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Surface reconstruction of GaAs (001) during OMCVD growth

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Surface reconstruction of GaAs (001) during organometallic chemical vapour deposition (OMCVD) growth has been investigated with reflectance-difference spectroscopy (RDS). RD spectra reveal that surface reconstructions similar or identical to (4 × 2), (2 × 4), and $c(4 \times 4)$ that occur on surface prepared by molecular beam epitaxy (MBE) in ultrahigh vacuum (UHV) occur even in atmospheric pressure OMCVD growth environments. Based on the RDS database we established on static surfaces in UHV, we studied the structure of surfaces under both static and dynamic conditions in non-UHV ambients. We find, in contrast to previous models, that the surfaces under various non-UHV conditions exhibit dimer formation. In addition, OMCVD growth and atomic layer epitaxy (ALE) typically occur under disordered $c(4 \times 4)[d(4 \times 4)]$-like conditions where the surface is terminated by multilayers of As. When trimethylgallium (TMG) and arsine (AsH_3) are supplied simultaneously, the surface structure varies as a function of the supply rates of TMG and AsH_3, and the substrate temperature.

1. Introduction

During the past few decades, the structure of GaAs (001) has been extensively studied for both technological and scientific interests. With the aid of surface analytical tools such as reflection high-energy electron diffraction (RHEED) and low energy electron diffraction (LEED), various surface reconstructions were found to occur on this surface in ultrahigh vacuum (UHV), when prepared for example by molecular beam epitaxy (MBE). From these measurements, it is known that the surface exhibits long-range ordering (LRO) of symmetries (4 × 2), (4 × 6), (1 × 6), (3 × 1), (2 × 4), $c(4 \times 4)$, etc. More direct information has recently been provided by scanning tunnelling microscopy (STM) (Pashley *et al.* 1988; Biegelsen *et al.* 1990) STM has allowed some of these structures to be observed directly, and together with information obtained by complementary techniques such as RHEED, LEED, or X-ray diffraction (XRD) (Sauvage-Simkin *et al.* 1989), has proven the presene of surface dimers and many of the speculated atomic arrangements.

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In contrast, very little is known about the structure of surfaces in non-UHV ambients that are encountered for example during organometallic chemical vapour deposition (OMCVD). This was mainly due to the fact that very few surface analytical techniques are compatible with non-UHV conditions. And even STM, one of the very few tools which in principle is operable in non-UHV, is not easy to use in dynamic situations such as crystal growth. For this reason, OMCVD growth has usually been analysed using *ex situ* measurements, for example XRD or photoluminescence. A new probe for monitoring surface processes on an atomic scale during growth was needed.

Reflectance-difference spectroscopy (RDS) has recently proven to be a suitable technique for studying the structure of surfaces in various environments from UHV to atmospheric pressure (AP), or even liquids (Aspnes *et al.* 1988, 1990; Kamiya *et al.* 1992*a*, *b*). Here we describe its application to the study of surfaces during atmospheric pressure OMCVD growth.

2. Experiment

The principle and methods of RDS have been described elsewhere (Aspnes *et al.* 1988). The spectrometer consists of a 75 W Xe short-arc lamp, front-surface spherical and plane mirrors, MgF_2 and quartz Rochon polarizers, a 50 kHz photoelastic modulator, a 0.1 m focusing-grating monochrometer with 0.5 mm slits, and an extended S-20 photomultiplier detector. These are all mounted on a 16×12 in^2 Al plate, which can easily be attached to various growth chambers for measurements. Under typical conditions, a spectrum from 1.5 to 5.5 eV is obtained in 25 s.

