

Role of kinetics and thermodynamics in alloy clustering and surface quality in InAlAs grown by molecular-beam epitaxy: Consequences for optical and transport properties

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We present results of a Monte Carlo computer simulation which was carried out to understand the molecular-beam epitaxial (MBE) growth of InAlAs. We focus on developing an understanding of the role of growth conditions on the short-range order (alloy clustering) in the system as well as the quality of the growth front during growth. We find that for common anion alloy systems for which *thermodynamics favor phase separation*, the conditions for high-quality alloy and high-quality surfaces (and heterointerfaces) are incompatible if the conventional MBE growth approach is used. We also examine the effect of the alloy clustering on the optical and transport properties of InAlAs.

I. INTRODUCTION

Due to rapid advances in epitaxial crystal-growth techniques, such as molecular-beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), heterostructure based technology has received a tremendous boost.^{1,2} An important feature responsible for the improved performance of heterostructure based devices is the ability to fabricate thin semiconductor structures with atomically abrupt interfaces.^{3,4} Heterostructures are being fabricated not only from binary compound semiconductors, but also from elemental ternary and quaternary compound semiconductors. For heterostructures based on alloys, not only is the quality of the interface important, but the quality of the epitaxial alloy is also important for device performance. The use of semiconductor alloys permits a wide range of choice in tailoring the optical/electronic properties of the heterostructures. An important structural parameter which describes the quality of an alloy is the short-range order parameter (to be described later) which contains information on the clustering present in the alloy. Alloy clustering can cause additional scattering effects which, in turn, can cause broadening of optical emission lines as well as reduce the mobility of charge carriers.

Although, conceptually one can form alloys from a variety of different semiconductors, the actual realization of high-quality alloys is not easy. From thermodynamic considerations, one can determine whether or not an alloy can be produced without clustering. However, even if according to *thermodynamic* considerations one may not be able to grow a cluster-free alloy, one may use a far-from-equilibrium growth technique to grow high-quality cluster-free alloys. MBE is a far-from-equilibrium growth technique which, in principle, can be used to grow alloys which according to equilibrium thermodynamic considerations are immiscible at the growth temperature commonly used. How-

ever, since the growth conditions also determine the quality of the growing surface/interface, one has to ensure that improvements in alloy clustering do not come about at the expense of poorer interfaces.

Due to recent interest in the $\text{In}_{0.52}\text{Al}_{0.48}\text{As}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ system for high speed devices, there is considerable interest in the quality of the MBE-grown InAlAs system.^{5,6} So far, experiments based on photoluminescence and transport have shown that the system is not of a high quality and may have alloy clustering present.⁷⁻¹⁰ Thus, an understanding of the MBE growth process of this system is expected to be quite useful. Due to the large difference between In and Al related bond energies, the InAlAs system is expected to show clustering at the low temperatures employed in MBE growth.^{10,11} In this paper we study the role of growth conditions in controlling the clustering. We also present a theoretical formalism which relates the clustering produced in the alloy grown under different conditions to optical and transport properties of the alloy. Development of such a formalism is important if the consequences of clustering are to be understood.

In the next section, we briefly describe the model used in our calculations and in Sec. III, we present the results and discussions of our computer simulations. In Sec. IV, we discuss the consequences of the alloy clustering on optical and transport properties of InAlAs. And finally, in Sec. V we state the conclusions.

II. MODEL FOR GROWTH SIMULATIONS

The details of our model have been presented elsewhere¹²⁻¹⁴ so here we will only focus on issues special to alloys. The energetics describing the lattice gas model used for the simulations are described by

$$H = \frac{1}{2} \left(\sum_{i \in C(\alpha)} C_{i_a} V_{AC(\alpha)} C_{i_{C(\alpha)}} + \sum C_{i_a} V_{AA} C_{i_a} + \sum_{i_{C(\alpha)} i_{C(\alpha)'} C(\alpha)} C_{i_{C(\alpha)}} V_{C'(\alpha)C(\alpha)} C_{i_{C(\alpha)}} \right), \quad (1)$$

where C_{i_a} and $C_{i_{C(\alpha)}}$ denote the occupation number at the anion and cation sublattices, respectively, and $V_{AC(\alpha)}$, V_{AA} , and $V_{C(\alpha)C(\alpha)}$ are the bond energies for the nearest-neighbor, second-neighbor-anion, and second-neighbor-cation bonds. The α denotes the two (or more) species of cations in the growth of the ternaries being considered.

