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The adsorption and decomposition of trimethylgallium and triethylgallium at GaAs(100) surfaces

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Abstract. This paper outlines the results of an investigation into the adsorption of trimethylgallium (TMGa) on GaAs(100) surfaces at 300 K and its subsequent thermal chemistry carried out using Auger electron spectroscopy, temperature programmed desorption methods and reflection–absorption IR spectroscopy (RAIRS). The data are compared to previously obtained data for triethylgallium adsorption at these surfaces and discussed in terms of reactions that lead to carbon deposition and the relative reactivities of As-rich and Ga-rich surfaces. Very preliminary RAIR data for TMGa adsorption at the Ga-rich surface reveal that some surface reaction does indeed occur at 300 K but that at least some of the methyl groups appear to remain intact. Thermal decomposition of the species formed by TMGa adsorption is found to be highly sensitive to experimental conditions and generally results in high levels of residual carbon, in marked contrast to the behaviour of TEGa.

1. Introduction

The need for a greater understanding of surface chemical processes involved in the vapour phase epitaxial growth of III–V semiconductors has resulted in considerable activity in recent years [1–4]. For the growth of GaAs on GaAs(100) substrates, we were the first to demonstrate that a typical Ga growth precursor, triethylgallium (TEGa) adsorbed at an As-rich GaAs(100) surface readily at 300 K and furthermore decomposed cleanly leaving little residual carbon [1]. Subsequent studies from our laboratories [3] and elsewhere [4] showed that both ethane (via hydrogen addition) and ethene (via β-elimination) are formed in the thermal decomposition of TEGa on GaAs(100) and that for the As-rich surface, two distinct desorption states for both products are observed. For this surface, analysis of AES intensities indicated that the surface species possessed the stoichiometry, 1 Ga : 4 C ± 0.25, consistent with the presence of a species such as diethylgallium (DEGa) presumably produced via *reactive* adsorption [3].

While TEGa is commonly used in high vacuum growth processes such as chemical beam epitaxy (CBE), growth of GaAs at higher temperatures (up to 1000 mbar) occurs quite successfully using trimethylgallium (TMGa) often using conditions which limit the possibility of gas-phase reactions, and again high quality n-type material results, indicative of clean decomposition pathways. However, there is very little known regarding the nature of these pathways. In this paper, we report some basic surface chemical studies of the nature of the interaction of TMGa with GaAs(100) surfaces and

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we contrast the behaviour of TMGa with that of TECa. We demonstrate that unlike the case of TEGa, the clean surface decomposition of TMGa must involve *intermolecular* reactions, most likely with adsorbed hydrogen resulting from the heterogeneous decomposition of the group V reagent, arsine gas.

2. Experimental procedure

The experimental system used in this work has been described in detail elsewhere as are the procedures for generating clean, Ga-rich and As-rich GaAs(100) surfaces [5] and the experimental arrangement for the RAIRS measurements [6]. Substrates were n-type GaAs(100), Si-doped to $1\times10^{17}\,\mathrm{cm}^{-3}$ of surface area approximately $1\,\mathrm{cm}^2$ (MCP Electronics) which were polished and chemically etched prior to mounting in the UHV system. Auger electron spectra were recorded in derivative mode using a primary beam of energy 2.5 keV with a surface current density of $1\text{–}5\,\mu\mathrm{A\,cm}^{-2}$.