In brief, for (001) surfaces of zinc-blende structure, the quantity measured in RDS is the relative difference between the complex near-normal-incidence reflectances $\tilde{r}_{\bar{1}10}$ and $\tilde{r}_{110}$ of light linearly polarized along the two principal axes $[\bar{1}10]$ and $[110]$:

$$\Delta\tilde{r}/\tilde{r} = \Delta r/r + \mathrm{i}\Delta\theta = (\tilde{r}_{\bar{1}10} - \tilde{r}_{110})/\tilde{r}, \tag{1}$$

where

$$\tilde{r} = \tfrac{1}{2}(\tilde{r}_{\bar{1}10} + \tilde{r}_{110}). \tag{2}$$

$\Delta\tilde{r}/\tilde{r}$ can be expressed by the surface dielectric anisotropy $(\epsilon_{\bar{1}10} - \epsilon_{110})\,d$ as

$$\frac{\Delta\tilde{r}}{\tilde{r}} = -\frac{4\pi\mathrm{i}d}{\lambda}\frac{\epsilon_{\bar{1}10} - \epsilon_{110}}{\epsilon_{\mathrm{s}} - 1}, \tag{3}$$

where ϵ_{s} is the bulk dielectric function of GaAs, $\epsilon_{\bar{1}10}\,d$ and $\epsilon_{110}\,d$ are the surface dieletric responses along the $[\bar{1}10]$ and $[110]$ axes, respectively, and λ is the wavelength of the light. For $\mathrm{Im}\,(\epsilon_{\mathrm{s}}) \ll \mathrm{Re}\,(\epsilon_{\mathrm{s}})$, which is the case for semiconductors for energies below the E_1 threshold, the real part of $\Delta\tilde{r}/\tilde{r}$ will be dominated by the anisotropic surface absorption properties. Because $\Delta r/r$ is also relatively free from experimental artifacts, such as effects due to strain birefringence of the UHV viewing ports, we use $\Delta r/r$ throughout.

Experiments were performed with our RDS system mounted on a Varian Gen II MBE station, a double-wall quartz horizontal-flow OMCVD reactor, and also a new horizontal-flow stainless-steel with optical ports that we recently developed for real-time optical studies of epitaxial growth. Cr-doped semi-insulating GaAs wafers oriented $(001)\pm 0.5^{\circ}$ were used after standard chemical treatments. For MBE, the surfaces were simultaneously characterized by RHEED. Precursors fluxes were

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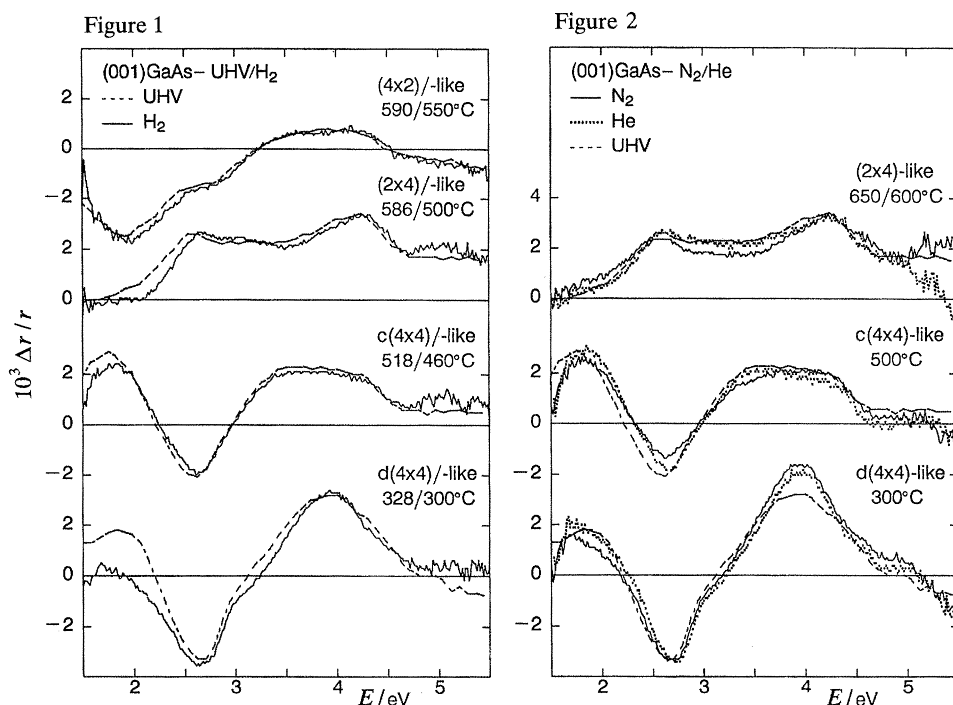

Figure 1. RD spectra of the primary reconstructions on (001) GaAs in UHV and AP H_2. $\Delta r/r$ is plotted as a function of photon energy. Surfaces in UHV were prepared under an As_4 beam equivalent pressure (BEP) of 5×10^{-9} Torr for the (4×2) reconstruction and 5.7×10^{-5} Torr for the rest.

