J. CHEM. SOC. FARADAY TRANS., 1991, 87(7), 995–1001

Low-pressure Photochemical Vapour Deposition of Gallium Metal from an Iodide Precursor

Stephen J. Lane† and Mino Green*
Department of Electrical Engineering, Imperial College of Science, Technology and Medicine, Exhibition Road, London SW7 2BT

A study has been carried out of the low-pressure photochemical vapour deposition of gallium thin films from a gallium triiodide vapour stream, as a function of temperature, precursor partial pressure and illumination intensity. Deposition was found to take place through the photodissociation of adsorbed GaI molecules derived from the thermal decomposition of the triiodide. The reaction system was essentially oxygen-free, as shown by negligible dark deposition rates over the experimental temperature range of 673–873 K. The deposition rate was modelled using thermodynamic data in conjunction with the deBoer and B.E.T. adsorption theories. The resulting gallium films, which oxidized *ex situ* on exposure to the atmosphere, were characterised by ellipsometry, profilometry measurements of thickness, and EDX analysis for film composition. The possible growth of GaAs by this method was investigated by introducing molecular arsenic or arsenic triiodide into the system. The negligible incorporation of arsenic into the films, even at high arsenic partial pressures, is consistent with the presence of a stable GaI monolayer covering the gallium surface: this layer is taken to inhibit the formation of GaAs. Film growth was found to be consistent with photodeposition from a submonolayer of GaI adsorbed onto the iodine monolayer covering the gallium surface. The deposition of other Group IIIb metals by this method should be practical.

The interaction of light with molecules is a subject of considerable interest.[1,2] In recent years the processing of materials by photochemical means has been studied and is of particular interest for low-temperature processes in semiconductor fabrication. These techniques should be distinguished from the effects caused by localised heating arising from photon interaction with the substrate. Recent texts by Boyd[3] and Bauerle[4] offer good reviews of photon-stimulated etching, deposition and doping. Much of the research to date has been concerned with gas-phase photodecomposition of precursors already in use for thermally activated processes, namely the organometallic compounds. The development of precursors from which thermal deposition does not occur, but which photodecompose to yield either the species to be deposited or a thermally unstable secondary precursor, is of some interest. Photodeposition from the adsorbed state offers the prospect of accurate process control in the fabrication of high-resolution structures. Surface diffusion has also been studied by measuring deposition from the adsorbed state.[5] Much of the work to date on photodeposition from adlayers[6–8] has been conducted under ultra-high vacuum, with no ambient gas to replenish the adsorbed layer.

Photodeposition from inorganic precursors is a neglected field. Geohegan and Eden[9] deposited thin films of In, Al and Tl by gas-phase photoionisation of the metal iodides in an electric field with 193 nm photons. The photochemistry of vapour-phase metal halides has been studied for a number of years.[10–21] Interest has been rekindled by research into metal-atom resonance-line lasers.[22] Lasing results from the relaxation of excited-state metal atoms generated by the photodecomposition of the metal iodides. Hemmati and Collins[23] observed emission at 417.2 nm from neutral atomic gallium photodissociated from the iodide by an ArF laser. The dominant gas-phase species was GaI_3; however, as suggested by Hemmati and Collins, the gallium atoms were probably generated from the photodecomposition of GaI. The monoiodide was either thermally or photochemically generated. Deutsch *et al.*[24] reported similar lasing action from the iodides of Bi, In, Ga and Al. It was found that a sequential, two-photon (193 nm) excitation of the triiodide produced excited-state metal atoms *via* a monoiodide intermediary. A recent review[25] lists a large number of metal iodides which have demonstrated metal-atom lasing *via* gas-phase photodissociation. Therefore, these compounds have potential as precursors for metal deposition by photochemical means. We are here concerned with the photolysis of gallium iodide species.