In addition to the energetics described by Eq. (1), one needs to define the kinetics of the crystal growth process. The important processes have been discussed in Ref. 14. Here we will only emphasize that since several different cations are being incorporated during alloy growth, the activation barrier for individual cations will be different. We have used the following general expression for the surface hops:

$$R_d^i = R_{0d} \exp\left(-\frac{(E_{tot}^i - E_{||}^i)}{kT_s}\right) \quad (2)$$

for the in plane hops and,

$$R_d^i = R_{0d} \exp\left(-\frac{(E_{tot}^i - E_{\perp}^i)}{kT_s}\right) \quad (3)$$

for interlayer hops. Here T_s is the substrate temperature, $E_{||}^i$ and E_{\perp}^i are the reductions in activation barriers for in-plane and interplane hopping for cation i , respectively. Here E_{tot}^i is the total binding energy for the cation and we have chosen

$$E_{||} = E_{\perp} = \frac{1}{2} E_c^f, \quad (4)$$

where E is the binding energy for a free cation (i.e., a cation which has bonds only in the lower layers). Here, it is assumed that for a free cation to hop to the neighboring site, it requires to break half of its surface bonds. This is expected to be a reasonable assumption and, along with the appropriate choice of R_{0d} , gives a close agreement with experimental observations of hopping rates on GaAs.¹⁵ Equations (3) and (4) can be scaled conveniently from one semiconductor to another.

It is difficult to assign accurate values to the various parameters involved in Eqs. (1)–(4). A reasonably accurate value can be obtained for the kink site bonding energy (energy when the atom has two nearest-neighbor and six next-neighbor bonds) from the temperature dependence of the cation vapor pressure. We have described a procedure that has been used to determine these parameters for GaAs.¹⁴ A similar procedure can be applied for other III-V's. For systems where it is difficult to obtain relevant information directly from experimental work, we have scaled the kinetic parameters by bond strength ratios.

The choice of various parameters used by us in the simulations is shown below (R_{0e} is the prefactor for evaporation rate):

$$R_{0d} = 4.0 \times 10^{10} \text{ s}^{-1}, \quad R_{0e} = 8 \times 10^{13} \text{ s}^{-1}, \\ V_{In-As} = 0.7 \text{ eV}, \quad V_{In-In} = 0.14 \text{ eV}, \quad V_{Al-As} = 1.0 \text{ eV}, \\ V_{Al-Al} = 0.2 \text{ eV}, \quad V_{In-Al} = 0.05 \text{ eV}.$$

It must be pointed out that for the InAlAs system we

have used a value of second-neighbor cation bond strengths such that the quantity

$$\Delta = \frac{1}{2}(V_{In-In} + V_{Al-Al}) - V_{In-Al} \quad (5)$$

has a positive value. An exact value of Δ is not known, but we find that small variations in Δ do not have much effect on our results. For example, we have used values of V_{In-Al} ranging from 0.05 to 0.1 eV and find almost no changes in the growth modes and rather small changes in cluster order parameters. However, if the value of V_{In-Al} is chosen close to 0.15 eV, the clustering effects disappear. We note, however, that since work done on LPE growth of InAlAs shows that clustering occurs in this material unless growth temperatures are raised high values¹⁰ (values at which MBE growth cannot take place due to high in evaporation). We believe the choice of parameters above is quite reasonable. We must emphasize, though, that very little is known about the kinetics of growth of InAlAs and hopefully this paper will provide incentive for microscopic study of the InAlAs system.

According to thermodynamics, if the bond energy parameters discussed above are used at temperatures employed in conventional MBE (~ 650 – 750 K), serious clustering effects must occur. However, since MBE is capable of far from equilibrium growth, it is possible to have growth conditions under which cluster-free growth of immiscible alloys can occur. These conditions are explored in the next section.

