Surface Science 50 (1975) 434–450
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INTERACTION KINETICS OF As_4 AND Ga ON {100} GaAs SURFACES USING A MODULATED MOLECULAR BEAM TECHNIQUE

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Received 13 January 1975; revised manuscript received 6 March 1975

A modulated molecular beam technique, using mass spectrometric detection of desorbed species, had been applied to a study of the kinetics of Ga and As_4 interactions on {100} GaAs surfaces. Time domain mass spectrometer signals were processed using fourier transform techniques to provide information on surface lifetimes, sticking coefficients, desorption energies and reaction orders. In the temperature range 300–450 K As_4 is non-dissociatively chemisorbed on Ga atoms from a weakly bound precursor state, but above 450 K there is a pairwise dissociation–recombination reaction between As_4 molecules adsorbed on adjacent Ga lattice sites. At temperatures higher than 600 K a temperature dependent Ga adatom population is formed by the desorption of As_2 from the surface. Thus above 450 K it is possible to produce GaAs from beams of the elements, but below this temperature the compound does not form.

1. Introduction

A knowledge of the interaction kinetics of vapour species of elements of Groups III and V with the surfaces of III–V compounds is of fundamental importance to the understanding of growth from the vapour phase of thin films of these materials. A large amount of work has been published on film growth methods, and a number of investigators have attempted to make an overall kinetic evaluation of film growth processes by the determination of growth rate as a function of substrate temperature, vapour phase concentrations and fluid dynamic conditions. However, more direct studies of detailed atomistic processes, such as adsorption, desorption and surface interactions have been far fewer in number and limited almost exclusively to GaAs. Arthur [1], using field emission microscopy, found that Ga migrates on the (111) A face of GaAs at temperatures above 525 K, and at somewhat lower temperatures (425 K) on the $(\bar{1}\bar{1}\bar{1})$ B. Arsenic from an As_4 beam was found to be mobile on both faces even at 77 K, and to desorb rapidly at 525 K. The same author [2,3] also studied the interaction of As_2 and Ga beams with {111} GaAs surfaces, using a pulsed molecular beam technique in which he measured the response of the desorption flux to a step function change in the intensity of the incident molecular beam. At temperatures in the range 870–950 K surface lifetimes for Ga of between 1 and 10 sec were measured, with a desorption energy of ~ 2.5 eV. There were minor quantitative differences between (111) A and $(\bar{1}\bar{1}\bar{1})$ B faces. Below 750 K the sticking coefficient of Ga was unity. Measurable sticking of As_2 was only observed when excess Ga was present on the surface, produced either from a second beam, or, at temperatures > 775 K, from a process occurring on the substrate itself. For monolayer Ga coverage, the As_2 sticking coefficient was unity.

Cho [4,5] studied by RHEED the surface structures formed on $(\bar{1}\bar{1}\bar{1})$ B and (100) GaAs substrates during adsorption of Ga and As_2. He found that at least two structures formed on each substrate orientation, probably corresponding to the varying surface stoichiometry formed by differing amounts of adsorbed gallium and arsenic. In a more recent publication, Arthur [6] has also discussed surface structural changes resulting from gain or loss of As_2 from the surface. From experiments in which desorption rate and surface composition were correlated, a model was proposed which assumes that As_2 is adsorbed into a weakly bound molecular precursor state, from which dissociation into atoms occupying arsenic surface sites occurs. The recombination–desorption process, from surface As atoms to desorbed As_2 molecules, occurs with decreasing activation energy as the As surface concentration increases.

Foxon et al. [7] have reported some preliminary results on the interaction of Ga and As_4 beams with {100} GaAs surfaces, using the transform analysis of modulated molecular beam measurements. That paper was basically concerned with the technique and the kinetic results were only presented to illustrate the application to a real system. The present paper, therefore, describes a comprehensive set of measurements based on the same transform analysis technique, from which surface kinetic parameters for the Ga–As_4–GaAs {100} system have been evaluated. Possible reaction mechanisms are then considered.

2. Experimental

The UHV system, together with the apparatus and techniques used for beam formation, detection, data acquisition, signal processing and surface analysis have all been described previously [7]. The only modification is that ion counting techniques have been employed for much of the present work, rather than using analogue to digital conversion of the current from the electron multiplier of the mass spectrometer. Base pressures of 5×10^{-11} torr were obtained after bakeout and a typical operating pressure, with beams on, was ~ 10^{-9} torr.

The substrates used were GaAs bars, 20 mm x 5 mm x 1 mm thick, oriented such that the widest face was {100}. They were bromine-methanol polished, and then autoepitaxial layers ~ 10 μm thick were grown on them in a conventional chemical vapour deposition system. The layers were n-type S-doped, with a free carrier concentration of ~5×10^{15} cm^{-3}. Examination by Auger electron spectroscopy before in-situ cleaning showed sub-monolayer coverages of oxygen and carbon. Heat treatment at ~850 K (i.e. well within the congruent evaporation region [8]) for a few minutes at a pressure of ~5 x 10^{-10} torr resulted in the removal of oxygen to below the detection limit (~0.01 monolayer), and although traces of carbon were still present, the coverage was less than ~0.1 monolayer. Substrate temperatures were measured with a thermocouple placed through a hole drilled ultrasonically in the centre of the narrow face of the bar.

The gallium and arsenic were both obtained from Mining and Chemical Products Ltd., the former having a stated purity of 99.9999%, and the latter 99.999%.

