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Comparative studies of the surface reactivity of triethylgallium on semiconductor and dielectric surfaces

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Abstract. The adsorption of triethylgallium (TEG) on GaAs in the presence of submonolayer quantities of Al or In has been investigated. It is found that these additives modify the reactivity patterns observed for TEG on the clean GaAs surface; the presence of Al suppresses the amount of diethylgallium (DEG) desorbing whereas In has the opposite effect. This arises since the kinetic parameters governing the desorption of DEG, which occurs in competition with its surface decomposition, are changed when Al or In are deposited on the surface. Comparative studies on the adsorption of TEG on Si_3N_4 have also been performed and the results are used to gain an insight into phenomena observed during the growth of III–V semiconductors by chemical beam epitaxy.

1. Introduction

Studies of the surface chemistry of metal organics have become more widespread in recent years—see, e.g., [1–4]. On the one hand these important inorganic compounds display a rich chemistry and an investigation of their reactivity at surfaces is therefore of intrinsic chemical interest. At the same time the surface decomposition of metal organics is central to a range of thin film deposition and epitaxial growth techniques; a knowledge of the surface chemistry involved should thus aid the future development of such processes [5]. This is particularly true in the area of chemical beam epitaxy (CBE) which involves the reactions of metal organics at surfaces under ultra-high vacuum conditions, a reaction regime which can be directly accessed using a UHV-based surface science approach.

In previous studies we have characterized the reactivity of triethylgallium (TEG) on the Ga-stabilized GaAs (100) (4×1) surface using a wide range of surface science techniques [1]. The results indicate that the reactions involved can be summarized by the scheme in figure 1. Below 250 K TEG is present in a molecularly chemisorbed state whereas reversible dissociation to form adsorbed diethylgallium (DEG) and ethyl radicals occurs at 300 K. At higher temperatures DEG either desorbs or cracks to release Ga atoms to the lattice and form further ethyl radicals which themselves desorb above 600 K, mainly as gas phase ethene and hydrogen. An important characteristic of this reaction scheme is the occurrence of processes (the desorption of TEG and DEG) which compete with the overall cracking of TEG to produce Ga atoms. This is of significance since it means that the efficiency at which TEG is converted to Ga in CBE growth processes depends very sensitively on the nature of the reacting surface

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involved, with consequent loss of control over the growth rate and stoichiometry of the deposited material [6]. In this paper we therefore briefly explore how the kinetics involved in the pathway in figure 1 vary with the addition of In or Al to a GaAs surface, and also how the reactivity of TEG on GaAs compares with the behaviour observed on Si_3N_4.

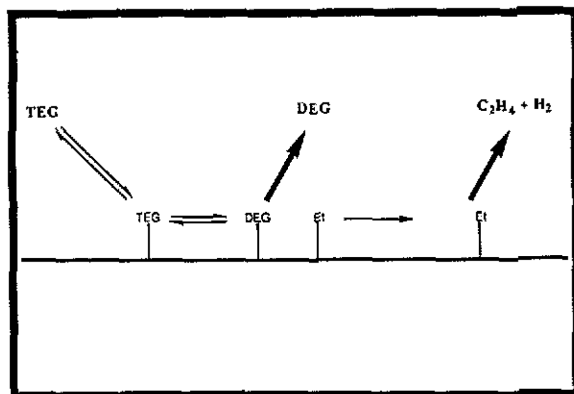

Figure 1. Reaction scheme describing the decomposition of TEG to produce ethene, hydrogen and lattice Ga on GaAs (100) (4×1).

2. Experimental details

All experiments were carried out in two UHV systems equipped with XPS, AES, HREELS, LEED and TDS which have been described in detail elsewhere [1]. The GaAs (100) sample used was n-type and was cleaned by Ar ion sputtering and annealing to produce a contaminant-free Ga-stabilized (4×1) reconstructed surface. The Si_3N_4 sample was deposited by CVD on GaAs wafers and was simply cleaned by annealing at elevated temperatures in vacuum to produce a surface which displayed the presence of significant quantities of oxygen as well as nitrogen when analysed by XPS, and which appeared disordered when examined by LEED. The TEG used was of electronic grade purity as supplied by Epichem Ltd. Al and In were deposited onto the surface from high purity metal evaporation sources.

3. Results

3.1. Influence of Al and In on the reactivity of TEG on GaAs

According to the reaction scheme in figure 1, TEG dissociates to form DEG and ethyl species on GaAs at 300 K, with both TEG and DEG desorption occurring in the range 350–600 K and ethyl decomposition releasing ethene and hydrogen into the gas phase above 600 K. Thermal desorption experiments following saturation TEG exposure to the GaAs surface in the presence of sub-monolayer concentrations of Al or In were therefore performed to probe for changes in surface reactivity. The results are qualitatively similar in the presence of both In and Al but the relative desorption yields of

Ga alkyls and ethene were found to vary considerably when these metals were evaporated onto the surface. The ethene desorption yield increases by almost an order of magnitude in the presence of this metal, whereas In reduced the ethene desorption yield by a factor of two.

