Surface Science 64 (1977) 293–304
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INTERACTION KINETICS OF As_2 AND Ga ON {100} GaAs SURFACES

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Received 12 October 1976; manuscript received in final form 10 December 1976

A modulated molecular beam technique, using mass spectrometric detection of desorbed species, has been applied to a study of the kinetics of Ga and As_2 interactions on {100} GaAs surfaces. In the temperature range 300–600 K a surface association reaction occurs, leading to the desorption of As_4 by a first order process. Above 600 K, As_2 is lost from the substrate itself by a dissociation reaction, which gives rise to a temperature dependent Ga adatom population, and this in turn results in a temperature dependent As_2 sticking coefficient which can reach unity.

1. Introduction

As a result of the application of the technique of molecular beam epitaxy [1] to the growth of thin films of III–V compounds, a considerable effort has been directed towards understanding those surface processes which are involved in film formation. Almost all of the early work was due to Arthur, who first showed by field emission microscopy [2] that gallium could migrate at quite low temperatures (~525 K) on {111} GaAs surfaces, and that arsenic from an As_4 beam was mobile down to 77 K, desorbing rapidly at 525 K. In subsequent investigations using a pulsed molecular beam technique [3,4] he measured surface lifetimes of Ga on {111} GaAs of between 1 and 10 s in the temperature range 870–950 K, corresponding to a desorption energy of ~2.5 eV. Below 750 K the sticking coefficient of Ga was always unity, but for As_2 (produced from a Knudsen source containing GaAs rather than elemental arsenic) the sticking coefficient was zero unless Ga atoms were present on the surface. The Ga surface population could be produced either from a Ga beam incident on the substrate, or, at temperatures >775 K, from the substrate itself as the result of desorption of As_2. In a more recent publication [5] Arthur has further investigated this aspect of surface stoichiometry by augmenting the pulsed beam technique with temperature programmed thermal desorption measurements, and by correlating desorption rates with surface composition he was able to propose a model whereby As_2 is adsorbed into a weakly bound molecular precursor state, from which dissociation into atoms occupying arsenic surface sites can occur. The recombination–desorption process, from surface As atoms to As_2 molecules in the vapour phase takes place with decreasing activation energy as the arsenic surface concentration increases.

Structural studies by Cho [6,7] and Chang et al. [8] principally using RHEED, have demonstrated that several surface structures can exist on both $(\bar{1}\bar{1}\bar{1})$B and {100} GaAs substrates, the particular structure obtained being a function of temperature and the arsenic to gallium flux ratio. The different structures probably correspond to changes in surface composition, and to some extent this effect is also apparent in Auger electron spectra of GaAs surfaces [5]. The surface composition is usually defined as being "As-stabilized" or "Ga-stabilized" according to whether the lattice is terminated by As or Ga atoms respectively.

The present authors have investigated the interaction of Ga and As_4 on {100} substrates in some detail [9], using a transform analysis of modulated molecular beam measurements [10]. It was found that at temperatures from 300–450 K As_4 has a measurable residence time on GaAs ($\sim 10^{-3}-10^{-5}$ s), with a desorption energy of ~0.38 eV and an activation energy for surface diffusion of 0.24 eV. When a Ga adatom population is available, non-dissociative chemisorption occurs by transfer from this weakly bound precursor state, with a temperature dependent sticking coefficient which tends to unity at the lower temperatures. Above 450 K, chemisorption is dissociative, again occurring only in the presence of a Ga surface population, but the sticking coefficient is always $\lesssim 0.5$, dissociation occurring by pairwise interaction of As_4 molecules. Above 600 K As_2 is lost from the substrate surface by dissociation of GaAs, but this can be replaced by interaction of incident As_4 molecules with the Ga surface atoms so formed. Within the experimental accuracy of this work it was also reported that incident As_4 molecules are completely thermally accommodated on the GaAs substrate during their lifetime in the precursor state, but Arthur and Brown [11] have recently published the results of a direct determination of the velocity distribution of desorbing As_2 and As_4 molecules by time-of-flight measurements, and it was shown that their translational energy is apparently lower than that corresponding to the substrate temperature, the kinetic energy deficit being carried in internal modes. However, the time-of-flight measurements depended on the assumption that the mass spectrometer acted as an ideal density detector, and it has recently been shown (12) that this assumption can be erroneous.