Measurements were made of accommodation coefficients, surface lifetimes, sticking coefficients and where appropriate reaction orders, for beams of Ga and As_4 impinging both separately and simultaneously on {100} GaAs surfaces. The techniques for these measurements have all been described previously in some detail [7].

3. Results

For convenience of presentation the results will be discussed according to the behaviour observed in three distinct substrate temperature regions: 300–450 K, 450–600 K, and 600–900 K.

3.1. The region 300–450 K

The thermal accommodation coefficient of As_4 in this temperature region was determined by modulation of the desorption flux of As_4 from a GaAs surface on which an As_4 beam was impinging. The range of modulation frequencies used was between 20 Hz and 100 Hz, and two approaches were used. Firstly it was found that variation of the effective temperature of the impinging beam by ~100 K did not measurably affect the mean flight time of desorbed molecules. Secondly, by variation of the substrate temperature over the whole 300K–450 K range it was found that the temperature dependence of the flight time was consistent with a thermal accommodation coefficient of unity. The details of the analytical technique used have already been reported [7]. The absolute accuracy of the time of flight measurements was limited, however, to ± 10%, so that small variations from unity of the thermal accommodation coefficient would not have been detected. Measurements were then made of the surface lifetime of As_4 as a function of substrate surface temperature, by modulation of the incident flux. The effect of a surface population of Ga on the As_4 surface lifetime was also investigated, under conditions of both a fixed initial Ga surface concentration and a simultaneously impinging beam of Ga. Lifetimes were determined from measurement of phase shift and also of the frequency dependent attenuation. The results are summarised in fig. 1. In the absence of a surface population of Ga, the surface lifetime, τ, of As_4 in this temperature region varies between 5×10^{-3} and 10^{-4} sec, with an activation energy of desorption, E_D, of 0.38 ± 0.03 eV, determined using eq. (1)

$$\tau = \tau_0 \exp (E_D/kT) \qquad (1)$$

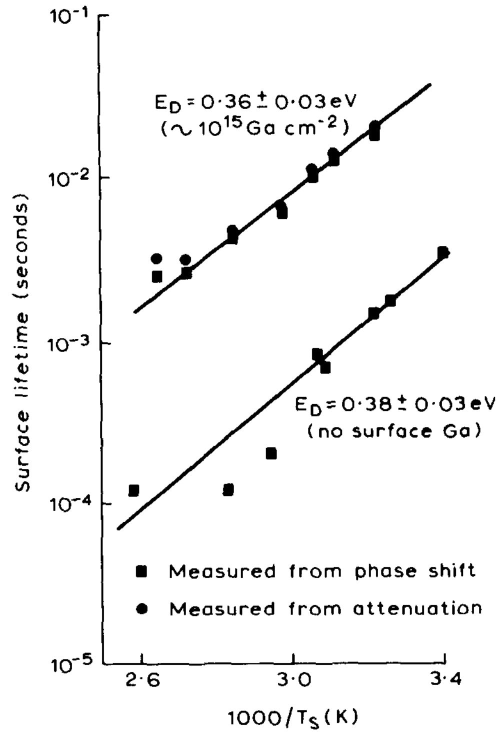

Fig. 1. Surface lifetime of As_4 on {100} GaAs surfaces, with and without excess Ga, as a function of temperature.

When the substrate is exposed to a Ga flux prior to the impingement of the As_4 beam, so that a specific concentration of Ga atoms is obtained on the surface, the surface lifetime of As_4 is increased considerably at all temperatures, but the activation energy for desorption remains the same as for a surface on which there is no excess Ga. The upper line in fig. 1 shows the result for the pre-deposition of 10^{15} Ga atoms cm^{-2}, corresponding to ~ 1 monolayer, but since the distribution of Ga was not known, the real coverage was also unknown. The pre-exponential factors for the gallium free and gallium populated surfaces are 9.0×10^{-10} seconds and 1.6×10^{-8} sec respectively.

By varying the amplitude of the modulated beam over quite a wide range ($\sim 10^{11} - 10^{13}$ molecules cm^{-2} sec^{-1}) and carrying out an harmonic contact analysis of the signal produced by the desorbed As_4, it was found that the system response was completely linear, i.e. there was $< 2\%$ of even harmonics present. The desorption process was therefore first order.

When beams of Ga and As_4 were impinged simultaneously, it was possible to measure surface lifetimes of As_4 having the same range of values as indicated in fig. 1. It was not possible, however, to obtain reproducible results at any one substrate temperature, because the duration of any preceding exposures to Ga influenced the absolute value of the surface lifetime. Since from the fixed Ga adatom population experiment the lifetime is known to be a function of the Ga surface concentration, and possibly also of its distribution, it seems most likely that one or both of these could have varied significantly during the experiment. Consequently, no quantitative data was obtained on the relationship between Ga beam flux and As_4 surface lifetime. It is simply known that higher surface concentrations of Ga result in longer As_4 lifetimes.

In the absence of a Ga adatom population, there was no measurable sticking coefficient of As_4 on {100} oriented GaAs substrates, i.e. there was no frequency independent attenuation of the signal from desorbed As_4. Previous observations [1,2] that the sticking coefficient of Ga in this temperature range was unity and independent of surface composition were also confirmed. When a modulated As_4 beam and an unmodulated Ga beam impinged simultaneously on a substrate, a temperature dependent sticking coefficient of As_4 (S_{As_4}) was measured, approaching unity at the lower temperatures, as shown in fig. 2. The rather large (maximum 15%) uncertainty indicated in the values of S_{As_4} occurs for the same reason as in the surface lifetime experiments; i.e. possible variations in the Ga adatom population and distribution. Nevertheless, S_{As_4} is clearly temperature dependent, with a value under these conditions which is always > 0.5, and the desorption process was linear with respect to the incident As_4 flux over the range investigated. (10^{12}–10^{13} molecules cm^{-2} sec^{-1}).