Experimental

Apparatus

Experiments were undertaken in a reactor where the precursor species were exposed only to silica, Pyrex glass and a small area of PTFE, the iodide gases being incompatible with stainless steel and other metallic components. The apparatus is schematically illustrated in Fig. 1. Argon carrier gas, purified through a molecular sieve and a molten Ga/Al alloy bubbler[26] at 473 K, was monitored into the two source columns by leak valves and flow meters. Carrier gas and precursor partial pressures within the system were controlled by a series of capillary tubes. These prevented the back diffusion of condensable precursor species from hot to cold zones. The partial pressure of argon in the reaction zone was calculated to be 2000 Pa. The apparatus was operated in an oven at an ambient temperature of 473 K to ensure that the precursor molecules were stable in the gaseous form. Individual sections of the apparatus were cooled or heated from this temperature. Gallium triiodide was synthesised *in situ* from the elements in order to obtain an oxygen- and water-free source; this was found to be difficult using a commercial compound. The elemental arsenic source contained grains *ca.* 0.5 mm in diameter. This was found to be a good compromise between the large surface area needed to produce a useful sublimation rate and the small surface area desirable to reduce the inclusion of arsenic oxides. The arsenic source was run at 473 K in a gas flow containing some hydrogen for a number of days to remove the volatile oxide species. The system could be leak tested and baked to ensure as low a level as possible of chemically reactive oxygen-bearing species. The sources were

---

† Present address: Department of Geology, University of Bristol, Wills Memorial Building, Queen's Road, Bristol BS8 1RJ.

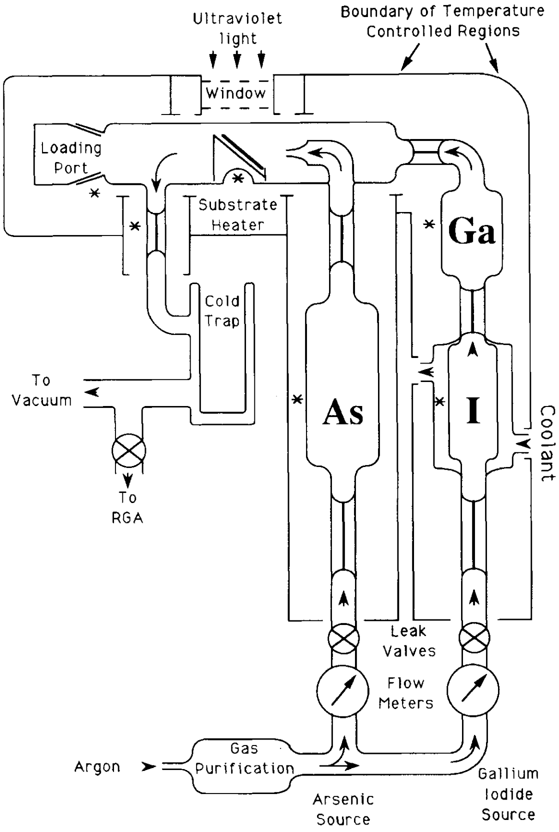

Fig. 1 Schematic diagram of low-pressure photochemical vapour deposition apparatus. Thermocouples are indicated by *. Carrier gas (argon) flow rate was controlled by leak valves. A differentially pumped residual gas analyser was fitted. A series of capillary tubes controlled the partial pressures of gaseous species. Argon pressures (in Pa): cold trap, 0.1; substrate, 2000, Ga and As, 2400 and 18900; supply, 120000

isolated from the atmosphere during substrate exchange by maintaining a flow of argon through the system. Heating was by resistive means, and the iodine source was cooled. Temperature measurement and control was obtained to within ±0.5 °C using three term controllers. Exhaust gases were condensed in a cold trap and pumping was provided by a rotary backed, oil diffusion pump. A differentially pumped quadrupole mass analyser was used to monitor system cleanliness. Illumination was provided from a 100 W high-pressure mercury arc lamp. An image of the arc, 5 mm in diameter, was focused onto the GaAs or Si substrate. The maximum available photon flux (Z_0) at the substrate between 200 and 300 nm, assuming a 5 eV average photon energy, was calculated to be 3×10^{21} quanta m^{-2} s.

