SOME INSIGHT INTO THE NATURE OF THE SURFACE CHEMICAL PROCESSES INVOLVED IN THE MOVPE GROWTH OF GaAs FROM ARSINE AND TRIMETHYL - OR TRIETHYL-GALLIUM

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ABSTRACT

A now established method of studying reaction pathways in GaAs growth is via the use of surface science and related techniques. This paper sets out to review progress made to date via the use of such techniques in terms of the two primary aims of any mechanistic investigation, the identification of reaction intermediates and the measurement of kinetic processes. A comparison is made between trimethylgallium (TMGa) and triethylgallium (TEGa) in terms of their behaviour upon adsorption at GaAs (100) surfaces. Both metallorganics adsorb readily at 300 K in a manner which depends only slightly upon the As-coverage of the substrate surface, indicating that there can be only small barriers to adsorption although clear differences in the subsequent chemistry are observed for As-rich and Ga-rich GaAs (100) surfaces, with more rapid uptake at the As-rich surface and the spontaneous loss of one alkyl unit (i.e. C_1 for TMGa and C_2 for TEGa). For TMGa, some evidence of multilayer formation at 300 K is presented. Triethylgallium adsorption and thermal decomposition on GaAs (100) surfaces under high vacuum conditions results in clean, intramolecular surface chemical pathways involving intermediates in which the ethyl groups remain intact. For trimethylgallium, the evidence suggests that adsorption leaves the methyl groups intact yet subsequent thermal decomposition does not occur cleanly in the absence of a source of surface hydrogen, although methyl radical recombination is clearly identified as a possible alternative route to the loss of surface carbon. Reflection IR spectroscopy has been used for the first time to study TMGa adsorption on GaAs (100) at 300 K and has produced vibrational data that are shown to agree with EELS data for the adsorption of TMGa on Si surfaces, also implying that the methyl groups remain intact.

As a source of surface hydrogen, arsine adsorption and reaction is shown to lead to a surface sub-hydride phase represented as AsH_n , which is shown to be consistent with the concept of stabilisation of GaAs (100) surfaces at high temperatures via an arsine (and not arsenic) overpressure. Finally, recent data obtained using the non-linear optical surface diagnostic technique of second harmonic generation are reported for the interaction of trimethylgallium with GaAs (100) surfaces at 300 K, which are discussed in the light of the available surface science data.

INTRODUCTION

The controversy regarding the relative importance of gas-phase and surface-phase reaction in GaAs MOVPE still rages [1-3]. Ultimately of course any semiconductor growth process must involve some surface chemistry, yet the extent to which this surface chemistry influences (a), the rate of reaction as indicated by growth rate and (b), the quality of the resulting epilayers, is still unclear. For the MOVPE growth chemist, the main goal remains the direct observation of both surface and gas-phase intermediates involved in the growth mechanisms. For the gas-phase, a number of in-situ, non-destructive methods are currently being exploited including coherent anti-Stokes Raman scattering [4] and IR spectroscopy [5]. For the surface-phase the choice of analysis methods available that can be applied under conditions of high temperatures and atmospheric or slightly reduced pressures is very limited. The way ahead is likely to be via the use of photon-based methods such as reflectance anisotropy (RA) [6,7], optical second harmonic generation (SHG) [7-9] and reflection IR spectroscopy (RIRS) [10] methods.

However, a lesson learned from other areas of surface chemistry such as catalysis and corrosion studies is that surface science studies of fundamental adsorption and reaction processes *can* provide some considerable insight into processes which normally occur at higher pressures and temperatures. With this in mind, we suggested in 1984 that the chemistry of III-V growth processes may be studied using surface science techniques. This has proved to be a powerful approach particularly in studies of the growth of GaAs on GaAs (100) and Si (100) substrates and many other groups are now actively involved in using traditional surface science methods in an attempt to understand the mechanisms of semiconductor growth [e.g. see the recent review papers, ref.s [11] and [12]. Much of this work is directed at MOMBE growth [13-15], since here surface science techniques may necessarily be applied in-situ. For such systems, the theoretical predictions of Robertson and coworkers for the MOMBE-growth of GaAs from triethylgallium [16] have provided direct inspiration for surface chemical studies employing static methods which may provide some insight into the nature of the available reaction pathways and/or somewhat crude molecular beam reactive scattering (MBRS) methods that utilise conventional hot filament mass spectrometry to detect desorbing or backscattered species [15]. Unfortunately there are many problems associated with the interpretation of data from such systems arising from reactions within the mass spectrometer ioniser. Thus while it may seem at least superficially that MBRS methods are ideally suited to such studies since they may be applied during growth, it has proven impossible to determine either the true nature of any *surface* species formed or indeed the true nature of any intermediate gas phase species via these methods. Until a detailed picture of the surface chemical processes involved in the growth is available, this system remains of interest at least to the surface chemist.