In order to determine if any dissociative adsorption–desorption of As_4 was occurring, unmodulated Ga and As_4 beams were impinged on the surface, and the flux leaving the surface was modulated. As_4^+, As_2^+ and As^+ signals were all detected, but As_2^+ and As^+ both appear in the normal fragmentation pattern of As_4, and it was

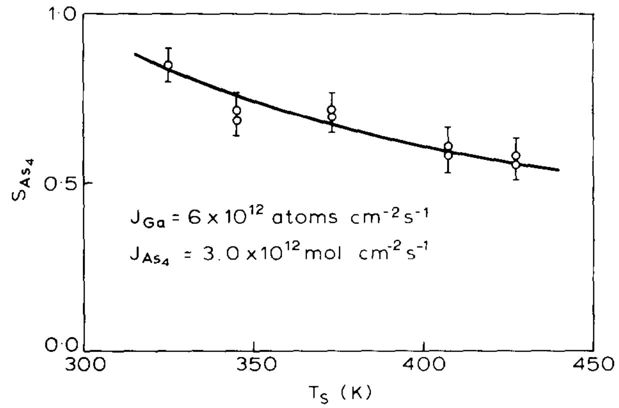

Fig. 2. Sticking coefficient of As_4 on {100} GaAs in the presence of a Ga beam, as a function of temperature below 450 K.

therefore necessary to establish the source of As_2^+ and As^+. It was first found that

$$(I_{As_2^+}/I_{As_4^+})_{\text{flux on}} = (I_{As_2^+}/I_{As_4^+})_{\text{flux off}}, \tag{2a}$$

$$(I_{As^+}/I_{As_4^+})_{\text{flux on}} = (I_{As^+}/I_{As_4^+})_{\text{flux off}}, \tag{2b}$$

where the left hand sides represent the appropriate ion intensity ratios produced from the flux arriving at the surface, and the right hand sides the same ratios from the flux leaving. This equality strongly suggests that As_2^+ and As^+ in the desorbed flux are simply fragment ions from As_4. This was further substantiated by the observed independence of the right hand terms on substrate temperature over the whole range. Finally, by a direct determination of the time of flight of the species between the modulator and the ioniser of the mass spectrometer, which was found to be the same for all three, it was confirmed that the only desorbed molecule was As_4.

3.2. The region 450–600 K

Over this range S_{Ga} was always unity, in accordance with previous experiments [1,2] and the surface lifetime of As_4 was too short to measure, i.e. $< 5 \times 10^{-5}$ sec. In the absence of a surface concentration of Ga, S_{As_4} was zero, but by impinging an unmodulated Ga beam with the modulated As_4 beam the results shown in fig. 3 were obtained. From this it is clear that S_{As_4} assumes a finite value in the presence of a Ga beam, but that it is independent of temperature over the whole range. The direction of temperature change during the course of an experiment in which fluxes of

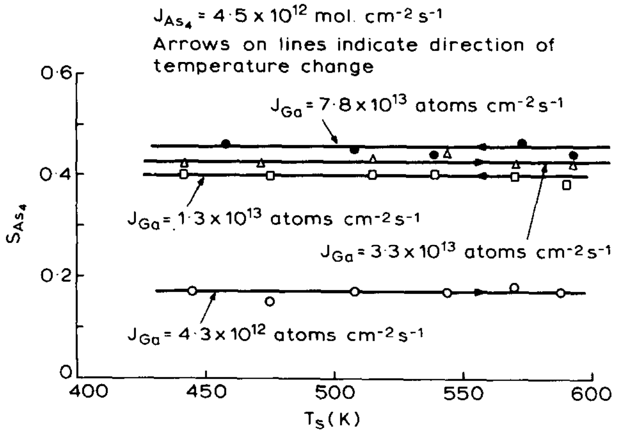

Fig. 3. Sticking coefficient of As_4 on {100} GaAs as a function of temperature between 450 K and 600 K for various Ga beam fluxes.

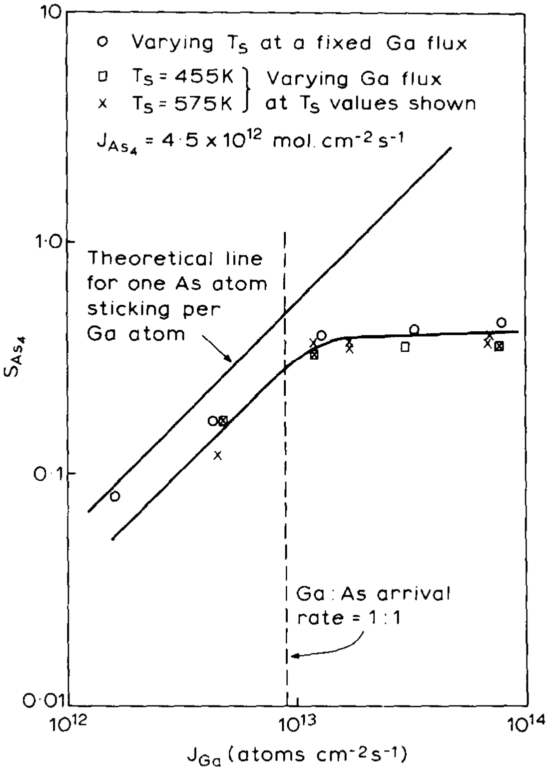

Fig. 4. Sticking coefficient of As_4 as a function of Ga beam flux in the temperature range 450–600 K.