Procedure

Substrates of Si and GaAs, *ca.* 15 mm by 15 mm, were cleaned in a reflux degreaser (isopropyl alcohol) and rinsed in deionised water. They were then dried at room temperature and loaded into the system. The apparatus was pumped down and the background heating applied whilst maintaining an argon flow of 8.3×10^{-8} m^3 s^{-1}. The system was baked for several hours. The arsenic and gallium triiodide sources were then activated to help getter oxygen from the reactor. Finally the substrate was heated to 100 °C above operating temperature for several minutes. The system was then stabilised to the required experimental conditions. This procedure took place with the substrate in dark conditions. The substrate was then illuminated for a measured period. The heaters were switched off and the system allowed to cool and fill with argon upon isolation from the pumping system. This comprised one experimental cycle.

System Characterisation

The system was subject to a series of trial experiments for characterisation and 'clean up' purposes. Gallium oxide in the deposition products, due to the presence of oxygen-bearing species reacting with the gallium iodide precursor, was reduced to insignificant levels within 25 experimental cycles. Thereafter, deposition took place only on illuminated regions of the substrate, deposition by thermal means being virtually undetectable by ellipsometry. The partial pressure of GaI_3 above the substrate was calculated to be 14 and 36 Pa at gallium triiodide source (Fig. 1) temperatures of 493 and 513 K, respectively. These values were obtained by collecting and weighing the amount of primrose yellow GaI_3 crystals forming in the cold trap. Illumination was varied using an adjustable aperture. Illumination intensity and substrate temperature rise, at atmospheric pressure, were both found to be directly proportional to aperture area. However, the substrate temperature rise was not measured by the substrate thermocouple in its experimental position (Fig. 1); it was measured only when bonded to the back of the substrate in a test experiment. Direct contact between the thermocouple and the substrate was not achieved during deposition experiments owing to the highly corrosive nature of the iodide precursor species.

Sample Analaysis

Sample analysis was carried out *ex situ*, since real-time *in situ* measurements were not available. Before removal from the system, photodeposited thin films had the metallic lustre of elemental gallium. The deposition of a continuous gallium film rather than the formation of gallium droplets, (as observed in conventional MBE/OMCVD systems with excess gallium fluxes) indicated the presence of a surface species which reduced the surface tension of the deposited gallium. The films were not moisture sensitive, as would be expected if a significant amount of iodine were present in the deposit. Such moisture sensitivity had been observed in experimental runs with a high overpressure of iodine in the system. The gallium films oxidized rapidly (minutes) in the atmosphere on removal from the experimental apparatus with the complete loss of metallic lustre. The resulting oxide films ranged in thickness from 175 to 2000 Å. The characteristic odour of iodine was not detected from the samples. All analyses were undertaken on this *ex situ* oxide film. Film thickness was measured using a Rudolf Research AutoEL nulling ellipsometer. The oxide films were a pale fawn in colour, irrespective of thickness, indicating a low level of absorption in the higher-energy end of the visible spectrum. In order to corroborate the ellipsometric data, measurements were made using a Talystep profilometer. This was used to measure steps where a section of the film had been etched from the substrate in an 0.5% HF solution for 5 s. The etch removed areas of film unprotected by an acetone soluble lacquer coating, but generated no detectable step in either Si or GaAs substrate slices. The two techniques agreed within experimental error (±50 Å), indicating that adsorption at 633 nm was insignificant. The ellipsometer was not capable of giving reliable results on some thicker samples, and these were measured by Talystep alone. The thickness measurements were combined with the illumination time to yield the growth rate *as oxide*. The oxide films were analysed in a JEOL T-200 SEM fitted with a Link Systems EDX analyser. The X-ray signal depth at electron energies of 25 keV was of the order of 2 μm, whereas film thicknesses were generally less than 0.1 μm. This yielded an X-ray spectrum dominated by peaks from the substrate material and so dictated the use of substrates containing different elements from those of the film when using this technique. The detection limit of this method was of the order of 1 at.%. The X-ray spectrum was collected for a time sufficient to allow the peaks characteristic of the film constituents to reach accurately measurable proportions.

