Comparative study of the growth processes of GaAs, AlGaAs, InGaAs, and InAlAs lattice matched and nonlattice matched semiconductors using high-energy electron diffraction

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We have examined the effect of growth temperature and growth interruption time on molecular-beam-epitaxial growth of GaAs, $Al_{0.3}Ga_{0.7}As$, and $In_xGa_{1-x}As$ on GaAs substrates and $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ on InP substrates using dynamical reflection high-energy electron diffraction as an *in situ* probe. We have studied the time taken for a rough growth front to recover in the absence of growth as a function of growth temperature for these compounds. It is found that while GaAs and InGaAs surfaces can recover in 15–20 s under ideal growth conditions, $Al_{0.3}Ga_{0.7}As$ surfaces take ≈ 45 s, and $In_{0.52}Al_{0.48}As$ surfaces take several minutes to recover. Our results also suggest that smoothening of the growth front occurs by rearrangement of the surface atoms, rather than by re-evaporation. We have also studied the effect of strain induced by mismatch on growth modes in the case of $In_xGa_{1-x}As$ on GaAs. Our studies suggest that the presence of strain inhibits the surface migration of adatoms during growth and thus tends to generate a rougher growth front.

I. INTRODUCTION

Molecular-beam epitaxy has emerged as a dominant growth technique which has demonstrated its ability to grow a variety of semiconductor heterostructures with hyperabrupt interfaces. This has led to the realization of novel concepts and devices. A critical region in a heterostructure is the interface between the two materials. The interface quality is particularly crucial in small period superlattices, devices based on perpendicular transport, etc. Poor quality of the interface can seriously undermine the potential advantages of these devices. It is therefore, important that growth occurs under optimal conditions. In this connection the atomistic nature of molecular-beam epitaxy (MBE) growth becomes important. Reflection high-energy electron diffraction (RHEED) is an important *in situ* analysis technique which is capable of giving semiquantitative and quantitative information about the growth process and its control.[1-4] A considerable amount of insight into the growth process has also been gained from computer simulation studies.[5,6] However, since there are a number of important unknown parameters used in the simulation models, it becomes necessary to estimate these from RHEED data.

It must be recognized that although the process of MBE growth appears to be conceptually simple, there are a number of critical details which need to be fully understood before the full potential of heterostructure technology can be realized. It must be recognized, for example, that even for the most studied semiconductor combination, GaAs/AlGaAs, the realization of perfect or near-perfect heterostructures is far from routine. The situation for other heterostructures such as InAlAs/InGaAs, InGaAs/GaAs, etc. is, of course, much worse. Computer simulations have shown that the growing surface remains smooth and atomically abrupt under growth conditions enabling a high surface cation migration rate. This allows the randomly impinging cations to move to a step edge so that growth takes place by a two-dimensional layer-by-layer mode. However, since migration rates are controlled by the surface bond strengths, the ideal growth conditions are different for different materials. This presents a difficulty in growing heterostructures which are formed by semiconductors with very different bond strengths. In such cases it may be useful to use unconventional growth approaches such as growth interruption, varying growth rate, varying growth temperatures, etc. *In situ* RHEED appears to be well suited for studying the effects of unconventional growth techniques on the nature of the growth front.

In this paper we report a comparative study of the growth of GaAs, AlGaAs, InGaAs, and InAlAs as monitored by dynamical RHEED oscillation studies. We also report results on the growth of strained InGaAs on GaAs and the effect of lattice mismatch on the growth. The effects of changing substrate temperature and growth interruption are also explored. In the next section we describe the experimental techniques. In Sec. III we briefly discuss some theoretical aspects of the work and in Sec. IV we present our results. Relevant conclusions are made in Sec. V.

II. EXPERIMENTAL TECHNIQUES

MBE growth was performed in a three-chamber RIBER 2300 system. Lattice-matched GaAs, AlGaAs, strained InGaAs layers, and InGaAs/GaAs strained-layer superlattices were grown on undoped GaAs substrates, while lattice-matched InGaAs/InAlAs single layers and heterostructures were grown on Fe-doped InP substrates. Both GaAs and InP substrates were initially solvent degreased. Mechanical damage resulting from polishing was removed by etching in (5:1:1) $(H_2SO_4:H_2O:H_2O_2)$. Surface oxides on GaAs substrates were removed by a quick etch in (1:1)

(HCl:H$_2$O), while oxides on InP substrates were removed by etching in 0.5% bromine methanol solution. The substrates were then rinsed in deionized water and mounted on the molybdenum blocks with indium solder.