In this paper we report the results of an investigation of the interaction of As_2 and Ga on and with a {100} oriented GaAs substrate, again using a transform analysis of modulated molecular beam measurements. In these new experiments particular attention has been paid to the identification of desorbing species by modulating the flux leaving the substrate and comparing the results with those obtained when the incident flux is modulated.

2. Experimental

The basic system, together with the apparatus and techniques used for beam formation, deteection data acquisition, signal processing and surface analysis have all been described previously [9,10], but fig. 1 shows the arrangement used for the particular experiments described in this paper. The important changes are the incorporation of two modulators, so that either the incident or the desorbed flux can be modulated without altering the sample environment, and the inclusion of a separate molecular beam source in line with the mass spectrometer so that a signal level from a direct beam of known intensity can be established and used to calibrate the signal produced after surface scattering. To carry out the calibration, the substrate is moved out of this direct beam, which can then also be modulated if required. In addition to these modifications, the RFA Auger spectrometer was replaced by a CMA. Base pressure after bakeout was $\sim 5 \times 10^{-11}$ Torr, and the operating pressure, with beams on, was $\sim 10^{-9}$ Torr.

The substrates used were GaAs bars, 20 mm × 5 mm × 1 mm thick, oriented such that the widest face was {100}. To produce clean surfaces (as determined by AES), epitaxial films ~1 μm thick were grown on the substrates from beams of Ga and As_4. The only contaminant then identified was carbon in trace quantities on some surfaces. Substrate temperatures were measured with a thermocouple inserted through a hole drilled ultrasonically in the centre of the narrow face of the bar.

Beams were produced from Knudsen cells containing Ga and GaAs, both obtained from Mining and Chemical Products Ltd., and of semiconductor grade purity. By using a Knudsen source containing GaAs, rather than elemental arsenic, the direct flux contains arsenic only as the dimer, As_2, there is no As_4 present. In addition there is also a flux of Ga from the source, which can be up 20% of the As_2 flux,

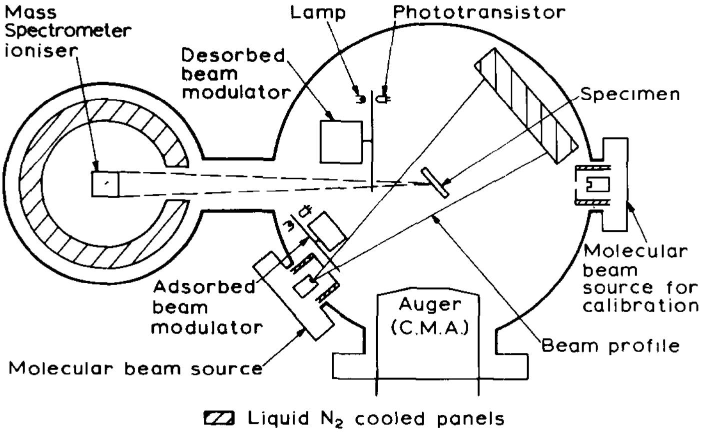

Fig. 1. Experimental arrangement, schematic.

depending on the source temperature used. This imposes a limitation that As_2 interaction in the complete absence of a surface Ga population cannot be studied.

The basic techniques used were the same as for the As_4 work [9,10], but where special circumstances dictated an operating modification, the procedure used will be described.