Results and Discussion

Results

Film growth rate D/Å min^{-1} measured as *ex situ* oxide, as a function of the (to be corrected) measured substrate temperature T_0/K, at maximum illumination intensity (Z_0) for partial pressures of GaI_3 [$p(GaI_3)$] of 14 and 36 Pa, is shown in Fig. 2. Fig. 3 shows film deposition rate as a function of illumination intensity factor Z, (Z scales the experimental light intensity between zero and the maximum value Z_0, giving a total illumination intensity of ZZ_0) at constant T_0 of 573 K and $p(GaI_3)$ of 36 Pa.

The iodine content of all grown films was below the detection limit of electron probe analysis. The growth rate results reported here were obtained in the absence of an arsenic-bearing phase. Separate experiments were undertaken in the presence of arsenic, either as the iodide or in elemental form, to investigate the incorporation of arsenic into the growing films. Arsenic was not detected in the films, even with arsenic partial pressures approaching saturation above the substrate. However, when using an AsI_3 precursor, iodine was detected; these films became moist on removal from the system and smelt strongly of iodine. Iodine X-ray peaks were present on the EDS spectra of these films. This excess iodine was attributed to the thermal decomposition of arsenic triiodide in the hot reaction zone.

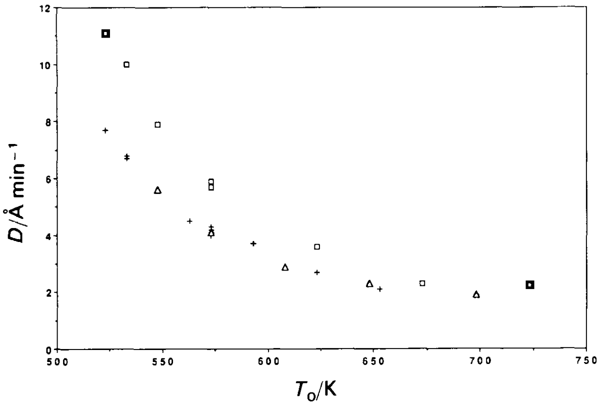

Fig. 2 Deposition rate (D) measured as *ex situ* oxide as a function of measured substrate temperature (T_0) at constant illumination intensity (scaling factor $Z = 1$). The open squares correspond to silicon substrates and $p(GaI_3) = 36$ Pa, the crosses to silicon substrates and 14 Pa and the open triangles to GaAs substrates and 14 Pa

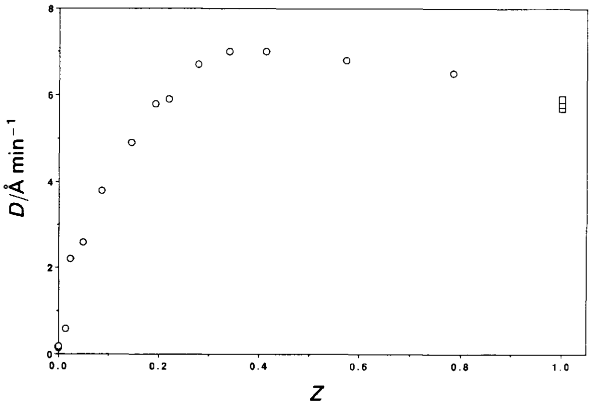

Fig. 3 Deposition rate (D) measured as *ex situ* oxide, as a function of scaled illumination intensity (Z). The true illumination intensity is given by ZZ_0. Experiments were carried out at a constant measured substrate temperature of 573 K. The open squares represent data from Fig. 2