Figure 2. As figure 1, but for AP He and N_2 ambients. The UHV data are the same as those of figure 1.

measured by beam equivalent pressure (BEP) for MBE, and partial pressure for OMCVD. Sample temperatures were measured for MBE by a thermocouple that was calibrated from the known oxide desorption temperature, and for OMCVD by optical pyrometry.

3. Results and discussion

(*a*) *Static surfaces*

We first performed measurements for surfaces prepared by MBE. By varying the As_4 flux and substrate temperature, we can create any of the various reconstructions on GaAs (001) that are mentioned above. Before RDS measurements, these reconstructions were confirmed by RHEED. By this means, we established our RD database for GaAs (001). Following this, we performed measurements on surface prepared by OMCVD in AP H_2, He, and N_2, with trimethylgallium (TMG) and arsine (AsH_3) supplied as necessary. The results are summarized in figures 1 and 2.

RD spectra obtained from OMCVD prepared surfaces are superimposed on those obtained from the primarily reconstructed surfaces prepared by MBE. The agreement is striking. It is clear that structure similar or identical to the (4×2), (2×4), $c(4 \times 4)$, and disordered-$c(4 \times 4)$[$d(4 \times 4)$] are formed even in AP OMCVD conditions. The $d(4 \times 4)$ is produced by excess As on $c(4 \times 4)$. Since structure in RD spectra originates from specific local atomic configurations (Aspnes *et al.* 1990; Chang & Aspnes 1990), we conclude that the surface terminations are locally identical, i.e., that dimers are also

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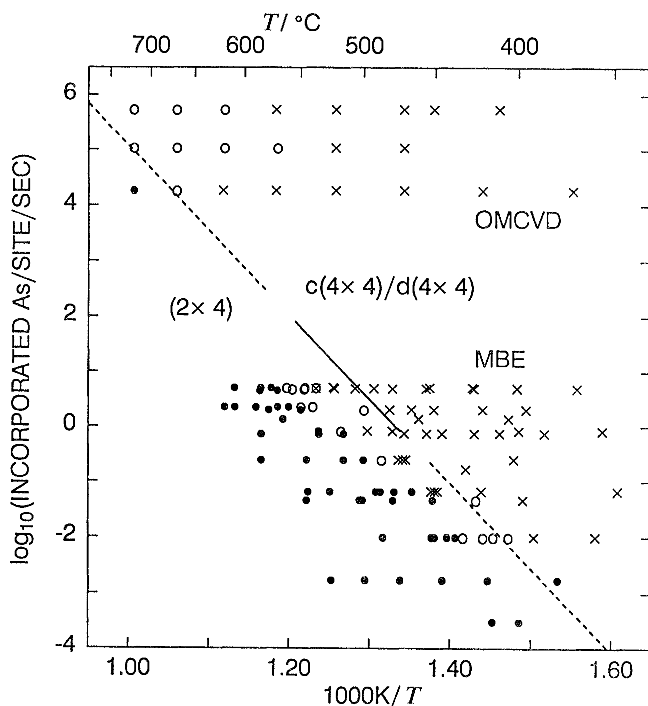

Figure 3. (2×4)-$c(4\times4)/d(4\times4)$ phase diagram as a function of substrate temperature and incorporation rate of As atoms, determined from partial pressures of As-containing precursors (see text). Dots, crosses, and circles represent (2×4), $c(4\times4)/d(4\times4)$, and marginal structures, respectively. The solid line is the (2×4)-$c(4\times4)$ boundary established by Van Hove *et al.* (1983) by RHEED.

formed in AP ambient. We term these surface reconstructions in AP ambient '-like' since LRO of the surface cannot be directly detected with RDS. However, under static conditions we expect LRO to be also identical as shown by XRD measurements under 100 Torr of H_2 (Fuoss *et al.* 1989; Kisker *et al.* 1990).