III. RESULTS

The Monte Carlo program was run on a 40×40 lattice and up to 20 monolayers were deposited in each growth run. Three different random number seeds were used to generate the results and the average of these are reported. We find that there are fluctuations of $\sim 3\%$ in the order parameters from one run to the next. In order to avoid the finite-size effects, we use periodic boundary conditions in the simulations. As noted earlier in this paper, we will focus on the InAlAs system. The conclusions arrived at for this system are generic in nature and will apply to other alloys as well. An important property of the semiconductor film being grown is the quality of its surface in terms of atomic abruptness. This quality is eventually responsible for the perfection of the interface formed between this semiconductor and another one. Before addressing the ternary InAlAs we present results for growth of InAs and AlAs by MBE.

In Fig. 1 we show dynamical coverage plots for the growth of InAs at three different growth temperatures. The growth rate corresponds to a deposition of one monolayer per second for the cation (under anion overpressure). The three temperatures correspond to 400, 520, and 700 K. We have plotted $d\theta_n/d\theta_{tot}$ which represents the fraction of arriving atoms going in a layer n . θ_n is the coverage on layer n and θ_{tot} the total coverage. We note that at lower temperatures, growth occurs at several layers simultaneously producing a rough surface. At $T_s = 700$ K, growth occurs by the layer by layer mode and produces a smooth surface (and interface). Similar results are observed for GaAs and AlAs, except that the corresponding temperatures for layer by layer growth are ~ 850 K and ~ 1000 K, respectively.¹⁴

In Fig. 2 we show the dynamic coverage results for

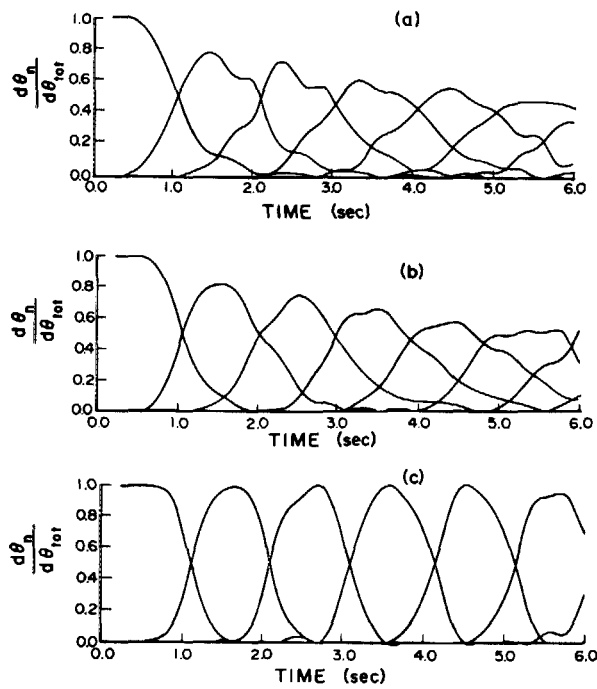


FIG. 1. Plots of $d\theta_n/d\theta_{tot}$ as a function of growth time for InAs grown at (a) 400 K, (b) 520 K, and (c) 700 K.

growth of $\text{In}_{0.5}\text{Al}_{0.5}\text{As}$ grown under the same conditions as for Fig. 1. We note that the profile for $\text{In}_{0.5}\text{Al}_{0.5}\text{As}$ growth front is slightly rougher than that for InAs. This arises primarily due to the low migration rate for Al atoms on the growing surface. Judging from Fig. 2 it seems logical to suggest that an increase in growth temperature would help the surface/interface quality of a heterostructure involving InAlAs. However, an increase in growth temperature has