Prior to initiation of growth, oxides were desorbed at 630 and 535 °C on GaAs and InP substrates, respectively, under an As$_4$ flux. RHEED was used to monitor desorption of the oxides. Appropriate undoped buffer layers, 0.3–0.5 μm thick, were grown prior to RHEED oscillation measurements. Arsenic to group II flux ratio of 20:1 and 60:1 was used for GaAs and In-based materials, respectively.

The RHEED system consists of a commercial 10-keV electron gun focused onto a phosphor-coated screen. Light from the diffraction patterns was collected by a lens/pinhole assembly mounted onto an X-Y-Z micrometer stage and focused onto a photomultiplier tube. The detected signal was suitably amplified and recorded.

III. THEORETICAL CONSIDERATIONS

It is important to discuss the physical nature of MBE growth and the information provided by the RHEED experiments. Much of the understanding of the MBE growth process has evolved from the work of Arthur[7] and Foxon and Joyce[8] on GaAs. Computer simulations based on Monte Carlo methods have also provided a great deal of insight into the atomistic nature of MBE growth.[5,6] By a combination of these experimental and theoretical techniques a conceptual picture of the MBE growth process involving a monatomic cation and molecular anion has emerged and is shown in Table I. Although the experiments which have led to this understanding have only been done on GaAs, it is reasonable to believe that the same picture is valid for other III–V compounds. Another important point to note in the MBE growth of III–V compounds is that the cation incorporation rate is close to unity. Under these conditions it has been demonstrated by computer simulations[5] that the growing crystal will retain a smooth and atomically abrupt surface only if the cation surface migration rate is very high ($\geqslant 10^4$ hops/s).

The cation surface migration rate can be expressed as

$$R_{\parallel}^i = R_{od} \exp\left[-(E_{\text{tot}}^i - E_{\parallel})/kT_s\right], \qquad (1)$$

for in-plane hops, and

$$R_{\perp}^i = R_{od} \exp\left[-(E_{\text{tot}}^i - E_{\perp})/kT_s\right], \qquad (2)$$

for interlayer hops. R_{od} is a prefactor which has negligible temperature dependence. E_{tot}^i is the total energy with which the cation at site i is bonded to the growing crystal and $E_{\parallel}$ and $E_{\perp}$ are the minimum energies with which the cation is bonded on the surface as it hops from site i to the next site. It is clear that the hopping rate is controlled by the surface bond strengths of the cations. Based upon computer simulations, the following picture has emerged for the MBE growth. Starting from a smooth surface, the initial atoms that impinge on the heated surface move towards each other forming a 2-D monolayer island which grows up to a size L_c after which the next monolayer starts to grow simultaneously. The RHEED intensity from such a growing surface is given by

$$I = \left|\sum_j \exp\left[i(k - k')r_j\right]\right|^2, \qquad (3)$$

where k is the momentum of the incident electrons, which form a collimated beam, and k' is the momentum in the direction of the detector. The summation in Eq. (3) is restricted to the surface atomic sites since the de Broglie wavelength for the electrons is ≈ 0.1 Å. It is easy to see that away from the Bragg angle, the intensity from surface atoms on successive monolayers will interfere destructively. Thus, under conditions in which growth is taking place in a layer-by-layer mode and the surface profile is changing (e.g., if one is growing on axis with no surface steps) one should expect the RHEED intensity to oscillate. These oscillations will eventually die out because of the increasing surface roughness and because of flux nonuniformities. If the flux nonuniformities are negligible, then the magnitude of the oscillation is representative of the quality of the growing front. We note, as has been pointed out by several workers,[3] that one may not see any oscillations on stepped surfaces even though one may be growing under ideal growth conditions. In this paper, we will only discuss results obtained during growth on (100) oriented substrates.

A rough surface can be smoothened by interruption of growth. Surface evaporation may also take place during interruption and can contribute to the improvement of the surface. The time it takes for the surface to smoothen depends on the initial roughness, surface bond strengths, and the substrate temperature. The recovery time is an important parameter which needs to be known if interruption of growth is to be used as a technique to achieve high quality interfaces.