In our laboratories, our primary concern is the elucidation of GaAs MOVPE growth mechanisms and as such our attention focusses on the higher pressure end of the growth spectrum. However for GaAs (100) surfaces we have obtained basic surface science data which agree at least intuitively with much of the expected chemistry of the MOVPE process and indeed MOMBE/CBE processes. We believe that this is the case because chemical thermodynamics necessarily limits the available reaction pathways such that the fundamental surface chemistry observed under idealised or high vacuum conditions may also occur under growth conditions. Neglecting gas-phase reactions, kinetics tells us that higher pressures will influence the *rate* of surface reactions but not necessarily the nature of the reactions. Gas-phase reactions are of course a problem. However, the increasing use of low-pressure MOVPE [17], localised substrate heating (cold wall reactors) and atomic layer epitaxy (ALE) [18], suggests that although gas phase reactions occur, they are not *prerequisite* for the production of high quality materials. This should not of course detract from the problem of detecting gas-phase species since some of these species may arise via specific surface reactions yet may be difficult to detect on the substrate surface.

In this paper, the chemistries of the GaAs MOVPE precursors trimethylgallium, triethylgallium, hydrogen and arsine on GaAs (100) surfaces are discussed in the light of possible decomposition pathways leading to the clean production of GaAs, using data obtained via the application of both conventional surface science methods e.g. Auger, thermal desorption and unconventional methods, specifically reflection IR spectroscopy (RIRS) and the pressure independent surface sensitive technique of optical second harmonic generation (SHG).

EXPERIMENTAL

The experimental system used in this work is described in detail elsewhere [19] but briefly consists of a stainless steel ultra high vacuum chamber (base pressure 5×10^{-10} mbar) equipped with facilities for Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and mass spectrometry. The system is also fitted with an isolatable reactor capable of operation over the pressure range $5 \times 10^{-10} - 10^3$ mbar. The experimental arrangement for the SHG experiments is described elsewhere [8], as are the experimental details of the RIR measurements [10]. The samples were cut from n-type GaAs (100) wafers (MCP Electronics) and were approximately $1\text{--}3\text{ cm}^2$. Surfaces were prepared in UHV by oxide desorption which leads to Ga-rich surfaces and by treatment in H_2 and AsH_3 using a procedure which generates Auger clean, As-rich surfaces [20], designed to mimic the pre-growth substrate bake employed in GaAs MOVPE.

RESULTS AND DISCUSSION

1. The Adsorption and Reaction of TMGa and TEGa at GaAs (100) Surfaces

The adsorption of Ga metallorganics has been discussed in several recent reviews [11,12]. The first clear evidence indicating that Ga-metallorganics would adsorb at GaAs (100) surfaces came from our laboratories [21]. Figure 4 of reference 21 reveals that TEGa adsorbs at an As-rich GaAs (100) surface at 300 K, the surface becoming saturated at relatively low exposures and, very importantly, subsequent thermal processing revealing essentially 'clean' decomposition pathways that left no residual surface carbon. Contrast this with the analogous data depicted in figure 1, for TMGa adsorption. In figure 1, AES spectra depicting Ga, As and C Auger transitions are shown after exposure of a clean, As-rich GaAs (100) surface to varying amounts of TMGa, followed by ramping the temperature slowly up to 850 K.