Significant Features

The thermal dissociation and photodissociation of gas phase GaI_3 to the elements[16,24,27,28] takes place as a two-step process, namely

$$GaI_3 \xrightarrow[\text{or heat}]{\text{photon}} GaI + 2I \qquad (A)$$

$$GaI \xrightarrow[\text{or heat}]{\text{photon}} Ga + I \qquad (B)$$

However, the thermal deposition of gallium was not observed over the temperature range investigated, indicating that the partial pressure of elemental gallium [$p(Ga)$] did not exceed the saturated value above the substrate. The small deposition rate observed in the absence of illumination (*ca.* 0.1 Å min^{-1}) was independent of substrate temperature, being most probably due to reaction of gallium iodide species with residual water and oxygen in the system, resulting in direct deposition of gallium oxide.

The optical absorption spectra[12,16,17,19,29,30] of selected Group IIIb iodides are shown in Fig. 4. The photodissociation of GaI_3 *via* reaction (A) requires a photon of <220 nm wavelength.[16,17] Absorption peaks at 245 and 265 nm were attributed to the dissociation of the bridged dimer[16] Ga_2I_6 to the triiodide. The photodissociation of GaI_3 molecules is therefore not possible with the photon energies available from a high-pressure mercury lamp. Gallium monoiodide, however, photodissociates on interaction with photons of <310 nm wavelength,[15–18] which are available from the experimental light source.

The non-inclusion of arsenic into the growing gallium film gives an important indication as to the nature of the gallium surface. Neither As_4 or As_2 is, on thermodynamic grounds, capable of rupturing a Ga—I bond, hence a surface iodide layer is a barrier to arsenic incorporation. It is highly probable that a layer of gallium metal in the presence of low concentrations of iodine will have a monolayer of dissociatively chemisorbed iodine atoms on its surface,[31] as illustrated for GaAs by Jacobi *et al.*[32]

The observed decrease in deposition rate with increasing temperature (Fig. 2) is indicative of a surface phase rate-controlling process. Analyses by Krchnavek *et al.*[33] and Chen and Osgood[34] have shown that the optical absorption of an adsorbed layer depends on surface coverage, which in turn is known to decrease with increasing temperature. If the rate of photodecomposition is proportional to the number of photons absorbed, then for a surface phase process one would expect the behaviour that has been observed in these experiments.[3] In contrast, gas-phase photoprocesses are only weakly temperature dependent, and tend to vary linearly with pressure.[3,5] A purely thermal process would show the opposite trend to that observed, *i.e.* increasing rate with increasing temperature. Hence, the deposition of gallium films from gallium triiodide vapour appears to be controlled by a surface-phase photodissociative process, probably of a

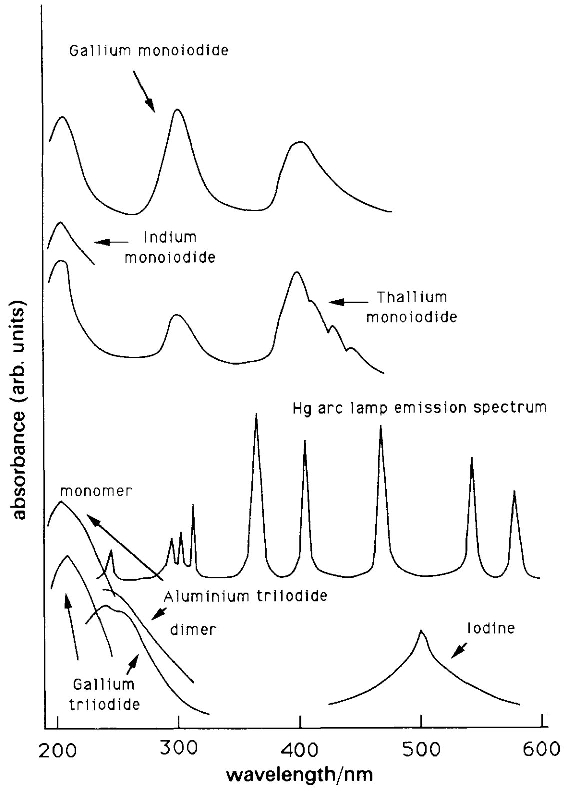

Fig. 4 The vapour-phase optical absorption spectra of selected Group IIIb iodides. For clarity the curves are displaced vertically from each other. The output spectrum of a high-pressure mercury lamp is superimposed. See text for references

monoiodide species generated from the thermal decomposition of the triiodide. Such a surface layer is consistent with the suppression of gallium droplet formation during deposition.