Variations in the DEG desorption spectra are shown in figures 2 and 3 for Al and In respectively. With regard to figure 2 it can be seen that Al reduces the DEG desorption yield and causes the high temperature tail to shift to higher temperatures. It was also found that the TEG desorption which occurs on the clean surface was completely suppressed, even by trace surface concentrations of Al. In figure 3 it can be seen that In increases the DEG desorption signal. Cracking pattern analysis monitoring TEG showed that the narrow peak which grows with In coverage in the 500–600 K range arises exclusively from DEG desorption whereas the broad peak at 350–500 K is associated with TEG desorption (TEG cracks to produce DEG in the QMS ion source). The narrow peak at 500–600 K shifts down in temperature as the In coverage rises.

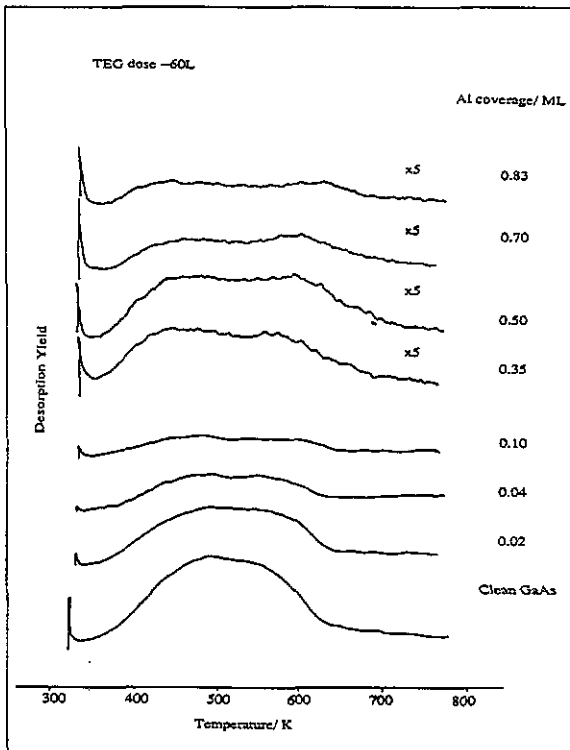

Figure 2. TDS spectra monitoring DEG desorption following 60 L exposure of TEG to GaAs at 300 K in the presence of the varying Al coverages shown. 1 ML corresponds to a physical monolayer of Al as estimated by AES.

3.2. The adsorption of TEG on Si_3N_4

XPS and thermal desorption experiments were carried out to examine the adsorption of TEG on Si_3N_4 at 300 K. An uptake curve derived by measuring appropriate XPS peak intensities as a function of TEG exposure in shown in figure 4. It is apparent from

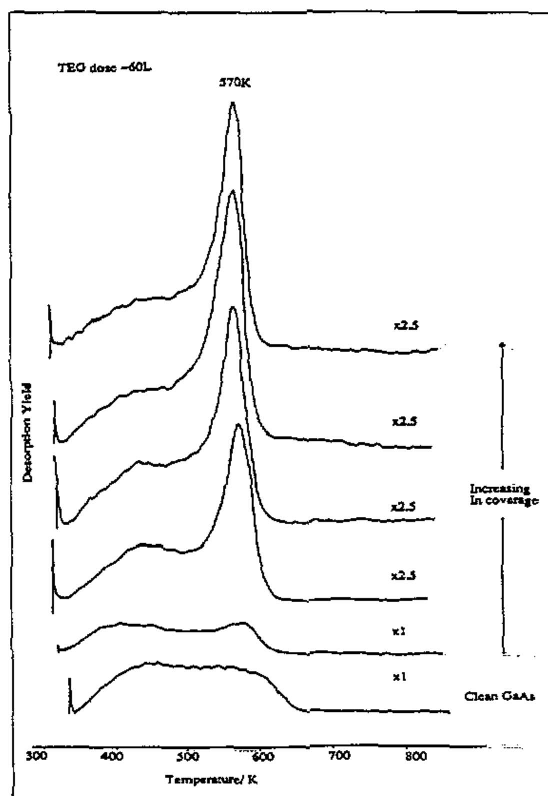

Figure 3. TDS spectra as for figure 2 but in the presence of increasing concentrations of In instead of Al.

these data that TEG does form an adsorbed layer on the surface in question since Ga and C peaks do grow in intensity. However, the saturation coverage is very low since the intensities of these peaks are small and the XPS transitions from the substrate are not attenuated. Thermal desorption measurements from the adsorbed layer are illustrated in figure 5 monitoring various Ga alkyl fragments $Ga(C_2H_5)_x$ ($x = 0$–3). The similarity of the peak profiles at differing masses suggests that the main desorbing species is TEG and this interpretation is consistent with the mass spectrum measured for the TEG dosing gas. XPS analysis following a thermal desorption sweep showed that all Ga was lost from the surface during such an experiment, within the limits of experimental detection.