Figure 1. Derivative AES spectra recorded from an As-rich GaAs (100) surface (a), clean surface spectrum, and after exposure at 300 K to (b), 0.3 L, (c), 3 L and (d) 30 L TMGa, followed by annealing to 870 K.

AES spectra were not taken prior to temperature ramping in order to eliminate the possibility of electron beam damage. From this figure it is clear that for TMGa unlike TEGa, the thermal treatment does not

give rise to clean decomposition reactions and the substrate surface remains contaminated with carbon after heating. The fact that residual carbon levels are seen to increase with increasing TMGa exposure up to 30 Langmuir is a possible indication that even at 300 K *multilayers* may form as discussed in more detail below. These data apparently conflict with the data of Yu and coworkers who studied the adsorption of TMGa on an As-stabilised GaAs (100) surface formed in a manner similar to that employed here, although the surfaces are reportedly reconstructed as (2x8) [22]. These workers found clean thermal decomposition above 570 K for the surface species which was believed to be dissociated TMG. The influence of adsorbed hydrogen on the desorption process was not considered by these workers, who favour the desorption of methyl radicals. We feel that given the low temperatures of these desorption processes, radical desorption is unlikely. At present we cannot reconcile our findings with those of Yu et al. but we note that when TMGa has been used for MOMBE growth, high levels of carbon incorporation have been reported for the deposited films, suggestive of incomplete decomposition as we have observed. Also, surface chemical studies of the growth of GaAs on Si (100) from TMGa have again revealed that surface decomposition results in residual carbon, most likely in the form of CH_x units [13]. This simple comparison of precursors is of enormous interest since it suggests that for TMGa unlike TEGa, an additional surface chemical reaction most likely involving another reactant is required in order to remove carbon from the substrate surface. The amounts of carbon left on the surface following TMGa adsorption and reaction are very high in doping terms and so this alternative reaction must be a major contribution to the overall growth mechanism in order to prevent the growth of p-type layers.

These data are believed to be the first direct comparison of the surface reactivities of TMGa and TEGa in terms of levels of residual carbon, (this system has been studied by McCaulley and coworkers from the viewpoint of the use of laser radiation to stimulate carbon removal but no mention of residual carbon levels resulting from a purely thermal treatment are made in their paper [23]) and clearly indicates the importance of the alternative first order decomposition pathway of β -elimination, which is available for TEGa but not TMGa. The implication of this last statement is that for TMGa, some process that is at least second order is required to remove residual carbon. If this is the case then to understand such pathways it is first necessary to understand the nature of the surface carbon species arising from TMGa adsorption and secondly to devise an experiment which indicates the role of a particular second species.

Figure 2. A comparison between (a), the carbon KLL AES lineshape for the surface species produced by TMGa adsorption on GaAs (100) at 300 K and (b), the carbon KLL AES lineshape for methane, taken from reference [24].

Considering the molecular nature of the surface species arising from TMGa adsorption at GaAs (100) surfaces at 300 K, figure 2 depicts an AES carbon lineshape taken from an As-rich GaAs (100) surface following exposure to 100 Langmuir TMGa at 300 K. Also shown is the gas-phase AES lineshape for methane taken from ref [24] and shifted along the electron energy axis for direct comparison.

AES lineshapes for simple atoms such as C, O, N, contain fingerprint information as to the nature of the chemical environment of the target atom [25]. The similarity in shape of the two lineshapes (not absolute energies which are not expected to be similar) is strong evidence in favour of an sp^3 hybridised carbon species, chemically very similar to methane.

This then is some evidence for the presence of intact methyl groups. A similar conclusion was reached by McCaulley and coworkers from XPS data for TMGa adsorption at a Ga-rich GaAs (100) surface at 300 K [23]. These data do not of course permit any comment as to the possibilities of dissociative or molecular adsorption. For adsorption of TMGa at Ga-rich surfaces the adsorption process is believed to be dissociative, yet without loss of carbon such that at least from XPS intensities the relative stoichiometry of the resulting surface species is 1 Ga : 3 C [23]. Figure 3 depicts the rate of uptake of TMGa on both As and Ga-rich GaAs (100) surfaces as a function of TMGa exposure at 300 K. From these data which may be thought of as involving the two extreme types of substrate surface possible under MOVPE or more likely ALE growth conditions, it is possible to note that (a), the rate of uptake is higher on the As-rich surface, (b), that there is a break in both uptake curves at low exposures followed by a slight rise over much higher exposures and (c), from the saturation intensities that the surface intensities for the As and Ga rich surfaces are 1 Ga : 2.0 C $\pm$ 0.3 and 1 Ga : 3.0 C $\pm$ 0.3, respectively.