We also note that Eqs. (1) and (2) may not be valid for the growth of strained systems. At present it is not clear how strain affects the surface kinetics and consequently the surface and interface quality. In this paper we will report on some studies of strained InGaAs/GaAs structures and the role of strain during their growth by MBE.

TABLE I. Conceptual picture of MBE.

Cation	Anion
Impingement from vapor	Impingement
↓	↓
Chemisorption	Physisorption
↓	↓
Surface evaporation	Surface migration/evaporation
↓	↓
Surface migration (in-plane;inter-plane)	Dissociative chemisorption
↓	↓
Incorporation	Surface migration/evaporation
	↓
	Incorporation

IV. RESULTS AND DISCUSSION

As mentioned earlier, in this paper we will report on growth studies of GaAs, AlGaAs, and InGaAs on GaAs

substrates and $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Ga_{0.48}As$ on InP substrates. InGaAs was grown on GaAs to study the effect of mismatch strain on the growth process. In Fig. 1, we show some typical RHEED oscillation data taken during growth of $In_{0.53}Ga_{0.47}As/InP$ and $In_{0.52}Ga_{0.48}As/InP$. The growth temperatures for both compounds was 480 °C.

In Fig. 2, we show the results of our interruption studies during growth of $In_{0.53}Ga_{0.47}As/InP$. The solid and dashed lines are joins of experimental data. In this series of experiments, we started growth with a smooth surface and measured the highest intensity of the RHEED oscillation, I_0. The growth was then continued till the oscillations disappeared. We then interrupted growth by varying time periods t_i. The growth was then initiated again and the initial intensity of the RHEED oscillation $I_i(t_i)$ was measured and compared with I_0. As the interruption time is increased, the two intensities approach each other signifying a better recovery with longer interruption time. From Fig. 2, it is evident that at low temperatures (440 °C), the recovery period appears to be of the order of minutes, but at higher temperatures, it decreases considerably. Thus, at 480 °C, the recovery is 90% after 20 s of interruption. At higher temperatures,

however, the sample surfaces indicate a degradation in morphology after interruption.

In Fig. 3, we show results of similar experiments done with GaAs and $Al_{0.3}Ga_{0.7}As$. Here we see a faster recovery, and more so for GaAs, when the crystals are grown at 640 °C. However, for GaAs, there is a degradation of the surface morphology beyond 30-s interruption, when grown at 640 °C. The ratio of the temperatures at which similar rates of recovery takes place for GaAs and InGaAs is in the ratio of the bond strengths of Ga–As and In–As, which is 1.14:1.0. This suggests that the recovery process of the alloy InGaAs is dominated by the migration of surface In atoms and does not substantially involve the surface Ga atoms.