Process Modelling

The thermal dissociation of GaI_3 *via* reaction (A) was studied experimentally by Kuniya and Chino.[27] Rearranging these workers' expression for the equilibrium constant of reaction (A) in terms of the partial pressure of GaI yields

$$p(\mathrm{GaI})/\mathrm{Pa} = 6.26 \times 10^{6} p(\mathrm{GaI_3})^{1/3} \exp(-1.17 \times 10^{5}/RT) \quad (1)$$

where R is the gas constant. Assuming, as previously discussed, that GaI is not generated photochemically, this expression describes the partial pressure of GaI in the experimental apparatus.

The electronic energy level diagram of GaI shown in Fig. 5, which is similar to those of the other Group IIIb monoiodides,[10–21] indicates that the monoiodide can undergo gas-phase photodissociation to the elements as in reaction (B), Assuming that adsorption into the photoactive layer does not radically change the GaI electronic configuration, then surface phase photodissociation is also possible.

The absorption of photons by a gas is described by the Beer–Lambert equation,

$$Z_t = Z_0 \exp(-\sigma n l) \quad (2)$$

where Z_t and Z_0 are the transmitted and incident photon fluxes, respectively. σ is the absorption cross-section, which for gaseous GaI has an approximate value of 2.5×10^{-22} m^2 at 310 nm. n is the gas particle density and l the photon path length through the medium of interest. The rate of photodecomposition is taken to be equal to the rate of absorption of photons.

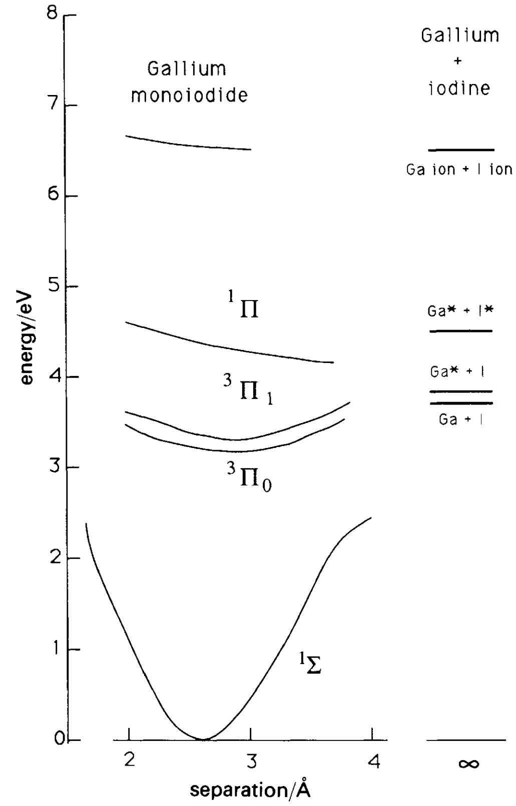

Fig. 5 The electronic energy levels of the GaI gas-phase molecule. * indicates the first excited electronic state. See test for references

Assuming $\sigma n l < -0.01$ and experimentally that pressure was constant, the gas-phase photogeneration rate of gallium is given by

$$\frac{\mathrm{d[Ga]}}{\mathrm{d}t} = \frac{Z_0 \sigma p(\mathrm{GaI}) l}{k_B T} \quad (3)$$

where k_B is Boltzmann's constant.