Figure 3. Variation of normalised carbon KLL AES signals as a function of TMGa exposure recorded from both gallium and arsenic rich GaAs (100) surfaces at 300 K

Thus for the As-rich surface the stable surface species has a stoichiometry consistent with that of dimethylgallium (DMGa). These figures were calculated using a procedure which is described in detail elsewhere but briefly consists of calculating the relative number of surface atoms as a fraction of the number of bulk Ga atoms in a slab of thickness defined by the escape depths of the Auger electrons in question [23,26]. These data indicate that the As-rich GaAs (100) surface is more 'reactive' in the sense that the sticking coefficient of TMGa on this surface is apparently higher than that for the Ga-rich surface, yet at least one C fragment is lost from each TMGa molecule upon adsorption at 300 K. Also, for both types of surface it would seem that the first 'layer' forms at low exposures followed by perhaps multilayer formation as indicated by the higher exposure portions of the uptake curves. This difference in reactivity of the two surfaces perhaps holds the key to the question of the fate of the surface carbon. The As-rich surfaces used here were prepared via treatment in H_2/AsH_3 overpressures and as such are believed to be rich in adsorbed hydrogen, via the formation of what we have termed an

AsH_n sub-hydride phase [12]. It is further believed that the presence of this 'active' hydrogen facilitates methane production via a second order chemical reaction with adsorbed species such as TMGa . In order to test this proposal we have performed thermal desorption measurements on this system: Figure 4 depicts thermal desorption data corresponding to methane production, $m/e = 16$ Daltons and ethane production, $m/e = 30$ Daltons, obtained from As-rich surfaces (a), as prepared and believed to be rich in adsorbed hydrogen and (b), after preparation and annealing in UHV at 670 K for 2 hours to drive off adsorbed hydrogen.

Figure 4, Thermal desorption spectra corresponding to the evolution of methane, $m/e = 16$, and ethane, $m/e = 30$, obtained from GaAs (100) surfaces after exposure to TMGa at 300 K. In (a) the surface was as-prepared via annealing in arsine and in (b), the surface had been annealed in UHV after cleaning in arsine in order to remove adsorbed hydrogen. The heating rate employed was 1 K s^{-1} .

The data depicted in figure 4 are poor quality since our experimental system is not specifically designed for such work yet it is clear that the production of methane is severely reduced by removal of surface hydrogen while the production of ethane is enhanced. These data show for the first time that both methane and ethane are formed via the surface chemical decomposition of TMGa on GaAs (100), lending further weight to the argument that adsorption leaves the methyl species effectively intact. These data are not intended to imply that methane and ethane are the only reaction products produced here. However, we have not been able to detect the desorption of TMGa itself in these experiments and for reasons of experimental difficulty have not attempted to look for Ga-containing decomposition products from TMGa .

Possibly the most exciting data available for TMGa on GaAs (100) surfaces comes via novel measurements made in our laboratories using reflection IR spectroscopy, an example of which is shown in figure 5. These data are among the first external reflection IR spectra obtained from compound semiconductor surfaces and serve to illustrate the enormous potential of this method for such studies. Unlike electron energy loss spectroscopy (EELS) which has been employed to study metallorganic adsorption elsewhere [11,13], IR methods are not inherently limited to low pressure operation and via the use of reflection methods can also be applied at high temperatures [10]. The spectrum depicted in figure 5 which was recorded in less than 500 seconds at a resolution of 8 cm^{-1} exhibits bands at 1170 cm^{-1} and 1420 cm^{-1} , which agree reasonably with the EELS data obtained by the groups of Luth [11] and Masel [13] for TMGa adsorption on Si surfaces, who assign such features to methyl vibrations of molecularly adsorbed TMGa . For reasons noted elsewhere, we believe

that some decomposition of the TMGa molecules may have occurred although it is not clear whether this is inherent in the chemistry of the system or whether it has been catalysed by surface contamination [10].