As_4 and Ga were kept constant did not affect the results, and the reproducibility was also much better than in the lower temperature region.

Although S_{As_4} is temperature independent, fig. 3 also shows that there is a strong dependence on the flux of Ga atoms, J_{Ga}, to the surface. The results are plotted in fig. 4 to indicate the form of this dependence, together with additional data points obtained by varying the Ga flux at two fixed substrate temperatures (455 and 575 K), showing that the method of performing the experiment (i.e. varying either J_{Ga} or T_S) did not affect the result.

In addition to the temperature independence of S_{As_4}, three other factors emerging from these results need to be emphasised. The first is that under no conditions did S_{As_4} exceed 0.5, even when the Ga flux far exceeded the As_4 flux. This is to be contrasted to the behaviour below 450 K, where S_{As_4} tended to unity. Secondly, the experimental results should be compared with the theoretical line plotted, which corresponds to one As atom sticking for each Ga atom supplied. It is seen that up to a relative arrival rate of one for As : Ga, the measured and calculated lines are parallel, and can probably be considered to superimpose within the limits of experimental error: i.e. when there is an excess of arsenic, each gallium atom supplied consumes an arsenic atom. The As arrival rate is 9×10^{12} atoms cm^{-2} sec^{-1} because the beam was composed of As_4 molecules, and had an intensity of 4.5×10^{12} molecules cm^{-2} sec^{-1}, but the mark–space ratio of the modulated beam was 1 : 1. The third factor relates to the sticking behaviour of As_4 in the region where an excess of Ga is being supplied, and the sticking coefficient of As_4 is 0.5. When the Ga beam is stopped, S_{As_4} does not return to zero until an amount of As_4 sufficient to account for each Ga atom already on the surface has been supplied. Thus although these Ga atoms do not provide sites on which the initial sticking coefficient of As_4 can increase beyond 0.5, ultimately they are all consumed if an As_4 flux is maintained.

To obtain an indication of the reaction mechanism involved in the As_4 adsorption–desorption process, the order of the desorption reaction was determined with respect to the As_4 incident flux at a fixed Ga flux. The basis of the method has been described previously [7]; briefly, a fixed amplitude modulated As_4 beam is directed at the surface, together with a second, unmodulated As_4 beam, whose intensity is varied. The modulated flux is kept sufficiently small that the total system response is always linear. If $H_S(f_1)$ is the transfer function describing the surface process, and V is the desorption rate, then:

$$|H_S(f_1)| = \frac{(V + \Delta V) - V}{(J + \Delta J) - J}\,, \tag{3}$$

which in the limit of small perturbation becomes:

$$|H_S(f_1)| = \partial V/\partial J, \tag{4}$$

and therefore:

$$V = \int |H_S(f_1)|\, \mathrm{d}J. \tag{5}$$

The actual measurement therefore corresponds to the differential desorption rate.

The integral curve (desorption rate) of As_4, calculated from the measured derivative curve, is plotted in fig. 5 as a function of J_{As_4} for a fixed value of J_{Ga}. This shows that at low As_4 fluxes (with respect to the Ga flux), desorption is a second order process, becoming first order at higher relative fluxes, with an intermediate non-integral order. The substrate temperature for these measurements was 550 K. It is also apparent from the two upper curves of fig. 3, where $J_{Ga} > 4J_{As_4}$, that S_{As_4} has a finite but variable value for this condition, confirming that the desorption process cannot be first order at low relative As_4 fluxes. The integral points determined from them in fact correspond precisely to a second order curve.

Measurements were also made of $|H_S(f_1)|$ as a function of Ga flux for constant modulated and unmodulated As_4 fluxes, and substrate temperature. The results are shown in fig. 6.

The $|H_S(f_1)| = 1$ line corresponds to a zero sticking coefficient of the modulated

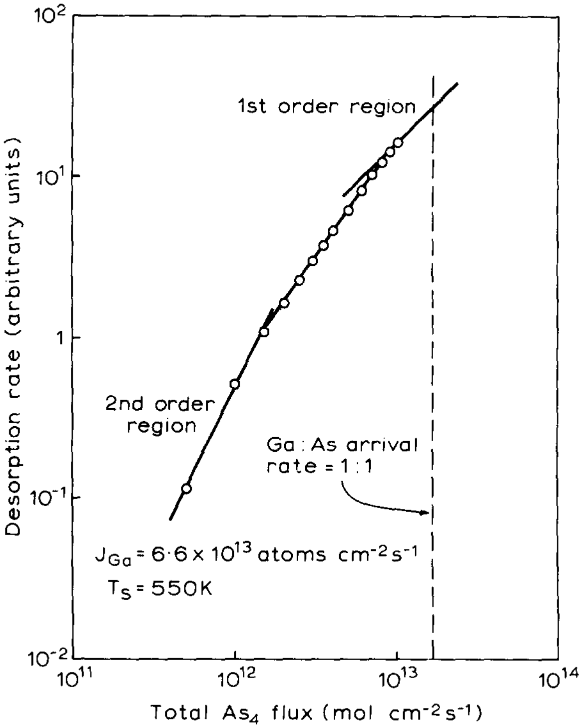

Fig. 5. Reaction order for As_4 desorption with respect to the As_4 flux to the surface of {100} GaAs in the presence of a constant Ga flux for a substrate temperature of 550 K.