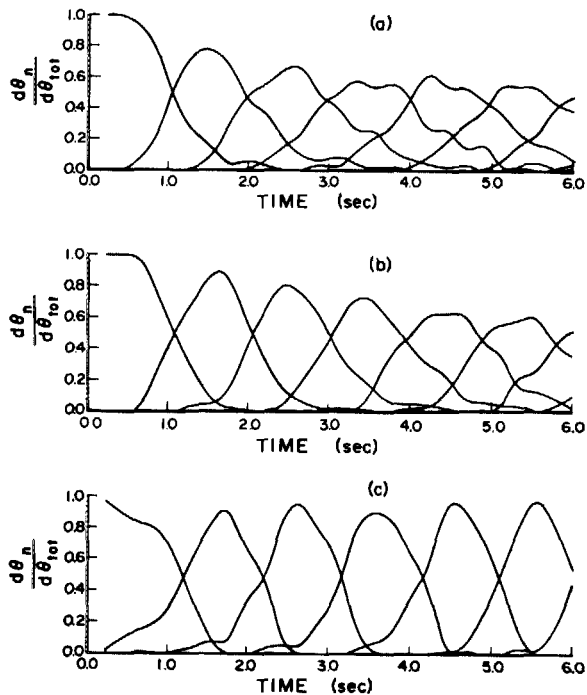


FIG. 2. Plots of $d\theta_n/d\theta_{tot}$ as a function of growth time for $\text{In}_{0.5}\text{Al}_{0.5}\text{As}$ at (a) 400 K, (b) 520 K, and (c) 700 K.

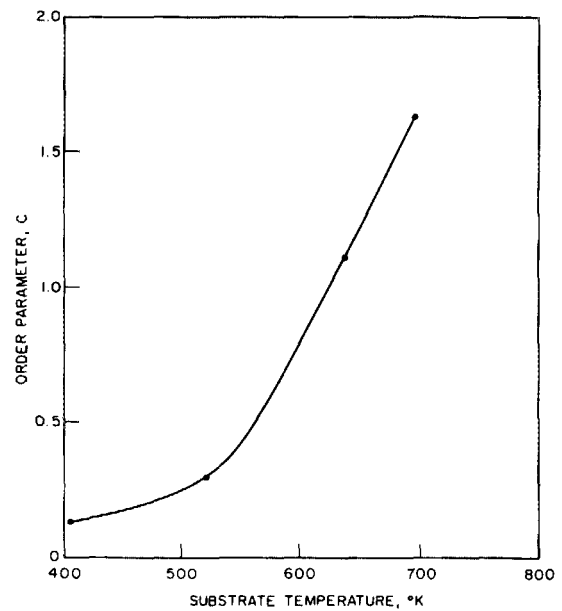


FIG. 3. Variation of short-range cluster order parameter C (defined in the text) as a function of growth temperature for $\text{In}_{0.5}\text{Al}_{0.5}\text{As}$.

important effects on the alloy quality itself as will be clear from the discussion below. In Fig. 3 we plot an order parameter C defined by

$$C = \frac{1}{2} \sum_{i,i'} c_i c_{i'} \quad (6)$$

where c_i 's are the occupation numbers for the cations (chosen to be +1 for In; -1 for Al). This order parameter represents the short-range order present in the alloy after growth. Note that for a perfectly random alloy (no clustering effect) one expects C to be given by

$$C(x) = Z\{x[x - (1-x)] + (1-x)[(1-x) - x]\} \\ = Z(4x^2 - 4x + 1), \quad (7)$$

where Z is the coordination (= 12 for tetrahedral III-V compounds) and x is the concentration of one component of the alloy. We also note that deviations from $C(x)$ given by Eq. (7) represent a clustering or ordered behavior. In Fig. 3 we have plotted the order parameter C for $x = 0.5$ ($C = 0$ for this random alloy) at the four different growth temperatures. We note that at the lowest temperature growth the system is indeed completely random, but as the substrate temperature is increased, more and more clustering occurs in the growing structure. Since a clustered alloy is expected to have poor optical and electronic properties, a lower temperature growth seems to be best for fabricating alloys with no clustering. Thus it is clear from Figs. 2 and 3 that the conditions for growth of structures with smooth surfaces (and sharp interfaces) and no clustering are not compatible if conventional MBE growth techniques are used.

The results presented here highlight the need to use "unconventional" growth techniques within the MBE technology. The unconventional techniques involve changing the growth rate and/or substrate temperature during the growth of a heterostructure. This will add an extra dimension to kinetics control in MBE growth and will be extremely useful

in overcoming the problem discussed above. In the next section we will discuss the effect of clustering observed in our simulations, on optical and electrical properties of the alloy.

