presented above. We are currently conducting more extensive experimental studies on GaAs/Co, GaAs/Ni and GaAs/Pt to firmly establish the reaction sequences already found in light of the above discussion.

2.2.4 Quantitative Layer-Growth of Phases

Up to this point, we have discussed only qualitative arguments for the formation of phases in a ternary diffusion couple such as GaAs/M. We now present the basic quantitative formulation for the growth of phases formed in a bulk diffusion couple in terms of ternary diffusion theory. Onsager[48-50] has shown that the diffusional flux, J_i, in a multi-component system may be expressed as a linear function of the chemical potential gradients. However, because chemical potential gradients are not convenient for experimental analysis, these equations are transformed, making use of the concentration gradients as independent variables. This leads to the generalized form of Fick's first law for a ternary system,

$$\tilde{J}_1 = - \tilde{D}_{11} \frac{\partial C_1}{\partial x} - \tilde{D}_{12} \frac{\partial C_2}{\partial x} \qquad [1.A]$$

$$\tilde{J}_2 = - \tilde{D}_{21} \frac{\partial C_1}{\partial x} - \tilde{D}_{22} \frac{\partial C_2}{\partial x} \qquad [1.B]$$

where $\tilde{D}_{11}$ and $\tilde{D}_{22}$ reflect the effect of the concentration gradient of a given component on its own flux and $\tilde{D}_{12}$ and $\tilde{D}_{21}$ represent the cross-effects, or the ternary diffusional interactions. The subscript 1 refers to component A (or 1) and 2 refers to component B (or 2). C_1 and C_2 are concentrations and x is a distance coordinate. Combining the above equations with the equations of continuity yields

$$\frac{\partial C_1}{\partial t} + \frac{\partial \tilde{J}_1}{\partial x} = 0 \qquad [2.A]$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial \tilde{J}_2}{\partial x} = 0 \qquad [2.B]$$