4. Discussion

The results show that the branching ratios involved in the reaction scheme in figure 1 vary significantly depending on the surface involved. Indium increases the DEG desorption yield very substantially illustrating that DEG desorption becomes favoured in comparison to DEG cracking to form Ga species. This could either occur because the DEG desorption energy is reduced or the cracking process is inhibited. Computer modelling of the desorption data indicates that the former explanation is at least sufficient to explain the data observed [7]. Al has the opposite effect and again it is found that

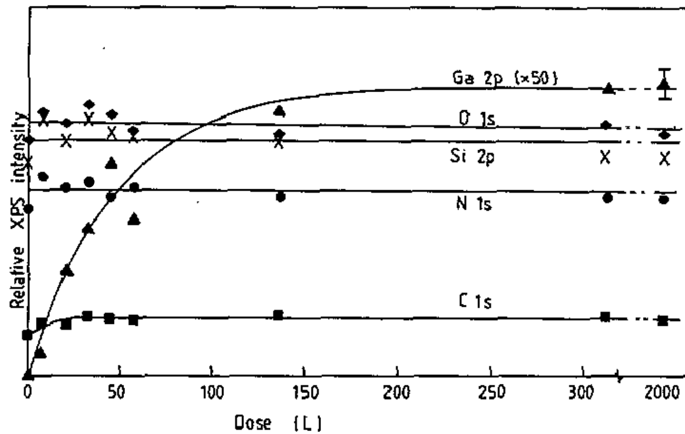

Figure 4. XPS uptake curve following TEG exposure to Si_3N_4 at 300 K.

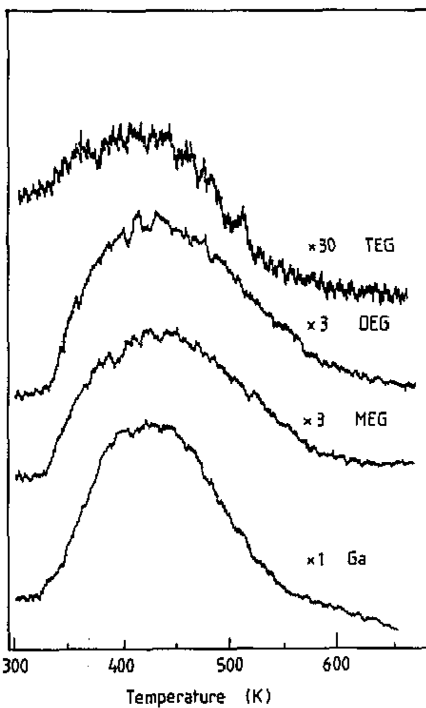

Figure 5. TDS spectra following saturation TEG exposure to the Si_3N_4 sample. TEG, DEG, MEG correspond to $Ga(C_2H_5)$ x species ($x = 1$–3) respectively.

an increase in the DEG desorption energy can explain the experimental data. A second effect produced by Al is the complete suppression of the TEG desorption signal. This arises on clean GaAs above 300 K from the associative desorption of DEG and surface ethyl species, suggesting that the presence of Al moves the equilibrium controlling the dissociation of TEG to the right. Surface spectroscopic studies [7] are indeed consistent with this explanation since they suggest that the ethyl species produced in the conversion of adsorbed TEG to DEG become trapped irreversibly at Al sites on the surface.

These modest changes in branching ratios governing surface reactivity patterns become enhanced when Si_3N_4 is substituted for GaAs. No irreversible cracking to produce Ga atoms on the surface is observed. Instead, the adsorbed layer desorbs as TEG indicating either that molecular adsorption occurs or that associative desorption dominates over other possible reaction pathways when the surface is heated. The very low adsorbate coverages seen also suggest that only a small fraction of sites on the Si_3N_4 surface are active in producing chemisorption.

The rate-limiting step in CBE growth processes of III–V semiconductors involving TEG is thought to involve the unimolecular conversion of TEG to Ga on the growing surface and it is now well established that the presence of Al increases the partial Ga growth rate whereas In reduces it [6]. The results presented here strongly suggest that this behaviour arises because of variations in the branching ratio controlling DEG desorption in comparison to DEG cracking. Similarly it is also known that GaAs growth on Si_3N_4 substrates does not take place under normal reaction conditions and again this is consistent with the data reported here which show that the conversion of TEG to Ga on this surface is very inefficient [8]. Surface science studies may therefore be used to obtain a mechanistic insight into the surface processes which underlie well-known semiconductor growth characteristics involving organometallic compounds.

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References

[1] Murrell A J, Wee A T S, Fairbrother D H, Singh N K and Foord J S 1990 *J. Appl. Phys.* **68** 4053

[2] Donnelly V M and McCaulley J A 1990 *Surf. Sci.* **238** 00

[3] Bent B E, Nuzzo R G and Dubois L H 1989 *J. Am. Chem. Soc.* **111** 1634

[4] Lin R, Gow T R, Backman A L, Cadwell L A, Lee F and Masel R I 1989 *J. Vac. Sci. Technol.* B **7** 725

[5] See for example *J. Cryst. Growth* **105** (1990) and **107** (1991)

[6] Skevington P J, Davies G J, Wee A T S, French C L and Foord J S 1991 *Appl. Phys. Lett.* submitted

[7] French C L, Fitzgerald E T and Foord J S 1991 *Surf. Sci.* in preparation for submission

[8] Kayser O 1991 *J. Cryst. Growth* **107** 1991