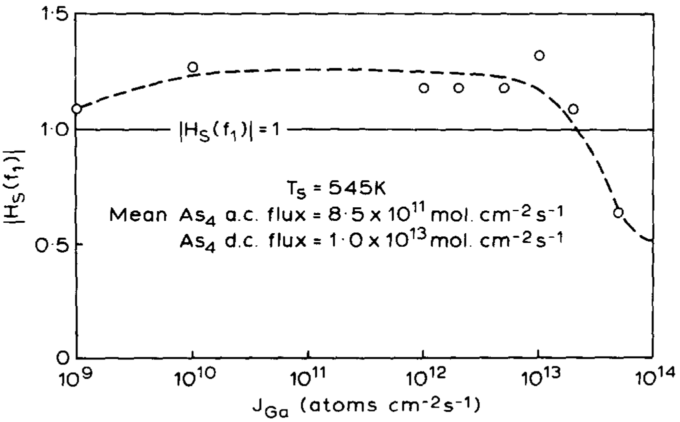

Fig. 6. $|H_S(f_1)|$, the transfer function describing the As_4 desorption process, as a function of the Ga flux to the {100} GaAs surface, for constant modulated and unmodulated As_4 fluxes at a substrate temperature of 545 K. For details see text.

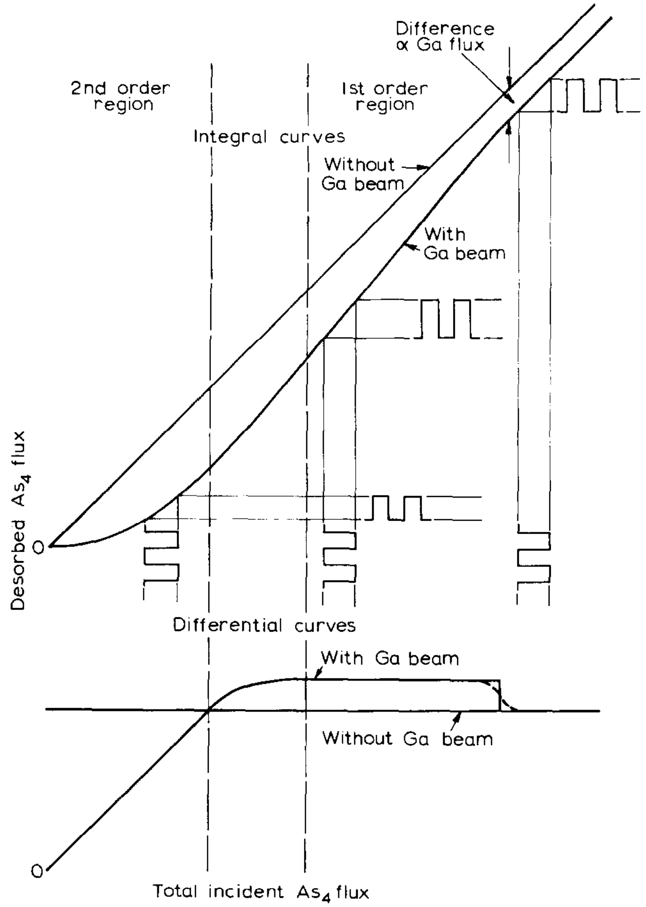

Fig. 7. Plots of differential and integral As_4 desorption fluxes as a function of total incident As_4 flux, illustrating the change from 2nd to 1st order kinetics, and the effect on the amplitude of the modulated desorbed flux with respect to the amplitude of the incident modulated flux.

As_4, and was defined by measurement of the transfer function in the absence of a Ga beam. Under these conditions it was shown to remain unity for a wide range of J_{As_4} values. The experimental observation that $|H_S(f_1)|$ can assume values greater than unity implies that in the presence of an unmodulated As_4 flux, a greater intensity of modulated material can leave the surface than arrives there. The explanation for the observed behaviour is illustrated schematically in fig. 7, which shows the differential and integral As_4 desorption fluxes as a function of the total As_4 incident flux, with and without a Ga beam. At low incident As_4 fluxes, desorption follows second order kinetics, but as the flux increases the slope of the integral curve becomes constant, i.e.

first order kinetics are obeyed, but the slope of the curve is greater than unity, corresponding, in the measured differential form, to an increase in the modulated desorbed flux with respect to the modulated incident flux, as illustrated for a rectangular pulse excitation. As the incident flux increases still further, the difference betwe incident and desorbed As_4 fluxes must become constant and proportional to the Ga flux supplied, i.e. the integral curve must become parallel to the curve for the integr total desorbed flux in the absence of Ga. In order for the curves to become parallel, a region must exist in which the slope of the integral desorbed flux curve exceeds that of the curve in the absence of Ga, and in this case it is in a region where first order kinetics are being obeyed. However, amplification of the modulated desorbed flux can only occur in a system where over some part of the incident flux range non linear kinetics are obeyed. Therefore, although amplification of the modulated signa is observed in a region where the desorption process is first order, this is a conseque of the basic non-linear kinetic behaviour of the overall system.

3.3. *The region 600–900 K*

Over this temperature range there is a measurable sticking coefficient for As_4 eve when there is no Ga flux to the surface. It is temperature dependent, S_{As_4} increasin with increasing temperature, and the value at any temperature is also dependent on the As_4 flux, but it never exceeds 0.5. The form of the temperature dependence for two values of J_{As_4} is shown in fig. 8. For a fixed substrate temperature S_{As_4} is time independent, as shown in fig. 9 for T_S = 733 K.