3. Results and discussion

AES reveals that a simple thermal treatment of the As-rich surface dose with TMGa at 300 K results in high levels of residual carbon [7], which is in marked contrast to our previous data for TEGa and is the first evidence of *differences* in the surface decomposition pathways of these two molecules. Figure 1 depicts the rate of uptake of TMGa at both Ga-rich and As-rich GaAs(100) surfaces at 300 K as a function of exposure, suggesting that (i), the rate of uptake (as determined by the exposures required to reach the plateau in the uptake curves) is slightly higher on the As-rich surface, (ii) that completion of the first stage of adsorption, which may be monolayer formation, occurs at low exposures indicating a relatively high sticking coefficient for TMGa on both surfaces and (iii) that adsorption may continue after this break resulting in multilayers. These data agree well with that of McCaulley and co-workers who found that both TEGa and TMGa adsorb readily at Ga-rich GaAs(100) surfaces at 300 K [8]. It would therefore appear that there is some similarity between the behaviour of TMGa and TEGa in that both molecules adsorb readily on both As-rich and Ga-rich GaAs(100) surfaces at 300 K. From figure 1 using simple layer formalism which calculates the surface stoichiometry of a particular species in terms of the fraction of Ga atoms in a slab of thickness equal to the escape depth of the Auger electrons in question, it may be shown that the surface stoichiometry of the species formed via TMGa adsorption at GaAs(100) at 300 K is 1 Ga : 2 C ±0.3 for the Ga-rich surface, in good agreement with the data of McCaulley and co-workers who employed XPS intensities in a similar calculation [8], but 1 Ga : 2 C ±0.3 for the As-rich surface, suggesting that spontaneous loss of at least one carbon fragment per TMGa molecule occurs upon adsorption at 300 K. Note here again the similarity with the data for TEGa adsorption described earlier. For the Ga-rich surface, the stoichiometry is consistent with the presence of molecular TMGa and analysis of the AES carbon 1s VV lineshape indicates that the species involves 'intact' methyl groups [7], but electron spectroscopy is not sufficiently reliable as a probe of molecular structure. To overcome this limitation we are exploring the potential of the RAIRS technique for use in the study of adsorbates at compound semiconductor surfaces.

As yet it has not been possible to obtain reliable RAIRS data for TMGa adsorption on GaAs(100) at exposures comparable to those required for monolayer information.

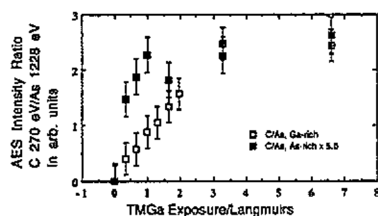

Figure 1. Carbon (270 eV) peak-to-peak Auger intensities normalized to the As (1228 eV) peak-to-peak intensity from both Ga-rich and As-rich GaAs(100) surfaces as a function of TMGa exposure at 300 K. The data for the As-rich surface is shown expanded by ×5, for ease of comparison.

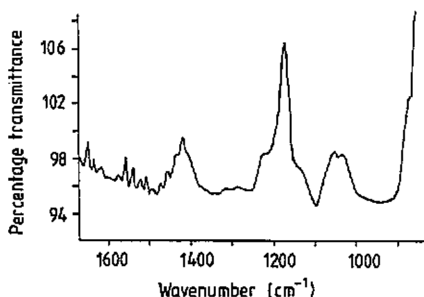

Figure 2. Transmittance spectrum recorded from a GaAs(100) surface in reflection–absorption geometry, following exposure to 10^5 L TMGa at 300 K. The spectrum was recorded at a resolution of 8 cm^{-1}, using 1000 scans, taking approximately 5 minutes to acquire both the background clean surface spectrum and the sample spectrum.

However, we have obtained good quality spectra resulting from much higher exposures of TMGa. Figure 2 shows what is believed to be the first reflection–absorption IR spectrum obtained from a compound semiconductor surface, for a Ga-rich GaAs(100) surface following exposure to 10^5 L TMGa at 300 K. These data are discussed in detail elsewhere [6], however, a preliminary analysis in comparison with gas and liquid phase data [9] together with EELS data for TMGa adsorbed at Si surfaces [2,10] suggests that the bands at 1174 cm^{-1} and 1420 cm^{-1} are possibly due to the symmetric and asymmetric CH_3 deformations of a multilayer of adsorbed TMGa species respectively [6]. Unfortunately the band at 1050 cm^{-1} is not consistent with this assignment and we have suggested that some decomposition of the TMGa must occur upon adsorption at 300 K. A possible assignment of the 1050 cm^{-1} band may involve the formation of C–C single bonds or perhaps loss of hydrogen to give rise to CH_x deformations. Obviously more RAIRS data are required particularly for the Ga–C stretching region and C–H stretching regions which were unfortunately outside of the range of the detector employed in these preliminary experiments. However at the very least, the data depicted in figure 2 indicate the potential of the RAIRS method for the *in situ* study of chemical processes occuring at compound semiconductor surfaces.