Similarities between the surfaces in UHV and in AP ambients can further be seen in the (2×4)-$c(4\times4)/d(4\times4)$ phase diagram shown in figure 3. This diagram summarizes the reconstructions determined by RD, and also with RHEED in UHV, under various substrate temperatures and As exposures. The As was provided by As_4 in UHV and AsH_3 in AP H_2. The extrapolation of the (2×4)-$c(4\times4)$ boundary established by RHEED on surfaces prepared by MBE (Van Hove *et al.* 1983) is indicated in the figure. This straight line also defines the boundary of the OMCVD régime. This is further evidence that the nature of the GaAs (001) surface is the same in both UHV and AP H_2 environments, and indicates that the surface structures in these ambients are determined mainly by the As supply rate and substrate temperature. This result also indicates that the main difference is the shift of equilibrium point due to the vastly different partial pressures of As-containing precursors between the two growth environments. These observations justify the applicability of chemical beam epitaxy (CBE) studies in UHV to OMCVD.

Another important result is that the structure of AsH_3-stabilized surface in typical AP OMCVD conditions is $d(4\times4)$-like. This eliminates previous models of OMCVD that were based on the assumption that the surface is terminated by hydrogen. Moreover, the surface is covered with multilayers of As in contrast to the single layer As (2×4)

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which is the As-stabilized surface under growth conditions in MBE. The role of these excess As atoms on the surface is not clear at the moment but some possibilities have already been discussed (Kamiya *et al.* 1992).

(*b*) *Atomic layer epitaxy*

As a step toward understanding surfaces under dynamic conditions, we first used these results to study the evolution of surface structure during atomic layer epitaxy (ALE) using multitransient spectroscopy approach. Here, we accumulate 81 single-wavelength transient spectra of 250 pixels each every 0.05 eV between 1.5 and 5.5 eV for a series of sequential gas exposures representing a complete ALE cycle. For 25-s cycles we achieve a time resolution of 100 ms. After these transients have been accumulated we rearrange the pixels to form 250 81-point spectra. An example taken with the sample at 450 °C is shown in figure 4. Figure 4*a* is the transient spectrum taken at 2.6 eV, and figure 4*b* summarizes the synthesized RD spectra at intermediate states indicated by the pixel numbers. The switching sequence of the precursor gases (2.3 Torr AsH_3 and 0.011 Torr TMG in AP H_2) are indicated in figure 4*b*. Again, the AsH_3-stabilized surface is $d(4\times4)$-like. The surface structure starts to change slightly as the supply of AsH_3 is terminated, and drastically as TMG is introduced. After supplying adequate TMG, in this case 7 s, the signal at 2.6 eV reaches a maximum. The spectrum of the surface at this stage is shown by 62 in figure 4*b*. At this point there is no indication that the surface is terminated by Ga dimers. In fact, features related to Ga dimers, negative peaks near 1.8 eV, begin to emerge only after an extended H_2 purge after the TMG supply has been terminated. Here, the growth rate was calibrated to be 1.4 ML per cycle. Since during a practical ALE cycle the H_2 purge is less than 5 s, the surface cannot be dominantly terminated by Ga dimers.

Spectra 62–82 represent the surface structure that is probably related to the self-limiting mechanism of ALE. These spectra show peaks at 2.5 and 4.3 eV, and share many features in common with a typical (2×4) spectrum. One of the previously proposed models attributed this surface to monomethyl radical termination on surface Ga atoms. However, some recent reports suggest that monomethyl radical desorption is too fast to account for the self-limiting mechanism. Hence the issue is still under discussion. To elucidate the structure of the surface from which spectra 62–82 were taken, further work is necessary, possibly using CBE in UHV where other complementary surface analytical tools can also be used.