Determination of the order of the desorption process for As_4 with respect to the As_4 flux to the surface by the techniques described in section 3.2 indicated the sam type of behaviour as observed in the 450–600 K temperature region, although in th case no Ga was supplied from an external source. The results are illustrated in fig. 1 and show a change from second order desorption kinetics at low As_4 fluxes to first order at high fluxes, with an intermediate non-integral order.

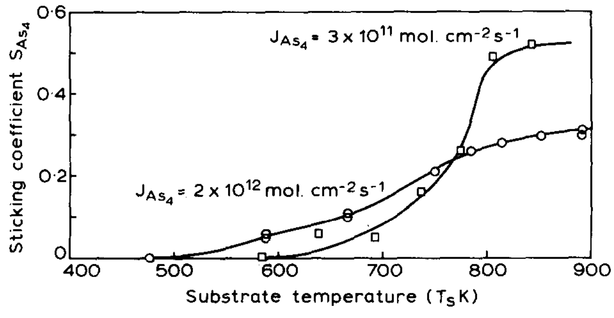

Fig. 8. Sticking coefficient of As_4 as a function of {100} GaAs substrate temperature > 600 K, in the absence of a Ga beam.

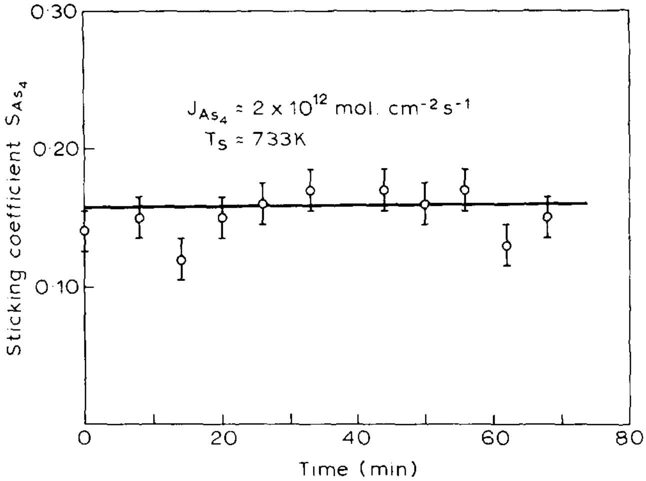

Fig. 9. Sticking coefficient of As_4 as a function of time on a {100} GaAs substrate at 733 K in the absence of a Ga beam.

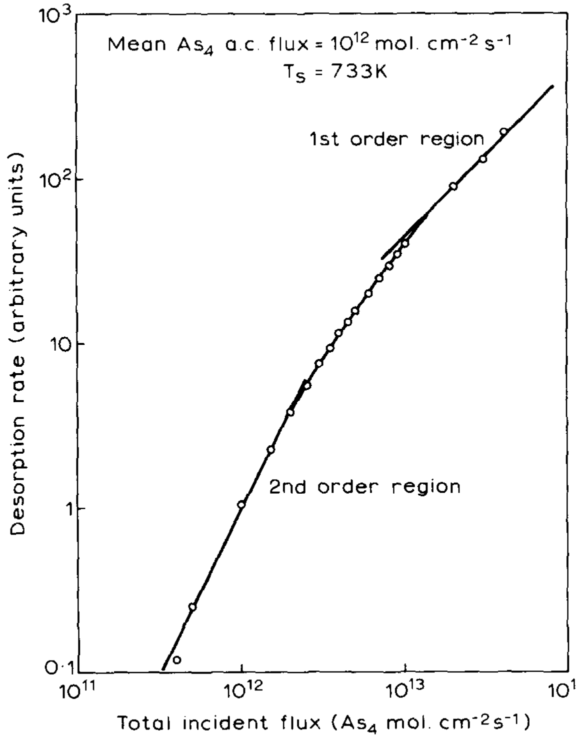

Fig. 10. Reaction order for As_4 desorption with respect to the As_4 flux to the surface of {100} GaAs in the absence of an external Ga flux for a substrate temperature of 733 K.

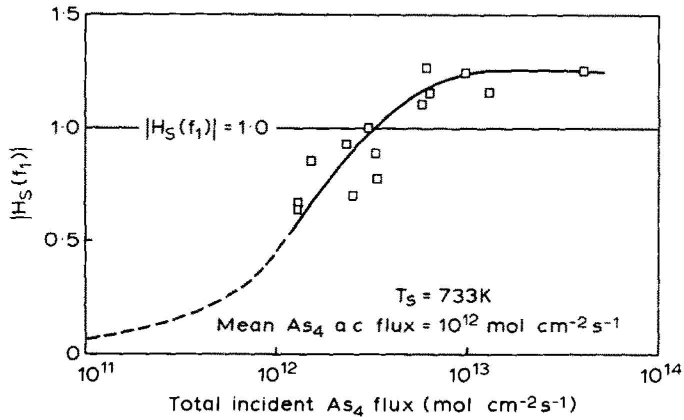

Fig. 11. $|H_S(f_1)|$ as a function of the total As_4 flux to the {100} GaAs surface in the absence of a Ga beam for substrate temperature of 733 K.

The increase of the modulated As_4 desorption signal with respect to the incident signal amplitude at high total As_4 fluxes, which was observed in the 450–600 K temperature region in the presence of an incident Ga beam, was also observed in this temperature region, but in the absence of any external supply of Ga. The result at $T_S = 733$ K is shown in fig. 11.