Figure 5. Transmittance RIR spectrum obtained from a GaAs (100) surface that was most likely Ga-rich, following exposure to $>10^4$ L TMGa at 300 K.

Turning now to TEGa adsorption, we have previously reported data for TEGa adsorption at the As-rich GaAs (100) surface at 300 K [21,26]. Auger lineshape data for this system revealed that the surface species is chemically very similar to ethane and not ethene, which may be taken as support for the existence of intact ethyl groups [21]. Analysis of AES saturation levels for the adsorption of TEGa on As-rich GaAs (100) at 300 K revealed a species with a relative surface stoichiometry of 1 Ga : 4 C, i.e. as with TMGa adsorption, spontaneous loss of one alkyl unit was inferred from the AES data [26]. This observation was also attributed to the presence of surface hydrogen although in this instance there are two possible sources of such hydrogen- one via arsine decomposition as noted above and the other via the β -elimination process to yield ethene, which may result in the formation of a convenient Ga-H bond. Data for TEGa adsorption at Ga-rich GaAs (100) surfaces obtained elsewhere suggests that at 300 K dissociative adsorption occurs [23] while thermal desorption studies obtained following low temperature adsorption (150 K) or high exposures at 300K, to simulate higher coverages believed to exist at higher pressures or continuous fluxes) reportedly indicate the production of H_2 , ethane, ethene and, as noted earlier, diethylgallium [14]. In contrast, for TEGa adsorption at the As-rich GaAs (100) surface at 300 K our thermal desorption studies have only detected ethene and ethane production, which occurs via at least two low temperature states, indicative of a *step-wise* decomposition process, figure 3 of ref [26].

The only evidence that we have noted for desorption of gallium-containing species comes via laser induced temperature jump experiments in which a peak at $m/e = 115$, i.e. consistent with DEGa (although this is far from definitive), was observed at an intensity of some 4 orders of magnitude lower than that for the peak at $m/e = 30$, which was used to detect ethane [27]. It would therefore appear that at least via static dosing at 300 K, the surface layer so produced is effectively chemisorbed such that subsequent desorption of Ga-containing species is unlikely. In this respect it should be noted that for TEGa adsorption at 300 K, our AES uptake curves do not provide any evidence of multilayer formation which is in marked contrast to the data for TMGa adsorption, whereas multilayers may well have formed in the low temperature/ high exposure adsorption experiments noted above [14], which may have been the source of the desorption of Ga-containing species. This point must not be overlooked since under conditions of higher pressures (e.g. MOVPE) or higher fluxes (e.g. MOMBE, CBE) it is

highly likely that the growth chemistry extends beyond the first layer, i.e. multilayer chemistry must play a significant role in the growth chemistry.

In mechanistic terms the detection of DEGa has become quite important for the reasons noted earlier. However, as can be seen, the only *surface chemical* data in specific support of the formation of DEGa diethylgallium on the substrate surface, has come from our laboratories [26], via the analysis of the relative surface stoichiometries and indirectly with the thermal desorption data, which are consistent with, but not proof of the sequential decomposition of a species such as DEGa. EELS data for adsorption at a Ga-rich GaAs (100) surface have been reported but lack the spectral resolution to adequately identify DEGa unambiguously [28]. RIR experiments currently underway should provide sufficiently detailed information to be able to solve this problem.

To summarise the implications for growth; for TMGa and TEGa adsorption on GaAs (100) surfaces it would appear that intramolecular decomposition pathways are entirely sufficient for the clean, sequential reaction of TEGa whereas for TMGa this is not the case, and additional surface species such as adsorbed hydrogen are involved in providing additional pathways not available to the TMGa molecule alone. In MOVPE, adsorbed hydrogen is provided by heterogeneous and homogeneous arsine decomposition but in CBE and MOMBE, atomic hydrogen is produced only at the arsine cracker, which may not be sufficient for efficient scavenging of surface methyl groups. This would explain the fact that the use of TMGa under MOMBE growth conditions results in the deposition of p-type material. TEGa of course has an alternative pathway available which also provides a source of adsorbed hydrogen.