Thermal decomposition of the species formed via TMG adsorption at GaAs(100) surfaces at 300 K is of great interest since for the formation of methane, which is the major reaction product obtained during the growth of GaAs from TMGa and arsine, a source of hydrogen is needed. For TMGa adsorption at Si surfaces there is some evidence of hydrogen abstraction from one methyl group to another to produce methane and CH_x (ads) (x = 0 to 2) [10]. However, during growth, isotopically labelled experiments have shown that the most likely source of adsorbed hydrogen is the co-reactant, arsine [11]. Previously we have shown that arsine decomposes heterogeneously at Ga-rich GaAs(100) surface to produce a surface which is As-rich [5]. There is now some evidence that this surface is also rich in adsorbed hydrogen, since we have found that from such a surface, the thermal desorption of methane is enhanced [7]. In contrast, where the surface has been annealed in UHV to drive off excess hydrogen, the production of ethane is enhanced. These data are described in greater detail elsewhere but it is noteworthy that the thermal desorption profiles for

both methane and ethane are poorly defined, in marked contrast to the well-defined sequential desorption of ethane and ethene noted for the decomposition of TEGa [3,4]. It is suggested that for TMGa decomposition this is a real feature of the experiment which is indicative of surface kinetics of order > 1, and a highly variable supply of $H_{(ads)}$. In contrast, for TEGa, the β-elimination reaction is an intramolecular source of hydrogen which may be used to produce ethane.

4. Conclusions

This work has highlighted some important similarities and differences between the chemistries of the GaAs growth precursors TMGa and TEGa at GaAs surfaces which have clear implications as far as the incorporation of carbon into the growing layers is concerned. It would seem that the As-rich surface is more reactive towards the adsorption of both metallorganics than the Ga-rich surface. TEGa is able to undergo clean intramolecular decomposition while decomposition of TMGa is likely to result in surface carbon unless there is an additional source of surface hydrogen. While in practice the levels of carbon incorporation obtained via the use of TEGa and TMGa are much lower than those indicated by the surface chemical data, the reactions observed here are undoubtedly representative of some of the processes leading to carbon incorporation under growth conditions. Preliminary RAIR data for TMGa adsorption at the Ga-rich surface at 300 K suggest the presence of at least two chemically distinct surface species, one of which may be TMGa itself, and are further an illustration of the potential of this technique for the identification of potential growth intermediates.

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References

[1] Pemble M E, Buhaenko D S, Francis S M and Goulding P A 1989 *Mechanisms of Reaction of Organometallic Compounds with Surfaces (NATO, ASI Series, Series B* 198) eds D J Cole-Hamilton and J O Williams (New York: Plenum)
[2] Luth H *J. Vac. Sci. Technol.* A 7 696
[3] Buhaenko D S, Francis S M and Pemble M E 1990 *Vacuum* 41 972
[4] Murrell A J, Wee A T S, Fairbrother H, Singh N K,Foord J S, Davies G J and Andrews D A 1990 *Vacuum* 41 955
[5] Buhaenko D S, Francis S M, Goulding P A and Pemble M E 1989 *J. Cryst. Growth* 97 591
[6] Patel H and Pemble M E 1991 *Proc. EuroCVD (Strathclyde, UK, 1991)* (Les Editions de Physiques) at press
[7] Buhaenko D S and Pemble M E submitted to *J. Cryst. Growth.* at press
[8] McCaulley J A, McCrary V R and Donnelly V M 1989 *J. Phys. Chem.* 93 1148
[9] Coates G E and Downs A J 1964 *J. Chem. Soc.* 3353
[10] Lee F, Gow T R, Lin R, Backman A L, Cadwell L A and Masel R I 1990 *Vacuum* 41 951
[11] Larsen C A, Buchan N I and Stringfellow G B 1988 *Appl. Phys. Lett.* 52 480