3. Results and qualitative interpretation

The first series of experiments was concerned with determining the nature and relative intensities of species desorbing from the {100} oriented GaAs substrate as a function of its temperature, for an incident As_2 flux, but without a separate Ga beam. The measurements were made by examining the response of the mass spectrometer while modulating the desorption flux, with an unmodulated As_2 incident intensity of 10^{13} molecules cm^{-2} s^{-1}. The results are illustrated in fig. 2, the most important feature being that below ~600 K an association reaction occurs, with the formation of As_4. There is a consequent decrease in the desorption rate of As_2 below 600 K, while at higher temperatures it remains constant. The decrease in the As_4 desorption rate below ~450 K is probably associated with the non-dissociative chemisorption of As_4, which is formed on the surface, on to those Ga atoms

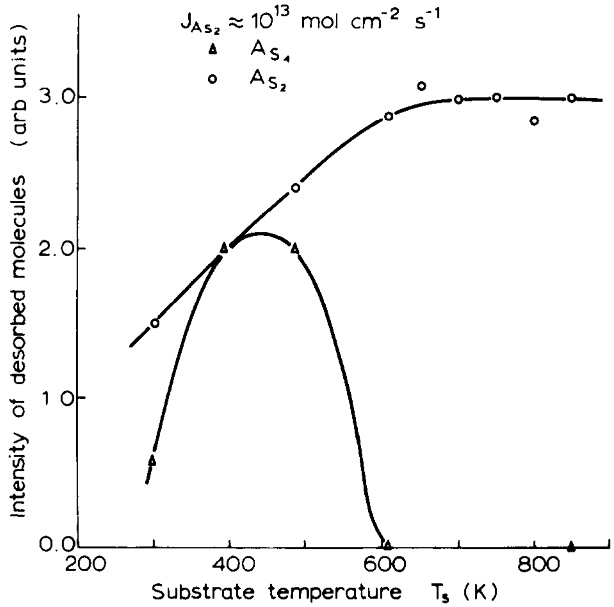

Fig. 2. Relative desorption rates of As_2 and As_4 for an incident As_2 flux as a function of substrate temperature.

which arrive with the incident As_2 beam. This type of chemisorption is precisely the same as that observed [9] when beams of As_4 and Ga are directly incident in this temperature region, with the As_4 sticking coefficient approaching unity at ~300 K if there is a sufficiently high Ga adatom population.

The absence of any As_4 desorption flux above 600 K probably implies that there is no association reaction above this temperature, since it is known [9] that the sticking coefficient for $As_4 \leq 0.5$, and that it does not dissociate to give As_2. Thus if any As_4 were formed on the surface, some would appear in the desorption flux.

The association reaction was investigated in more detail at a substrate temperature close to that corresponding to the maximum observed desorption rate for As_4 (485 K). The As_4 desorption rate was measured as a function of the incident As_2 flux, from which the order of the process was found to be unity for a wide range of incident fluxes, as shown in fig. 3. This implies that the rate limiting step in the association reaction is not the surface diffusion of pairs of As_2 molecules to adjacent sites since this would be a second order process, but rather that the actual associative interaction, or the desorption step itself must be rate controlling. This result was confirmed by determination of the As_4 surface lifetime, the measurement being made by modulation of the incident As_2 flux. It was found that even for modulation frequencies down to 0.5 Hz, the desorbing As_4 produced a signal which was effectively demodulated, which means that the surface lifetime of As_4, or more correctly the time constant for its formation plus desorption, was ≥ 1 s. Correspondingly the surface lifetime of As_2 was too short to measure ($< 10^{-4}$ s). Since the surface lifetime of As_4 present as such on the surface is known to be quite