The alternative way of reconciling these differences would be to propose that gas-phase decomposition of TMGa occurs under MOVPE conditions and not under high vacuum conditions. For MOVPE, this would then result in lower surface carbon levels since fewer carbon fragments will be generated at the substrate surface. For atmospheric pressure growth in a hot wall reactor this is most likely true to some extent, however the data presented here indicates that surface reactions such as those identified in this work must also be considered as possible routes to carbon removal since these processes will become particularly favourable under reduced pressure, cold wall and ALE growth conditions.

2. The Chemistry of Arsine and Hydrogen on GaAs (100) Surfaces

Previously we demonstrated that on GaAs (100) substrates that were depleted of As via thermal treatment in UHV, that surface As levels could be restored via annealing in arsine at substrate temperatures of 770 K as illustrated by the low energy AES data depicted in figure 3 of reference [20]. These data were the first surface chemical evidence of the *heterogeneous* decomposition of arsine which had been proposed previously in the growth literature [1,29]. These results have since been confirmed in the work of Yu et al. [22] who were able to obtain the As-rich c(2x8) surface reconstruction indicative of an As coverage of approximately 0.85 [30]. The relatively high pressures of arsine required, (typically 10^{-5} mbar) and long reaction times ($10 - 10^2$ minutes) suggested that the sticking coefficient of arsine on the GaAs (100) surface was very low. This statement accounted for the fact that for adequate growth rates in MOMBE, an arsine cracker has to be used in order to obtain a suitable flux of As_2 to the surface. Heterogeneous decomposition of arsine will generate a surface rich in adsorbed hydrogen. This is consistent with the generally accepted belief that this hydrogen is able to scavenge surface methyl groups produced by TMGa adsorption before they are able to react to produce some stable carbide species. The other possible source of hydrogen is of course the carrier gas. The work of Larsen et al. using D_2 as carrier gas demonstrated that the carrier gas is not involved in the reaction when both TMGa and arsine are present [31]. Previously we have shown that high overpressures of dihydrogen (H_2) are required in order to produce a surface reaction leading to the production of clean, yet As-depleted surfaces [20]. High pressures are believed to be necessary due to the very low sticking coefficient for dihydrogen adsorption on GaAs (100) surfaces, which contributes to a high barrier to dissociation. Others have noted that this is also the case, although the extent to which the surface reaction with hydrogen occurs appears to be variable [32]. When atomic hydrogen is deliberately formed in the chamber such as via a hot filament, clean GaAs (100) surfaces are generated relatively easily and are again found to be depleted of surface As [33], presumably via arsine formation. In comparison with dihydrogen, the adsorption and reaction of arsine occurs relatively easily. Since this process will generate adsorbed hydrogen, it will necessarily also limit dihydrogen adsorption via simple kinetic arguments. Thus when sufficient amounts of arsine are present we expect no surface chemical involvement of dihydrogen. These arguments also account for the fact that an overpressure of arsine gas

successfully prevents As loss from the substrate surface during the pre-growth substrate bake employed in MOVPE, since the proposed mechanism of As loss is via arsine formation and not simply via arsenic sublimation.

3. Optical Second Harmonic Generation Studies of GaAs (100) Surfaces

Previously we have reported the first application of the non-linear optical technique, second harmonic generation (SHG) to the study of III-V growth processes, monitoring the dynamic adsorption of TEGa on GaAs (100) at 300 K [8] and modelling the SHG intensity variation in terms of a simple Langmuir isotherm [9]. Not too surprisingly this latter treatment did not result in a good fit between the calculated and experimental data, suggesting that more complex adsorption kinetics are followed.

Here, we present recent data obtained for TMGa adsorption on GaAs (100) at 300 K for comparison to that obtained for TEGa. Figure 6 depicts an SHG transient obtained from a GaAs (100) surface recorded at near normal incidence during dynamic exposure to TMGa at 1×10^{-9} mbar.