IV. EFFECT OF CLUSTERING ON OPTICAL AND TRANSPORT PROPERTIES

In order to understand whether or not the alloy clustering discussed in the previous section has any detrimental effects, it is important to study the consequences of clustering on the optical and electrical properties of InAlAs. In this section we will discuss the effects of clustering on photoluminescence line width of excitonic transitions and mobility of electrons through the semiconductor. The expression for the excitonic linewidth in a perfectly random alloy is given by¹⁶

$$\sigma = 2[(C_A^0 C_B^0 r_c^3 1.4)/R_{ex}^3]^{1/2} \Delta_1 (0.327), \quad (8)$$

where C_A^0, C_B^0 are the mean compositions of InAs and AlAs in the system, r_c is the radius associated with a cation volume, R_{ex} is the exciton radius and Δ_1 is the direct bandgap difference between InAs and AlAs ($\Delta_1 = 2.0$ eV). For no clustering $r_c = 2 \times 3 \text{ \AA}$ one finds that $\sigma = 4$ MeV assuming $R_{ex} \approx 200 \text{ \AA}$.

The mobility limited by alloy scattering can be written as¹⁷

$$\mu_0^{all} = \frac{32 \sqrt{2} e \hbar^4}{9 \pi^{3/2} (m^*)^{5/2} V_a C_A^0 C_B^0 \Delta E^2 (kT)^{1/2}}, \quad (9)$$

where m^* is the effective mass in the alloy, V_a is the atomic volume associated with each cation, ΔE is the alloy scattering potential, and T is the temperature.

These expressions have been written for an alloy with mean composition C_A and C_B and *no clustering*. In case there is clustering in the system, the expressions are modified in a straight forward manner. A simple way to describe the alloy clustering is to describe the smallest scale n_c over which correlations exist ($r_c = n_c r_0$). Thus, we have two types of regions each containing $(4\pi/3)n_c^3$ cations which have concentrations different from the bulk values C_A^0 and C_B^0 (we have chosen C_A^0 and C_B^0 to be 0.5 in our work).

Let us assume that the clustering is manifested in the concentrations of these clusters being different from C_A^0 and C_B^0 . We assume that the concentration of A-type cations is C_A^1 in one type of cluster and C_A^2 in the other kind of cluster. If $C_A^1 = 1.0$ and $C_A^2 = 0.0$, then the clusters are purely dA type or purely B type. But we find from our simulations that this does not occur due to the nature of MBE growth (i.e., random impingement of cation and finite migration distances on the surface). With the above simple model for the clustering the short-range order parameter C can be calculated as follows. Within the clusters, the value of C is simply

$$C_{max} = Z(C_A^1 - C_A^2)^2. \quad (10)$$

The atoms in the cluster can be divided into "core" atoms and "surface" atoms. The core atoms have an average C value equal to C_{max} , while the surface atoms on average have a C value equal to $\frac{1}{2}C_{max}$. Since the fraction of the core and surface atoms is approximately

$$\left(\frac{n_c - 1}{n_c}\right)^3 \quad \text{and} \quad \frac{3}{2} \left(\frac{n_c^2 - n_c}{n_c^3}\right)$$

we get

$$C = Z(C_A^1 - C_A^2)^2 \left[\left(\frac{n_c - 1}{n_c}\right)^3 + \frac{3}{2} \left(\frac{n_c^2 - n_c}{n_c^3}\right) \right]. \quad (11)$$

This expression is quite accurate when n_c is large (> 4), but has errors when n_c is small due to the fact that the cluster is chosen to be spherical.

The expression for PL linewidth can now be generalized to the clustered case by the transformations $r_c \rightarrow n_c r_0$ and $\Delta_1 \rightarrow \Delta_1 |C_A^1 - C_A^2|$ leading to the following expression:

$$\sigma = \sigma_0 n_c^{3/2} |C_A^1 - C_A^2|. \quad (12)$$

Similarly the expression for mobility due to alloy scattering is given from Eq. (9) by the replacements

$$V_a \rightarrow n_c^3 V_a, \quad \Delta E \rightarrow \Delta E |C_A^1 - C_A^2|.$$

This gives

$$\mu^{-1}(C_A^1, C_A^2, n_c) = n_c^3 |C_A^1 - C_A^2|^2 (\mu_0^{all})^{-1}. \quad (13)$$