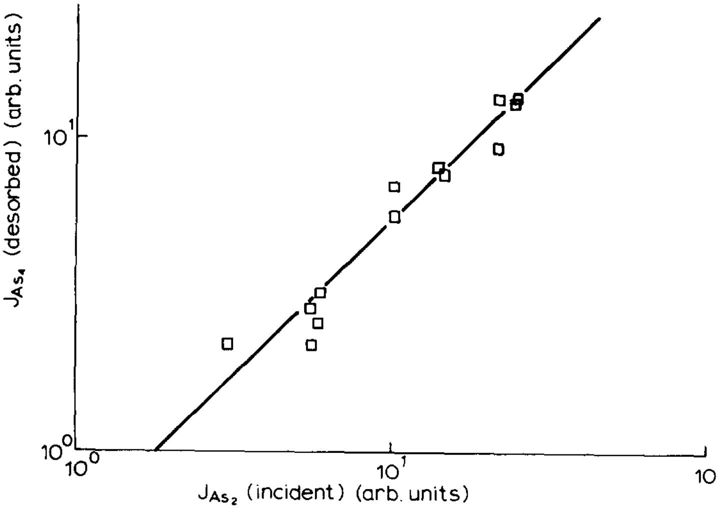

Fig. 3. Order of the association reaction of As_2 to As_4 on a {100} GaAs surface, J_{As_2} varied from 3×10^{12} molecules cm^{-2} s^{-1} to 4×10^{13} molecules cm^{-2} s^{-1}.

short at 485 K [9], some other slow step prior to desorption must be envisaged. This could involve surface rearrangement and diffusion of As_4, or alternatively a long-lived surface intermediate may occur.

Having estabished that no As_4 was desorbed above 600 K, the interaction of an As_2 beam with the GaAs surface in the absence of a separate Ga beam was investigated more quantitatively over the substrate temperature range 600–900 K. Experiments were performed in which either the incident flux or the desorption flux was modulated, and the results are summarised in fig. 4. Modulation of the desorption flux shows that when an As_2 beam is incident, the total As_2 flux from the surface is independent of temperature in the range 600–900 K. If the incident flux is modulated however, the amplitude of the correlated response decreases with increasing temperature, from which the temperature dependent sticking coefficient of As_2 can be calculated, and this is also shown in fig. 4. It is clear that it tends to unity, which may be compared to the limiting value of 0.5 observed for As_4 in the same temperature region. By harmonic content analysis of the signal it was established that all processes were linear.

By comparing these results with those obtained for As_4 in the same temperature range, a rather simple explanation can be proposed. As the temperature of the substrate is increased, an increasing Ga adatom population is formed by loss of As_2

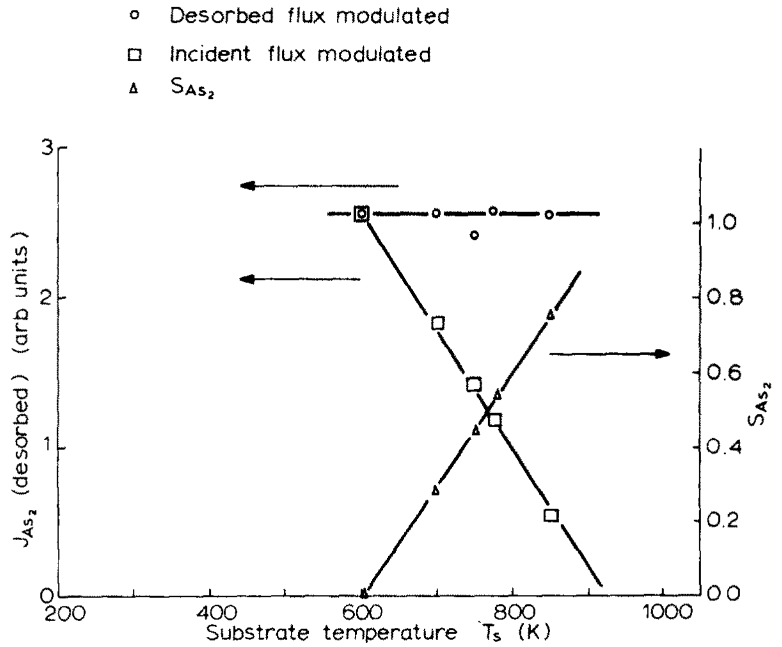

Fig. 4. Desorption flux and sticking coefficient of As_2 on {100} GaAs as a function of substrate temperature; no separate Ga flux. $J_{As_2} = 1 \times 10^{13}$ molecules cm^{-2} s^{-1}.