In Fig. 4, we show the recovery rate for $In_{0.52}Ga_{0.48}As$ at 480 °C. Note that at 480 °C, the recovery time for InGaAs was ≈ 20 s. However, for InAlAs even after a 2-min interruption, there is only a 70% recovery. These results are consistent with our recent photoluminescence studies involving growth interruption in InGaAs/InAlAs quantum wells.[9] From these studies it was concluded that a 3-min interruption was required to smoothen the InAlAs surface from a four-monolayer roughness to a two-monolayer roughness. It
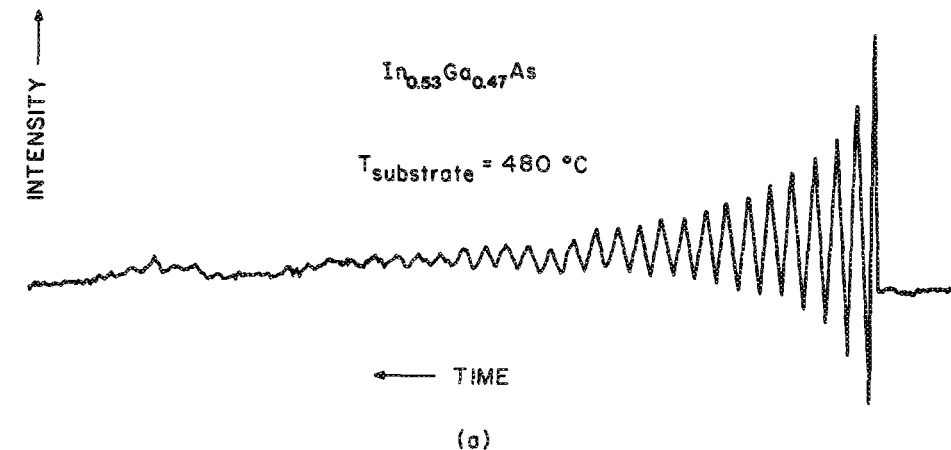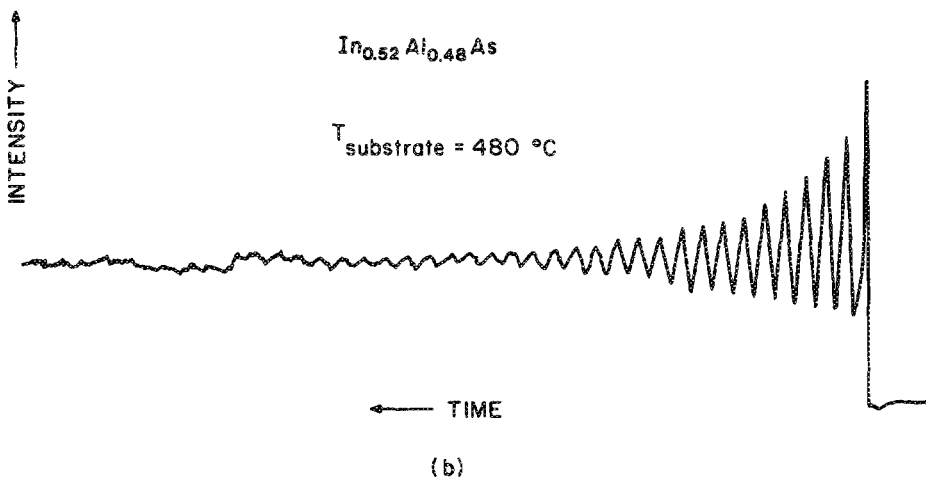

(a)

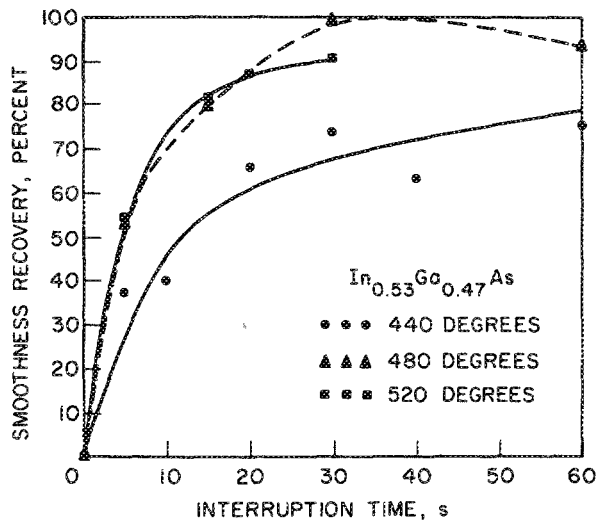FIG. 1. Typical RHEED oscillations observed for growth of (a) $In_{0.53}Ga_{0.47}As$ and (b) $In_{0.52}Al_{0.48}As$ on InP substrates.

(b)

FIG. 2. Surface recovery time after interruption during growth of $In_{0.53}Ga_{0.47}As$ at various substrate temperatures.

is clear that the presence of surface Al atoms strongly interferes with the smoothening process since the Al-As bond is $\approx 30\%$ stronger than the In–As bond.