Both these expressions are valid if the spatial extent of the cluster is *less than* the exciton size in the alloy ($\sim 200 \text{ \AA}$) and the electron wavelength. Our simulations show that the cluster sizes obey these restrictions and

$$\frac{1}{\mu^{all}} = \left(\frac{\sigma}{\sigma_0}\right)^2 \frac{1}{\mu_0^{all}}. \quad (14)$$

From Eqs. (10)–(13), we can see that the clustering in the alloy system can be very detrimental to both the PL linewidth and electron mobility. We also note that C by itself is not able to provide information to calculate σ and μ^{all} . We have therefore estimated C_A^1 and C_A^2 for the $\text{In}_{0.5}\text{Al}_{0.5}\text{As}$ alloy grown in our simulation. These values are typically 0.7

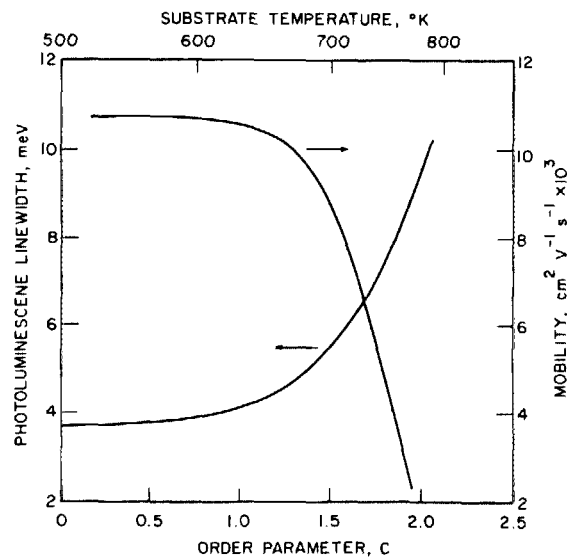


FIG. 4. Variation of alloy limited low temperature PL linewidth and 300-K electron mobility in $\text{In}_{0.5}\text{Al}_{0.5}\text{As}$ as a function of alloy clustering or substrate temperature. Note that the improvement at low temperatures may be reduced by the intrinsic defects that may be produced due to the poor growth front quality.

and 0.3. We are now in a position to estimate the linewidth and mobility from Fig. 3 and Eqs. (11) and (13). In Fig. 4 we present the results for $\text{In}_{0.5}\text{Al}_{0.5}\text{As}$ PL linewidth 300 K alloy scattering limited mobility. These results are plotted as a function of growth temperature, using the clustering information from our simulations. The effect of clustering is quite severe and we find the alloy limited PL linewidth increasing from 3.8 to ~ 12 meV as the growth temperature is raised to 800 K. The room-temperature alloy limited mobility changes from mobility changes from 13 000 to 2000 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. At room temperature we have to add the effects of phonon limited mobility to the above values according to Mathieson's rule to get the total mobility. It is clear that a small amount of clustering can seriously hurt the electrical and optical properties of InAlAs.

We must emphasize, however, that although clustering may be suppressed at low temperatures, the poor quality of the surface during growth may cause a high density of native defects which may form nonradiative centers as well as trapping centers. Thus, ideally one would like to reduce clustering without sacrificing the quality of the surface. This may require use of novel growth approaches as mentioned earlier.

V. CONCLUSIONS

In this paper we have examined the role of growth conditions in growth of common anion ternaries with a focus on $\text{In}_{0.5}\text{Al}_{0.5}\text{As}$. We find that a high cation surface migration rate is needed to grow smooth films, but for immiscible systems, the high migration rate causes clustering. We have also developed formalism for estimating the effects of alloy clustering on optical and electrical properties of the alloy. These results are important in identifying the importance of alloy quality on device related properties. We find that even small amounts of clustering can be very detrimental to the material properties. It is clear from the studies presented that novel

growth approaches are needed within the MBE-growth framework to produce high-quality alloys from components which favor alloy clustering according to thermodynamic considerations. These approaches may involve changing substrate temperature during growth, interrupting growth, etc., and we are carrying out computer simulations to study their effectiveness in overcoming the problem mentioned above.

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