Figure 6. Optical second harmonic generation signal intensity at 532 nm recorded from a GaAs (100) surface as a function of TMGa exposure at 300 K. An Nd:YAG laser provided the fundamental wavelength at 1064 nm, with pulses of 10 ns duration and powers of < 5 mJ unfocussed.

Figure 5 reveals that a steady decrease in SHG intensity occurs over a period of time corresponding to a TMGa exposure of approximately 1 Langmuir which from figure 3 would correspond to approximately one monolayer for an As-rich surface, and perhaps one third monolayers for a Ga rich surface. This decrease in intensity indicates that the non-linear surface susceptibility is decreasing during TMGa adsorption. This result contrasts with previous data obtained for TEGa adsorption, in which an increase in SHG was observed [8]. At the present time we are not able to fully explain these data apart from stating that the adsorption process must lead to a reduction in the surface electron density, i.e. an increase in work function, correlating with the presence of an electron-withdrawing overlayer [34]. We note that in these TMGa experiments it was not possible to remove all residual surface carbon before exposing the surface to TMGa. This may have resulted in a misleading SHG response since it is to be expected the SHG intensity will be critically dependent upon the state of the substrate surface. Unlike the RA technique, SHG does not require any macroscopic surface structural changes to occur before providing a response, i.e. a random adsorption process generating a disordered overlayer on a disordered substrate is just as likely to result in a significant SHG change as that for an ordered substrate/overlayer system. In addition to being able to monitor adsorption and desorption phenomena, the SHG technique is capable of providing detailed information regarding the 2D symmetry of the substrate surface [7,35]. As an illustration of this which is relevant to GaAs growth, consider the data shown in figure 8. This figure reveals the rotational anisotropy in the SHG response from a GaAs

(100) surface as shown in the variation of SHG intensity as a function of the angle made by the polarisation vector of the laser beam with the surface crystallographic axes.

Figure 7. Variation of SHG intensity at 532 nm as a function of the angle of polarisation of the laser with respect to a $\langle 110 \rangle$ direction on the GaAs (100) substrate, recorded in UHV, at 300 K using laser pulses of 10 ns duration and powers of < 5 mJ unfocused.

Analysis of these polar plots is not trivial as McGilp has shown [35]. However, at its basic level this data reveals that there is preferential ordering along at least one $\langle 110 \rangle$ azimuth, which is hardly surprising for a GaAs (100) surface. The presence of the orthogonal axis may be perceived from the weak features located at $\pi/2$ and $3\pi/2$, although better data are required before this may be confirmed. Nonetheless, the possibility of using such data to determine overlayer symmetry under high overpressures has been illustrated, which of course has enormous potential for growth studies. We believe that with more detailed analysis, SHG data such as that depicted in figures 6 and 7, and those discussed in reference [8] are likely to prove complementary to RA data for the in-situ monitoring in real-time of semiconductor growth processes over the complete range of pressures employed, i.e. atmospheric to UHV.

CONCLUSIONS

In this paper, we have demonstrated that via the use of surface science and related methods it is possible to begin to understand the fundamental surface chemistry associated with MOVPE and related growth techniques. The surface chemistry of the Ga-metallorganics such as TMGa and TEGa is now becoming clear. It would appear that the most likely surface processes to occur are those which could have been predicted from simple chemistry, i.e. hydrogen addition plus methyl recombination for TMGa and hydrogen addition plus β -elimination for TEGa. The role of arsine is also becoming clearer in that V/III ratios $\gg 1$ are to be expected for stoichiometric GaAs growth via surface reactions on the basis of the vast differences in sticking coefficients between the metallorganics (where it is near unity) and arsine, where it is perhaps several orders of magnitude lower. Arsine decomposition also produces surface hydrogen, which allows an explanation of the lack of participation of the hydrogen carrier gas in the reaction and also accounts for the efficiency of arsine overpressures in preventing surface degradation at high temperatures. This surface hydrogen is most likely responsible for scavenging of surface methyl groups during TMGa decomposition.

Finally new results for the two in-situ 'optical' surface probes RIR and SHG have indicated the enormous potential of such methods for future studies of surface processes in MOVPE.

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