(*c*) *Standard* OMCVD *growth*

The evidence of dimer formation which follows from our static and ALE results already has significant implications for elucidating surface processes of OMCVD. However, a complete solution to the OMCVD growth problem requires us to monitor the standard growth processes in which group III and V precursors are simultaneously supplied to the surface. To overcome the technical difficulty of windows being coated with deposits, such that optical probes can no longer be used, we designed and developed a new horizontal-flow stainless steel reactor that features H_2 purging of window port to prevent these deposits from occurring. This reactor also has optical ports for real-time studies of epitaxial growth by spectroellipsometry and by infrared and ultraviolet gas phase absorption as well as RDS. The details of the reactor are given by Kamiya *et al.* (1993). Using this reactor we studied the structure of surfaces during growth under various supply rates of TMG and AsH_3 at various growth temperatures. The results are summarized in figures 5–7.

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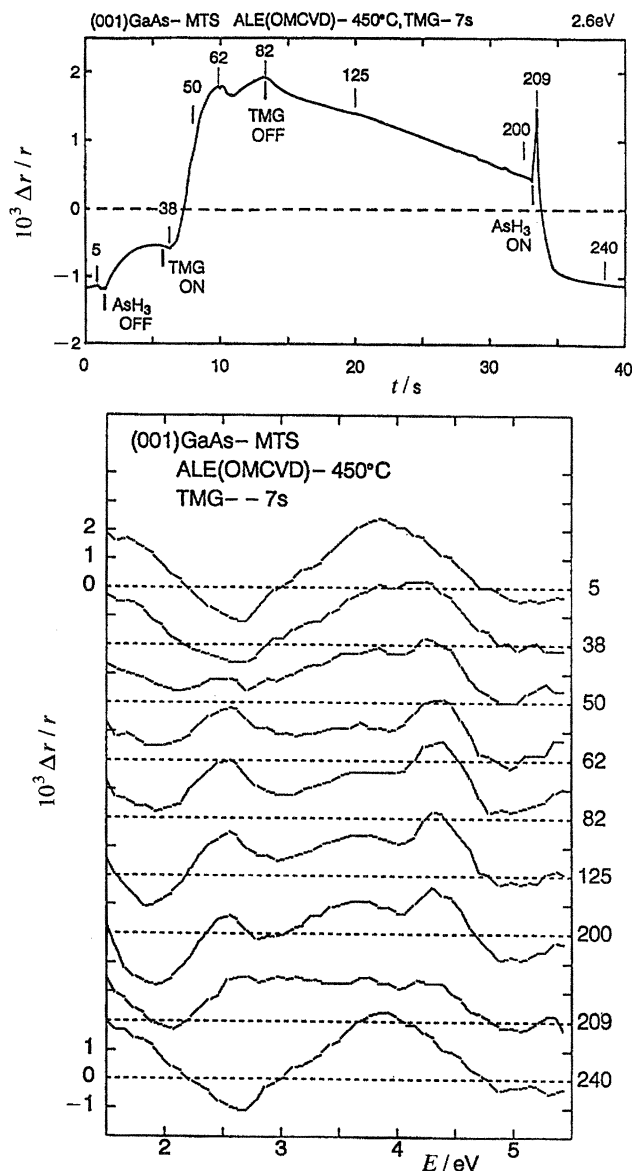

Figure 4. (a) RD transient at 2.6 eV during multitransient measurements on cyclic ALE sequences at 450 °C. TMG (0.011 Torr) exposure of 7 s is followed by a 20 s long H_2 purge period. (b) RD spectra of transient stages synthesized from 81 transients obtained at every 0.05 eV between 1.5 and 5.5 eV.