Adsorbed phase photodecomposition can be described in a similar fashion. Let the surface molecular density be θ and α be a correction factor for changes in σ upon adsorption.[3,34,35] This yields a surface photogeneration rate for gallium of

$$\mathrm{d[Ga]}/\mathrm{d}t = Z_0 \alpha \sigma \theta \quad (4)$$

Unlike their organometallic counterparts, the products of thermal- and photo-dissociation of the iodides undergo rapid recombination.[22,36] Gas-phase recombination of the monoiodide is given by the expression

$$\frac{\mathrm{d[GaI]}}{\mathrm{d}t} = \frac{-\mathrm{d[Ga]}}{\mathrm{d}t} = j_{\mathrm{rec}}[\mathrm{Ga}]^m \quad (5)$$

where [Ga] is the gas-phase gallium concentration, m is the kinetic order and j_{rec} the kinetic rate constant. At equilibrium the photodissociation and recombination rates must be equal to generate a steady value of [Ga]. Assuming second-order kinetics, [Ga] generated *via* the thermal decomposition of the triiodide followed by the photodissociation of the monoiodide to the elements, using eqns. (1), (3) and (5) is given by

$$[\mathrm{Ga}] = BT^{1/2}p[\mathrm{GaI_3}]^{1/6} \exp[-5.83 \times 10^{4}/RT] \quad (6)$$

where B is a constant incorporating all other non-variables. Assuming that the deposition rate from the gas phase is pro-

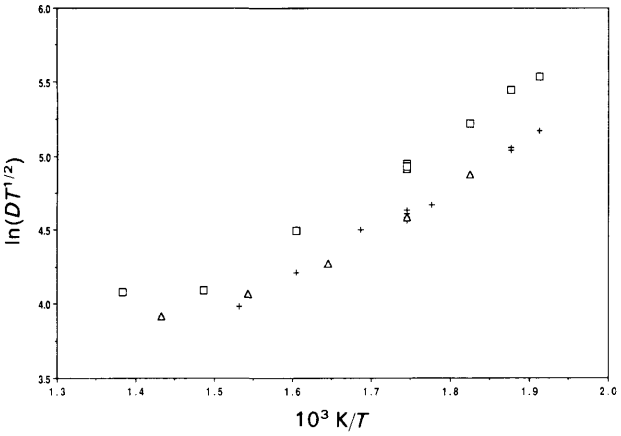

Fig. 6 Plot of $\ln(DT^{1/2})$ against $1/T_0$ for the data shown in Fig. 2. The linear trend is predicted by eqn. (7)

portional to [Ga], it is expected that growth rates *via* this process would rise as temperature increases. This is not observed in practice.

The recombination of products from surface-phase photodissociation reactions is difficult to model. However, the most likely fate of a photogenerated surface gallium atom is to combine with the surface causing film growth, since the adsorbed species is in contact with the surface more than any other phase. Expressing the surface coverage (θ) using the deBoer equation[37] in conjunction with eqns. (1) and (4) gives the surface photodecomposition rate as

$$\frac{d[\mathrm{Ga}]}{dt} = \frac{6.26\times10^{6} Z_0 \alpha\sigma p[\mathrm{GaI_3}]^{1/3}}{(2\pi m k_B T)^{1/2}} \times \tau_0 \exp\left(\frac{Q_i - (1.17\times10^{5})}{RT}\right) \qquad (7)$$

where τ_0 is the desorption attempt time and m is the mass of the GaI molecule. Q_i is the heat of adsorption of the photoactive layer. From eqn. (7), when $Q_i > 117$ kJ mol^{-1}, the surface photogeneration rate (d[Ga]/dt) will drop as the temperature rises. Fig. 6 shows the experimental data of Fig. 2 plotted as $\ln(DT_0^{1/2})$ against $1/T_0$, where T_0 is the measured substrate temperature, and illustrates the linear relationship predicted by eqn. (7). Modelling the deposition of gallium by the surface phase photodecomposition of GaI in thermal equilibrium with a GaI_3 vapour flow is qualitatively consistent with the experimental results.