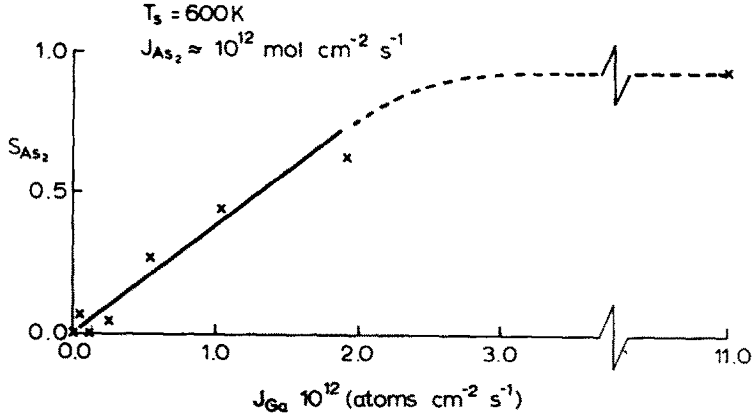

Fig. 5. Sticking coefficient of As_2 on a {100} GaAs surface at 600 K as a function of the Ga flux.

from the surface. This As_2 is replaced by the incident flux, leading to a temperature dependent As_2 sticking coefficient, as measured with respect to the incident flux. The total desorption flux is then composed of two parts, i.e. the evaporation flux from the GaAs, plus the fraction of the incident beam which desorbs. The sum of these two parts is a constant, independent of temperature (in the 600 K–900 K range), and the steady state surface composition is consequently also maintained constant with time, provided the incident flux intensity is high enough to compensate for the evaporation flux. In general, the specific surface composition is a function of both temperature and incident As_2 flux.

The behaviour at 600 K, where the detected As_2 flux intensities for both incident and desorption flux modulation are the same, represents an important check of surface reproducibility. The measured fluxes are only equal if there is not an excess surface Ga population, so in practice, all experiments are preceded by a check that at a substrate temperature of 600 K the measured desorption flux is the same whether the incident or desorption flux is modulated, and all results may be referred to this surface condition.

The sticking coefficient of As_2 was also measured at a substrate temperature of 600 K in the prsence of an incident flux of Ga. As explained above, both the association reaction and the rate of formation of a Ga adatom population by evaporation of As_2 are negligible at this temperature, and this therefore corresponds to the least complex interaction behaviour. The results are shown in fig. 5, the important point being that S_{As_2} tends to unity, compared to the asymptotic value of 0.5 for As_4 under similar conditions [9]. For comparatively low Ga fluxes, S_{As_2} is also directly proportional to the Ga flux, and within experimental accuracy each Ga atom supplied interacts with one As atom (for low Ga fluxed). At higher fluxes, the excess Ga probably accumulates on the surface.

4. Discussion and process modelling

It is interesting to compare the results described in the previous section before further analysis, with those reported by Arthur [3–5]. Firstly there is agreement that in the presence of an adequate Ga adatom population (i.e. approaching a monolayer), the sticking coefficient of As_2 tends to unity. Arthur also found a temperature dependent As_2 sticking coefficient at the higher temperatures as a surface population of Ga was formed; there is a considerable quantitative difference however, in that he found this effect commencing at ~775 K, compared to ~600 K determined in this work. This probably only represents different levels of detection sensitivity and accuracy of temperature measurement, however, and is not of fundamental significance.

Of greater importance, from both the theoretical and practical aspects, is the association reaction to form As_4 on the substrate surface below 600 K, which Arthur mentioned [3] but did not take account of in his kinetic model [5].

Failure to do so would lead to the measurement of an As_2 sticking coefficient which was too high, and the mass balance equation must contain a term which incorporates this effect. Qualitatively, the overall mechnism can be summarized as follows:

As_2 is adsorbed, possibly dissociatively from a physisorbed precursor state, onto {100} GaAs surfaces provided surface Ga atoms are present; if not, the sticking coefficient is zero. Below ~600 K there is a competing association reaction, leading to the desorption of As_4 by a first order process, while above 600 K desorption of As_2 from the substrate provides a Ga adatom population, but As_2 molecules which are lost can be replaced on a one-for-one basis by incident As_2 molecules. The time constant for the formation plus desorption of As_4 is very long (>1 s), while the surface lifetime of As_2 in the absence of a Ga surface population is very short ($<10^{-4}$ s).