Under AsH_3-stabilized conditions where TMG is not present, all data show that the surface is qualitatively $d(4 \times 4)$-like, consistent with our results shown in the previous section and also with XRD studies (Lamelas *et al.* 1992; Kisker *et al.* 1992). However, quantitatively, the amplitude of the signals depends on the substrate temperature and partial pressure of AsH_3. To lowest order, we believe this is a thermodynamic effect related to the surface density of As dimers. The highest surface dimer concentration is achieved with the highest AsH_3 partial pressures and the lowest substrate temperatures. This can be seen by comparing the spectrum of figure 5a

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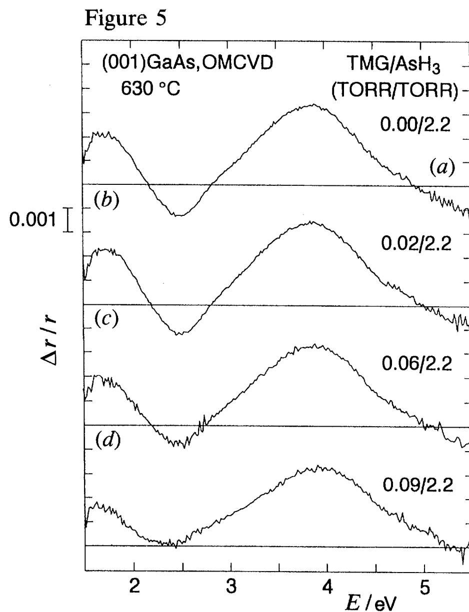

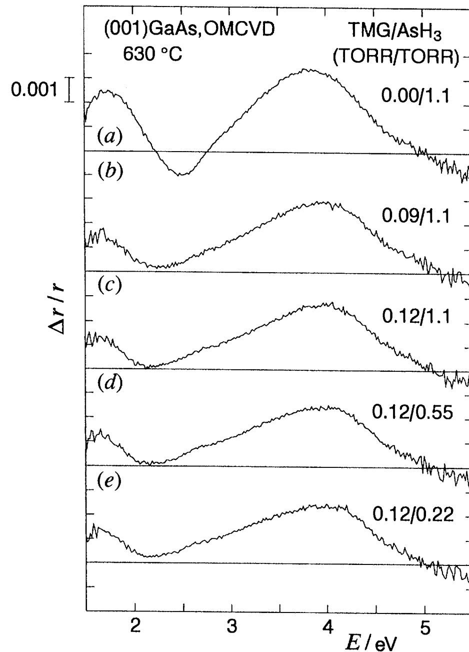

Figure 5. RD spectra $\Delta r/r$ of (001) GaAs obtained in AP H_2 with 2.2 Torr AsH_3 and various partial pressures of TMG as indicated at a substrate temperature of 630 °C.

Figure 6. As figure 5, but with various partial pressures of both TMG and AsH_3.

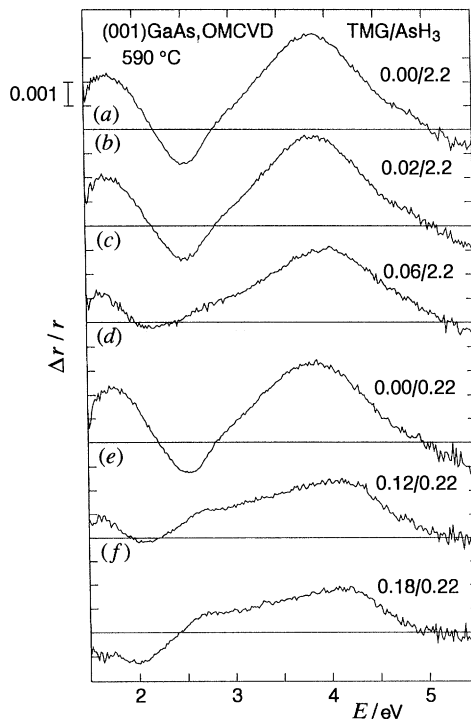

Figure 7. As figure 6, but at a substrate temperature of 590 °C.

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with that of figure 7*d*, which represent a difference of an order of magnitude in AsH_3 partial pressure.