Data recorded for interruption with and without an impinging arsenic flux are shown for growth of GaAs and
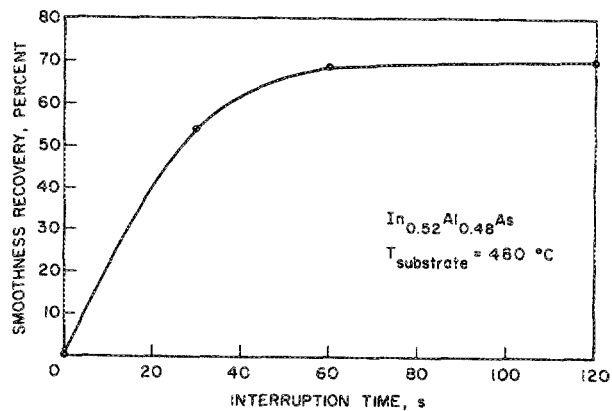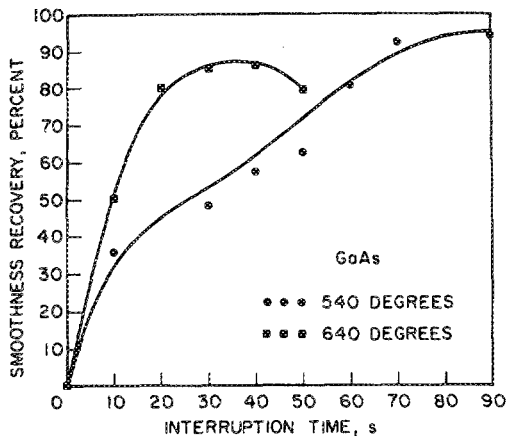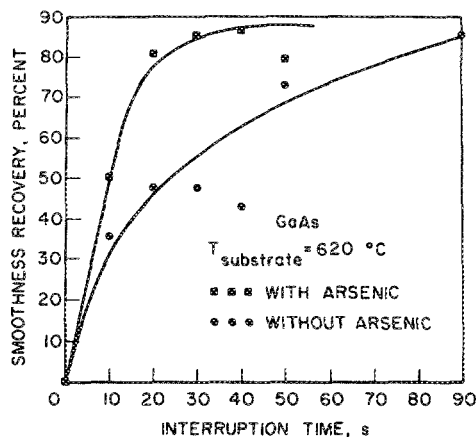

FIG. 4. Surface recovery time for growth of $In_{0.52}Al_{0.48}As$ at 480 °C after interruption.

$In_{0.53}Ga_{0.47}As/InP$ in Fig. 5. In both cases, the recovery period is longer without aresenic flux. This result suggests that smoothening of the growth front occurs by a rearrangement of the surface atoms rather than by re-evaporation and that the effective migration rate of cations on the surface seems to decrease in the absence of aresenic. This may be due to the evaporation of surface arsenic, so that available sites on which cations can migrate to reach step edges is reduced.
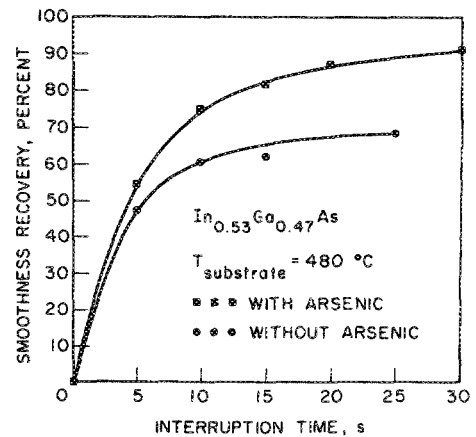

(a)
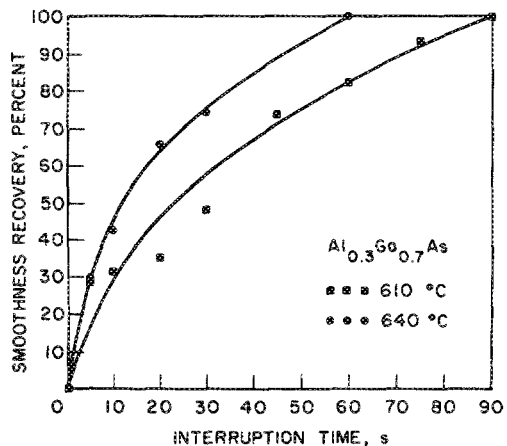
(b)

FIG. 3. Surface recovery time after interruption during growth (a) GaAs and (b) $Al_{0.3}Ga_{0.7}As$ at various substrate temperatures.

(a)

(b)

FIG. 5. Surface recovery time for (a) GaAs, and (b) $In_{0.53}Ga_{0.47}As$ with and without impinging As_4 during growth interruption.