Having proposed this qualitative description, the next stage is to attempt to model the reaction sequence so that we can predict the phase and amplitude behaviour of the measured signal in terms of surface processes. It will be convenient to treat separately the reaction sequences above and below 600 K. Consider first the high temperature case, where the experimental result is an attenuation of the As_2 signal with respect to a modulated incident As_2 flux, independent of frequency over a wide range. The basic reaction steps can be represented by eqs. (1):

$$\begin{tikzcd} {} \arrow[r, "J_{As_2}"] & As_2(p) \arrow[rr, "\overset{+\text{ Ga atom pair}}{k_2}"] \arrow[d, "k_1"] & & (As + As)(c) \\ & As_2(v) & & {} \arrow[ll, "k_3"'] \end{tikzcd} \qquad (1)$$

The nomenclature used in these equations is as follows: J_{As_2} is the incident As_2

flux, (p) represents a precursor state on the surface, (c) a chemisorbed state and (v) a vapour phase state. The terms k_i are rate constants for the various reactions. If we refer to coverages in the As_2 (p) state as θ_p and the As chemisorbed state As(c), i.e. with respect to As atoms, as θ_c, we can write the following mass balence equations:

$$\frac{d\theta_p}{dt} = \frac{J_{As_2}}{n_a}(1-\theta_p) - k_1\theta_p - k_2\theta_p(1-\theta_c)^2 + \tfrac{1}{2}k_3(1-\theta_p)\theta_c^2\,, \tag{2}$$

and

$$\frac{d\theta_c}{dt} = -\frac{J_{Ga}}{n_a} + 2k_2\theta_p(1-\theta_c)^2 - k_3(1-\theta_p)\theta_c^2\,, \tag{3}$$

where J_{Ga} is the external Ga flux to the surface, and n_a is the number of available surface sites per unit area. For ease of manipulation, the normalized fluxes (J_{i/n_a}) will be written as J'_i. Two other simplifying assumptions can be made. Firstly, because the lifetime, τ, of As_2 in the precursor state is very short, $\theta_p = J'_{As_2}\tau \ll 1$, and therefore $(1-\theta_p) \approx 1$. Secondly, we will assume that because single crystal GaAs is being produced by dissociation of As_2 molecules on Ga atoms in the {100} GaAs surface, following dissociation the As atoms do not occupy random sites, but there is in fact a pair correlation, with each As atom of the As_2 molecule being bonded to the same Ga atom, thus maintaining the correct surface structure. With this assumption, squared terms in θ_c and $(1-\theta_c)$ become first order. Under steady state conditions, the right hand sides of eqs. (2) and (3) can be equated to zero, and incorporating the above simplifications this gives:

$$k_1\theta_p = J'_{As_2} - \tfrac{1}{2}J'_{Ga}\,, \tag{4}$$

i.e. the desorption rate of As_2 is simply the difference between the incident As_2 flux and half the production rate of sites for As chemisorption.

Now consider a small perturbation from steady state, brought about experimentally by modulating J_{As_2}, and expressed by writing the surface concentrations in the mass balence equations as power series expansions which can be truncated at the first order term for small perturbations, i.e. there are time dependent concentration terms, and so the overall system response to the perturbation can be obtained by transformation to the frequency domain to give:

$$j\omega\theta_p(\omega) = J'_{As_2}(\omega) - k_1\theta_p(\omega) - k_2\theta_p(\omega)\,(1-\theta_c) + k_2\theta_p\theta_c(\omega) + \tfrac{1}{2}k_3\theta_c(\omega)\,, \tag{5}$$

and

$$j\omega\theta_c(\omega) = 2k_2\theta_p(\omega)\,(1-\theta_c) - 2k_2\theta_p\theta_c(\omega) - k_3\theta_c(\omega)\,, \tag{6}$$

where ω is the angular frequency of the perturbation. The measured quantity corresponds to the desorption of As_2, and the reaction probability for this desorption, i.e. the transfer function $H(\omega)$ is given by:

$$H(\omega) = k_1\theta_p(\omega)/J'_{As_2}(\omega) = k_1k'_3/[k_1k'_3 - j\omega(k_1 + k'_2 + k'_3) - \omega^2]\,, \tag{7}$$

where $k'_3 = k_3/(1 - \theta_c)$ and $k'_2 = k_2(1 - \theta_c)$. Eq. (7) can be rewritten as:

$$H(\omega) = [1 + jA(\omega/\omega_0)]/[1 + jB(\omega/\omega_0)) - (\omega/\omega_0)^2] , \tag{8}$$

where $\omega_0^2 = k_1 k'_3$, $A = k_1/\omega_0$, $B = (k_1 + k'_2 + k'_3)/\omega_0$. This is a standard form of transfer function, which for certain values of A and B shows attenuation with negligible phase shift over a wide range of ω. This qualitatively corresponds to the observed experimental behaviour, for particular values of the rate constants, k_i. Using the numerical values of the rate constants given below which we believe to be physically reasonable, the attenuation and phase shift as a function of frequency are shown in fig. 6, where it can be seen that over more than 3 decades of frequency, the attenuation is constant and the phase shift is negligible. The k_i values chosen were $k_1 = 10^6\ s^{-1}$, $k_2 = 5 \times 10^6\ s^{-1}$, $k_3 = 10^{-4}\ s^{-1}$, i.e. k_1 is a fast desorption rate, k_2 is a transfer rate from a precursor to a chemisorbed state and k_3 the slow dissociation process of GaAs. Unless $B \gg A$, such behaviour is not observed.

From fig. 6, $\omega/\omega_0 = 1$ corresponds to a set of conditions for which there is a large attenuation and negligible phase shift, i.e. typical of the experiments, and for these conditions,

$$H(\omega) \approx A/B \approx k_1/k'_2 ,$$

and the sticking coefficient = $1 - H(\omega) = 1 - k_1/k'_2$. Since measured values of S_{As_2} are in the range 0.1 – 1.0, k'_2 (= k_2 for low coverages) $\lesssim 10\ k_1$, implying that k_2 corresponds to a diffusion rate, not a simple transfer to the chemisorbed state.

We can now consider reaction sequences which occur on the surface below 600

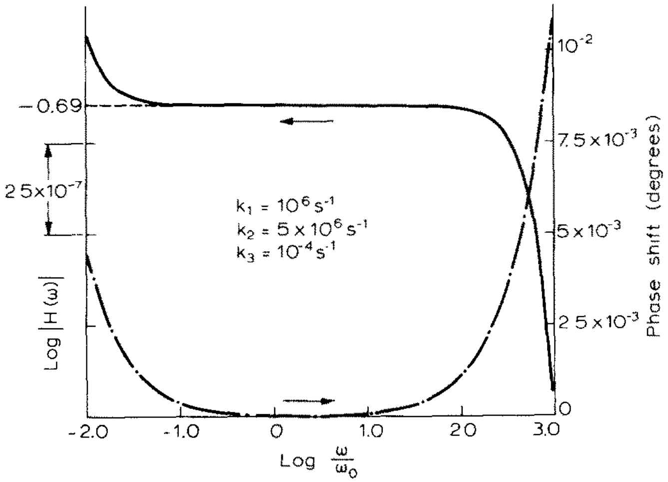

Fig. 6. Transfer function $H(\omega)$, i.e. the reaction probability, and phase shift as a function of reduced frequency for the desorption of As_2 above 600 K.