When the surface is simultaneously exposed to TMG and AsH_3, which is the condition encountered during standard OMCVD growth, the spectra exhibit both quantitative and qualitative changes. At a substrate temperature of 630 °C and 2.2 Torr partial pressure of AsH_3, 0.02 Torr of TMG has no effect on the RD signal (figure 5*b*). From previous calibrations, it has been found that this TMG partial pressure corresponds to a supply that would result in a growth rate that exceeds 1 μm h^{-1} at 650 °C, indicating that Ga incorporation is substantial. However, the change in the RD spectrum is miniscule. This leads us to the following conclusions: (1) Very little TMG is chemisorbed on the surface at any given time, since chemisorption involve breaking of dimer bonds at the surface, which is not seen. (2) The reaction of TMG and the incorporation of Ga atoms occurs on a time scale far shorter than that required to grow a semiconductor bilayer. As a result, surface is continuously healed as is seen in the RD spectra.

However, if the partial pressure of TMG is increased, the RD signal starts to change. At a TMG pressure of 0.06 Torr the signal intensities becomes smaller (figure 5*c*) and at 0.09 Torr even smaller (figure 5*d*). At a substrate temperature of 590 °C the results show the same trend, but the effect of TMG is much more enhanced. This is clearly seen by directly comparing the curves (*a*), (*b*) and (*c*) in figures 5–7. The qualitative change in the lineshape seen in figure 7*c* indicates that at this point the supply of Ga is exceeding the rate that the surface can accommodate it and still retain the original $d(4\times4)$-like reconstruction. At this stage, the chemistry changes, and the chemistry is determined by the TMG supply rate. This is clearly shown in figure 6. Under a constant supply of AsH_3 (1.1 Torr), the surface evolves as the TMG supply is increased as seen in (*a*), (*b*) and (*c*). However, once the spectral lineshape reaches that of (*c*), no further significant change can be observed by reducing the AsH_3 supply (figure 6*c*–*e*). This indicates that under these conditions, the supply of As is more than sufficient, and the TMG supply rate is the determinant.

The effect of TMG becomes even more prominent as the TMG/AsH_3 supply ratio is increased. Curves (*b*)–(*e*) in figure 6 are distinct from $d(4\times4)$-like surfaces not only by their general lineshapes but also from the shift in the peak energy from 2.5 eV to 2.1–2.2 eV. These lineshape resemble the ones seen at the crossover conditions from $c(4\times4)$ to (2×4) observed on surfaces prepared in MBE (Kamiya *et al.* 1992) suggesting that the surface is probably mixed with single and double layer As dimer termination. By lowering the substrate temperature to 590 °C, further changes begin to take place in the spectra. At TMG and AsH_3 partial pressures of 0.02 Torr and 0.22 Torr, respectively, the change is clearly seen by comparing figure 5*f* and figure 6*e*. By further increasing the TMG supply to 0.18 Torr at 590 °C, the spectrum evolves to a lineshape similar to that seen during ALE at 410 °C. The morphology of the layers grown under this condition was extremely poor, as could be established by visual inspection. This clearly demonstrates that growth should be carried out under As rich conditions, and at the same time shows that RD spectra can be used for optimizing growth conditions.

The recent XRD result by Lamelas *et al.* (1992; Kisker *et al.* 1992) concluded that there are no reconstructions on this surface during OMCVD growth. Since our conditions are not identical to theirs, we cannot make a direct comparison of the results. However, our present data clearly show that under typical growth conditions the surface is dominantly $d(4\times4)$-like, and that this can be changed with the supply

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rates of TMG and AsH_3 and the substrate temperature. We believe that the possible explanations are (1) the LRO is not formed despite the $d(4\times4)$-like termination, (2) the difference in growth conditions. The reaction of TMG at the surface already breaks dimer bonds as we have discussed above, and depending on the speed and the nature of the reaction the LRO can be affected.

4. Conclusion

In conclusion, we have observed surface reconstructions involving dimer formation on GaAs (001) in atmospheric pressure OMCVD ambients using reflectance-difference spectroscopy. The spectra obtained under static conditions on surfaces prepared by MBE in UHV were used as database for the study of dynamic processes that occur during ALE and standard OMCVD growth. We show that both OMCVD and ALE take place basically under disordered-$c(4\times4)[d(4\times4)]$-like conditions, but depending on the TMG/AsH_3 supply rates and substrate temperature, the detailed structure can vary and this accounts for the discrepancy between the RDS and XRD measurements.

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