All of these results imply that in the temperature range 600–900 K there is a temperature dependent Ga adatom population, as suggested by Arthur [2], but the interaction with As_4 on GaAs surfaces is the same as at lower temperatures, where the Ga must then be supplied externally. The mechanism responsible for the formation of this Ga surface concentration cannot be determined unequivocally from the experiments described above. Two possibilities seem to exist, either (a) it resulted from the outdiffusion of Ga to the surface from the bulk, or (b) arsenic was being desorbed from the GaAs as As_2 [8], which creates Ga surface atoms, and the desorbed arsenic is replaced, under steady state conditions, by arsenic from the As_4 beam. The time independence of S_{As_4} lends support to the latter mechanism, and by modulation of the flux leaving the surface it was possible to identify precisely the species which were desorbing, as described previously.

It was found that $(I_{As_2^+}/I_{As_4^+})_{\text{flux on}}$ and $(I_{As^+}/I_{As_4^+})_{\text{flux off}}$ remained sensibly constant over the whole temperature range. [The symbols have the same meaning as in eqs. (2a) and (2b).] However, at temperatures > 600 K the equalities represented by those equations no longer hold, and values of $(I_{As_2^+}/I_{As_4^+})_{\text{flux off}}$ and $(I_{As^+}/I_{As_4^+})_{\text{flux off}}$ as a function of temperature are plotted in fig. 12. It is seen that there is a significant increase in the As_2^+ signal, and part of this As_2^+ signal was not therefore related to the As_4 fragmentation pattern. The As^+ signal arises as part of the fragmentation pattern of both As_4 and As_2; As does not leave the substrate surface as an independent species.

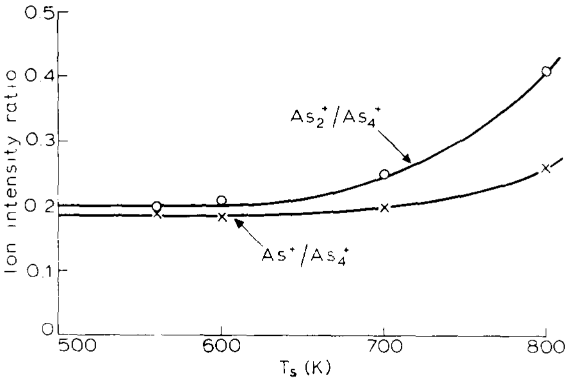

Fig. 12. Ion intensity ratios produced from the flux desorbing from a {100} GaAs surface as a function of temperature when there is an incident As_4 flux, but no incident Ga flux.

Finally, the effect on the As_4 sticking coefficient of an external Ga flux in this temperature region was investigated, and in general found to produce an increase. However, when S_{As_4} is already close to 0.5 in the absence of an external Ga flux, which is the case for high substrate temperatures and low As_4 fluxes, the Ga beam has little effect on S_{As_4}. Again, as in the 450–600 K temperature range, there is a region of relative flux intensities where every Ga atom supplied can consume an As atom, i.e, the relative sticking coefficient $S_{As}/S_{Ga} = 1$, but beyond a particular Ga flux at each temperature this falls below unity, and in this temperature range also, S_{As_4} never exceeds 0.5, irrespective of the surface concentration of Ga.

4. Discussion

In general terms the results indicate that there are two basically different mechanisms for the interaction of As_4 and Ga on GaAs surfaces, one below ~ 450 K, and one above. The behaviour in the low temperature region would seem to correspond to simple non-dissociative chemisorption of As_4 molecules onto Ga atoms on the surface of GaAs, via a precursor state. In the absence of surface Ga atoms only physisorption occurs. The evidence for this may be summarised as follows:

(i) All desorbed As_4 molecules have completely thermally accommodated with the surface, and there is a measurable surface lifetime with an activation energy for desorption (0.38 eV) which is commensurate with desorption from a weakly bound precursor state. In the presence of a Ga adatom population, where the sticking coefficient for As_4 becomes non-zero, the desorption energy obtained from lifetime measurements remains the same as when S_{As_4} is zero, only the pre-exponential factor changes. This implies that desorption always occurs from the same binding state.

(ii) All As_4 desorption processes follow first order kinetics.
(iii) The As_4 sticking coefficient in the presence of surface Ga atoms tends to unity, and increases with decreasing temperature.
(iv) Examination of desorbed species shows no evidence of dissociation.

The rate of chemisorption appears to be controlled by surface diffusion, in that an As_4 molecule only sticks (becomes chemisorbed) if during its lifetime on the surface in the precursor state it encounters a Ga atom. Now n, the number of sites visited during random motion on the surface, is given by Burton, Cabrera, and Frank [9] as

$$n = \exp (E_\mathrm{D} - E_\lambda)/kT, \tag{6}$$

where E_λ is the activation energy for surface diffusion. Thus provided that $E_\mathrm{D} > E_\lambda$, which is the usual situation, the higher the substrate temperature the fewer the number of sites visited, leading to the observed decrease in S_{As_4} with increasing temperature.