K, where the basic steps are represented by eqs. (9) below:

$$\begin{tikzcd}
 & \mathrm{As}_2(\mathrm{v}) \\
{} \arrow[r, "J_{\mathrm{As}_2}"] & \mathrm{As}_2(\mathrm{p}) \arrow[u, "k_1"'] \arrow[d, "k_4"', "+\mathrm{As}_2(\mathrm{p})"] \\
\mathrm{As}_4(\mathrm{v}) & \mathrm{As}_4(\mathrm{s}) \arrow[l, "k_5"']
\end{tikzcd} \tag{9}$$

All symbols have the same meaning as before, and in addition (s) refers to a surface molecule. We can write the following mass balance equations, again assuming that $(1-\theta_p) \approx 1$, and also that the surface Ga population is zero:

$$d\theta_p/dt = J'_{As_2} - k_1\theta_p - 2k_4\theta_p^2(1-\theta_s)\,, \tag{10}$$

$$d\theta_s/dt = k_4\theta_p^2(1-\theta_s) - k_5\theta_s\,. \tag{11}$$

At steady state, the R.H.S.'s of eq. (10) and (11) can be equated to zero, and the desorption rate of As_4, R_{As_4}, can therefore be written as:

$$R_{As_4} = n_a k_5 \theta_s = \tfrac{1}{2}(J_{As_2} - k_1 n_a \theta_p)\,. \tag{12}$$

At low temperatures, when $k_1\theta_p \ll 2k_4\theta_p^2(1-\theta_s)$,

$$R_{As_4} \approx \tfrac{1}{2}J_{As_2}\,,$$

i.e. the desorption rate of As_4 is first order with respect to the incident As_2 flux, as observed experimentally. The second experimental observation which the model is required to predict is that for small perturbations of the incident As_2 flux (i.e. when it is modulated) there is a large phase shift and attenuation associated with the detected signal from desorbing As_4 molecules. The time dependent behaviour can be obtained by transformation of eqs. (10) and (11), using the same first order approximation as before, from which it can be shown that the reaction probability for As_4 desorption, $H(\omega)$ is given by:

$$H(\omega) = 2k_4k_5\theta_p/(j\omega + k_5)(j\omega + k_1 + 4k_4\theta_p)\,. \tag{13}$$

At a substrate temperature of 485 K, it is experimentally observed that association to As_4 is highly favoured, and under these conditions eq. (13) can be written as:

$$H(\omega) = \tfrac{1}{2}/[1 + j(\omega/\omega_1)]\ [1 + j(\omega/\omega_2)]\,, \tag{14}$$

where $\omega_1 = k_5$ and $\omega_2 = 4k_4\theta_p$. There are therefore two distinct time constants involved, and for $\omega_1 < \omega_2$, a highly demodulated signal with a large phase shift for $\omega \geq \omega_1$ will be obtained, which is the experimental observation. The process chemistry must therefore involve a relatively fast association of As_2 to As_4, followed by slow rearrangement and/or diffusion steps, before eventual desorption. Rearrangement could involve a long-lived surface intermediate.

In semi-quantitative terms at least, the models are therefore able to predict the observed behaviour, but since none of the rate constants has a value in the experimentally accessible range, a fully quantitative model cannot be obtained.

References

[1] A.Y. Cho and J.R. Arthur, Progr. Solid State Chem. 10 (1975) 157.
[2] J.R. Arthur, J. Appl. Phys. 37 (1966) 3057.
[3] J.R. Arthur, in: Proc. Conf. on Structure and Chemistry of Solid Surfaces, Ed. G.A. Somorjai (Wiley, New York, 1969) p. 46.
[4] J.R. Arthur, J. Appl. Phys. 39 (1968) 4032.
[5] J.R. Arthur, Surface Sci. 43 (1974) 449.
[6] A.Y. Cho, J. Appl. Phys. 41 (1970) 2780.
[7] A.Y. Cho, J. Appl. Phys. 42 (1971) 2074.
[8] L.L. Chang, L. Esaki, W.E. Howard and R. Ludeke, J. Vacuum Sci. Technol. 10 (1973) 11.
[9] C.T. Foxon and B.A. Joyce, Surface Sci. 50 (1975) 434.
[10] C.T. Foxon, M.R. Boudry and B.A. Joyce, Surface Sci. 44 (1974) 69.
[11] J.R. Arthur and T.R. Brown, J. Vacuum Sci. Technol. 12 (1975) 200.
[12] C.T. Foxon, B.A. Joyce and S. Holloway, Intern. J. Mass. Spectr. Ion Phys., 21 (1976) 241.