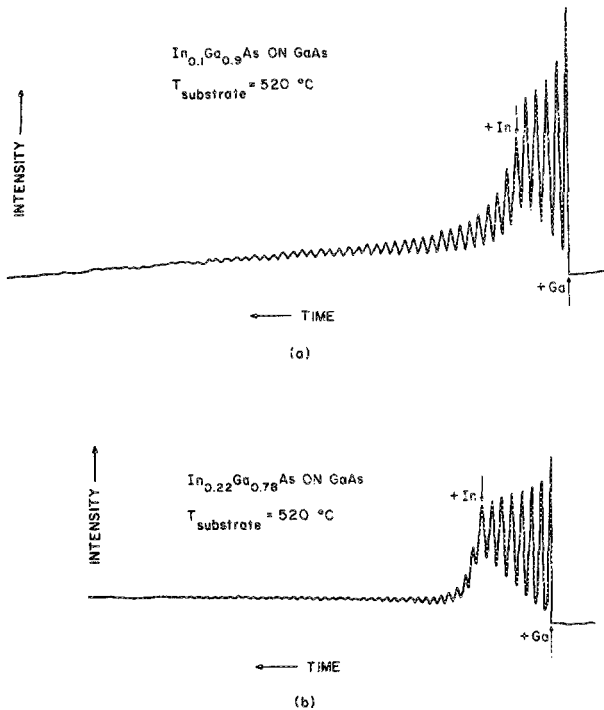FIG. 6. RHEED oscillation data for (a) $In_{0.1}Ga_{0.9}As$, and (b) $In_{0.22}Ga_{0.78}As$ (on GaAs substrate) at 520 °C.

FIG. 7. Surface recovery time after growth interruption for different compositions of strained $In_x Ga_{1-x}As$ on GaAs.

In Fig. 6, we show RHEED oscillation data for growth of $In_{0.1}Ga_{0.9}As$ and $In_{0.22}Ga_{0.78}As$ on GaAs substrates. These structures are strained and the purpose of these studies is to understand the effect of strain on growth. The data indicate RHEED oscillations during growth of the initial GaAs layer. Oscillations are continuously recorded during growth of $In_x Ga_{1-x}As$ after opening the In shutter. For the alloy with low In content, we see that there is almost no change in the intensity of the oscillations. However, for higher In content the oscillations decay rapidly. Since there is $\approx 1.2\%$ mismatch in the latter case, it appears that the strain is strongly inhibiting surface migration of the atoms during growth. Figure 7, shows the smoothness recovery time after growth interruption under As_4 flux for various alloy compositions with increasing In, up to 30%. The data support our observations in that the increased strain inhibits cation migration. It is clear that strain plays a very important role in the surface kinetics and hence in the growth mode and, therefore, may have considerable influence over the ideal growth conditions. Growth of high quality strained structures may require use of novel growth techniques to overcome this additional strain-related problem.

V. CONCLUSIONS

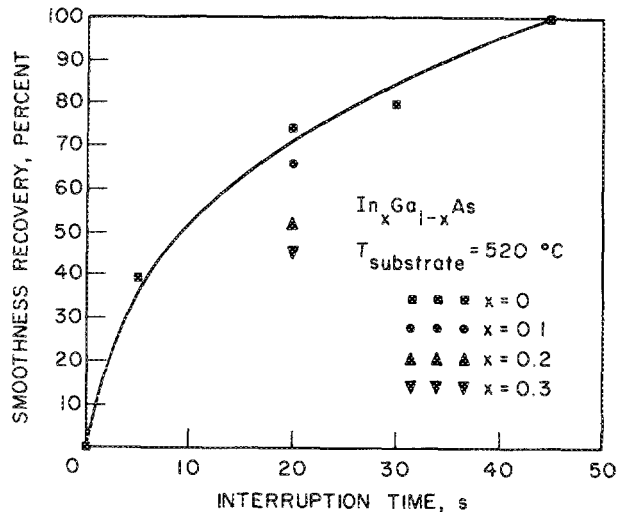We have studied the RHEED oscillations observed during growth of several III–V semiconductors to understand the MBE growth process and its control. In lattice-matched systems the ideal growth conditions are closely tied to the surface bondstrengths. Thus, in GaAs the ideal growth temperature (with our substrate temperature measurement system) is ≈ 620 °C while for $In_{0.53}Ga_{0.47}As$ it is ≈ 480 °C. In the case of $In_{0.52}Ga_{0.48}As$, we find that the stronger Al–As bondstrengths force the growing surface to roughen and in order to get a smooth surface, several minutes of interruption are required. In the case of lattice-mismatched InGaAs on GaAs, we find that the presence of strain in the growing surface has a very strong influence on the growth process. In the case studied by us (expansive strain), surface migration of atoms is severely inhibited by the presence of strain. We are now in the process of carrying out a more detailed investigation of the effects of strain on MBE growth.

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