Adopting the formalism of Ehrlich [10] for the precursor state model for chemisorption gives

$$S_{\mathrm{As}_4} = 1 - k_1/(k_1 + k_2), \tag{7}$$

where k_1 is the rate of desorption of physisorbed As_4 and k_2 is the rate constant for chemisorption. This equation is perfectly general, and makes no assumptions about the rate limiting step in chemisorption. For diffusion controlled kinetics, which must be considered if every atom site does not constitute an adsorption site, and that is clearly the case here, where the "sites" (Ga atoms) are being supplied at the same time as the adsorbate, Ehrlich [10] has shown that

$$\frac{\partial \ln [S_{\mathrm{As}_4}/(1 - S_{\mathrm{As}_4})]}{\partial (1/kT)} = (E_\mathrm{D} - E_\lambda)\left(1 - \frac{S_{\mathrm{As}_4}}{2} + \frac{S^2_{\mathrm{As}_4}}{3} - \ldots\right). \tag{8}$$

In fig. 13 log $[S/(1 - S)]$ is plotted as a function of $1/T$, producing a good straight line, and assuming the validity of eq. (8), the value of $E_\mathrm{D} - E_\lambda$ obtained from it is 0.14 eV. Since E_D has been determined to be ~ 0.38 eV, E_λ ~ 0.24 eV, which seems a reasonable value. Although a surface diffusion rate limitation is not proven the results are at least consistent with it.

It must also be emphasised that in this temperature region GaAs is not formed, since the adsorption is non-dissociative.

Turning now to the higher temperature regions, the apparent differences above and below ~ 600 K can simply be accounted for by the formation of an intrinsic surface population of Ga atoms at temperatures in excess of 600 K, in addition to any supplied from an external source. Apart from this factor the As_4–Ga–{100} GaAs surface interaction chemistry is the same over the whole temperature range from 450 to 900 K.

The Ga surface population at the higher temperatures is created by the desorption of As_2 from the outermost layer of GaAs, and if As_4 is being supplied to the surface

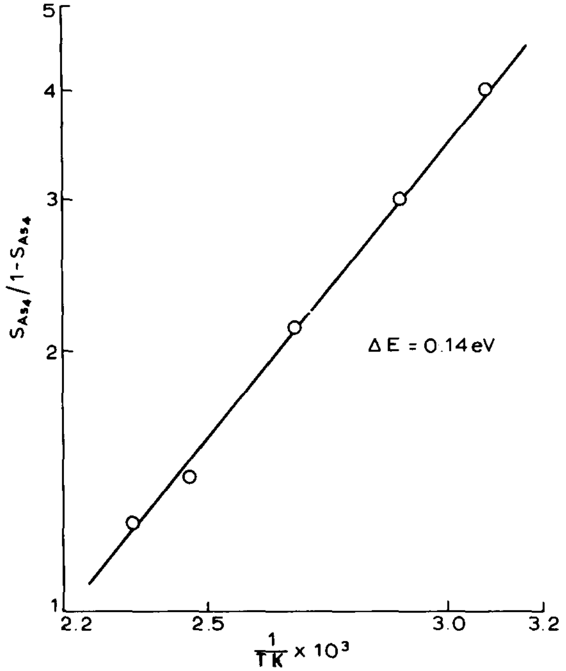

Fig. 13. $S_{As_4}/(1 - S_{As_4})$ as a function of reciprocal temperature for the {100} GaAs substrate temperature region 300–450 K, in the presence of a constant Ga flux to the surface. ΔE = 0.14 eV.

a steady-state desorption-replacement situation is set up. This maintains the non-thermally stable surface discussed by Cho [5], but in the absence of a supply of As_4, a "gallium stabilised" surface is produced, which is then stable.

The final stage is to attempt to deduce a mechanism for the interaction of As_4 and Ga on {100} GaAs surfaces at temperatures > 450 K from the kinetic results presented in section 3. In constructing any model several important factors must be taken into account:

(i) The sticking coefficient of As_4 is always < 0.5, irrespective of the Ga flux, and As_4 adsorption is non-activated ($S_{As_4} \neq f(T)$).

(ii) When there is an excess of arsenic, each Ga atom supplied consumes one As atom.

(iii) Any Ga supplied which is in excess of that producing the maximum value of 0.5 for S_{As_4} is eventually consumed if an As_4 beam is maintained after the Ga beam is turned off.

(iv) The order of the desorption process with respect to As_4 changes from second at low As_4 coverages (relative to the Ga coverage) to first at high coverages.

(v) There is no measurable desorption of As_2 (or any species other than As_4) below 600 K.

Tha fact that there is a region where desorption kinetics are second order and that S_{As_4} never exceeds 0.5 implies that chemisorption must be dissociative, with a pairwise, rather than a single As_4 molecule interaction with Ga sites. This is substantiated by the absence of species other than As_4 in the desorbed flux, until the GaAs substrate surface begins to dissociate, i.e. a single molecule cannot of itself dissociate. The hysteresis effect, whereby all Ga supplied is eventually consumed if an arsenic supply if maintained, suggests that only specific Ga atoms can act as adsorption sites, and it is postulated that these are actually GaAs lattice sites.

It is suggested, therefore, that starting from the same precursor state as in the low temperature region, chemisorption at these higher temperatures becomes dissociative, involving interaction between a pair of As_4 molecules adsorbed on adjacent Ga atoms. This would account for the maximum value for S_{As_4} of 0.5, and the second order kinetics is in accord with a pairwise interaction, when the As_4 precursor state population is small compared with the number of Ga sites, so that the desorption rate limitation is imposed by the encounter/reaction probability of pairs of As_4 molecules. When the As_4 population is high, the desorption rate becomes proportional to the number of molecules being supplied to the surface – i.e. a first order process.

Thus at all temperatures > 450 K it is possible to prepare GaAs from beams of As_4 and Ga, but above 600 K the steady state replacement of As_2 being lost from the arsenic stabilised GaAs surface must be considered in relation to the total Ga adatom population.

Acknowledgements

This work has been carried out with the partial support of Procurement Executive, Ministry of Defence, to whom thanks are due.

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