Eqn. (7) predicts the deposition rate to be proportional to the illumination intensity. This was not observed in practice (Fig. 3). However, an illumination dependent substrate heating effect took place and is taken to explain this behaviour. The true level of substrate heating is not known experimentally. Eqn. (7) can be re-expressed as the dependence of measured film growth rate (D) on temperature, to yield

$$D/\text{Å min}^{-1} = \frac{W}{(T_0 + \Delta T_0)^{1/2}} \exp\left(\frac{G}{T_0 + \Delta T_0}\right) \qquad (8)$$

where T_0 is the measured substrate temperature and ΔT_0 is the temperature rise at full illumination, $Z_0(Z = 1)$ and

$$D = M\mathrm{d[Ga]/d}t \qquad (9)$$

The conversion constant M is calculated to be 1.47×10^{-17}.

Normalising eqn. (8) to two experimental values (runs 52 and 62 in Fig. 8) of the deposition rate (D) at constant illumination intensity (Z_0) and $p(\mathrm{GaI_3}) = 36$ Pa, and incorporating the illumination intensity factor (Z), which expresses illumination intensity as a fractional value of Z_0, the deposition rate can be calculated with varying Z for different values of ΔT_0. This is plotted in Fig. 7 and compared with the experimental data in Fig. 3. A ΔT_0 value of 150 °C was found to yield a reasonable representation of the experimental data. This yields, from eqn. (8), values for W and G of 0.11 and 5300, respectively. Incorporating $p(\mathrm{GaI_3})$ as a variable yields the deposition equation as

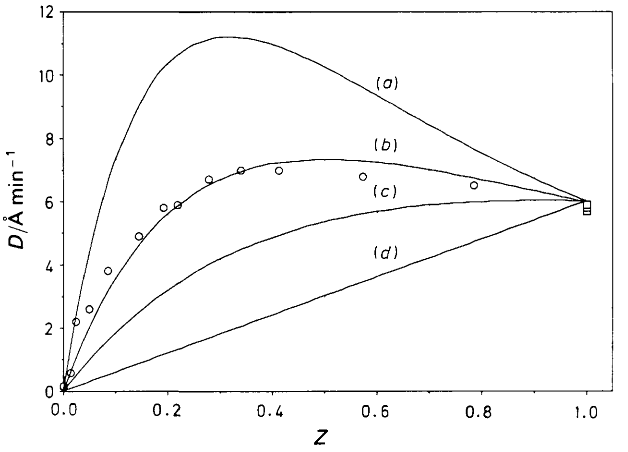

Fig. 7 Plot of deposition rate (D) against illumination intensity factor (Z). The lines represent theoretical plots for the marked value of substrate heating (ΔT_0) (*a*), 200 °C; (*b*), 150 °C; (*c*), 100 °C; (*d*), 0 °C; due to illumination at maximum illumination intensity ($Z = 1$). The symbols represent experimental data taken from Fig. 3

$$D/\text{Å min}^{-1} = \frac{0.033Zp(\mathrm{GaI_3})^{1/3}}{(T_0 + 150Z)^{1/2}} \exp\left(\frac{5300}{T_0 + 150Z}\right) \qquad (10)$$

Eqn. (10) is plotted in Fig. 8 as $\ln(DT^{1/2})$ against $1/T$ for a Z value of 1.0 and is compared with the experimental data for Fig. 2, where $T = T_0 + 150$. Theoretical and experimental data show good agreement.

The G value of 5300 yields a heat of adsorption (Q_i) for the photoactive layer of 160 kJ mol^{-1}. This is somewhat higher than the heat of evaporation given in the vapour-pressure data for GaI.[38] However, Cox *et al.*[39] found the desorption energy of YCl_3 from a chlorinated yttrium surface to be considerably higher than the heat of vaporisation. The value of G gained by fitting the theoretical expression (8) to experimental data is therefore considered to be reasonable.

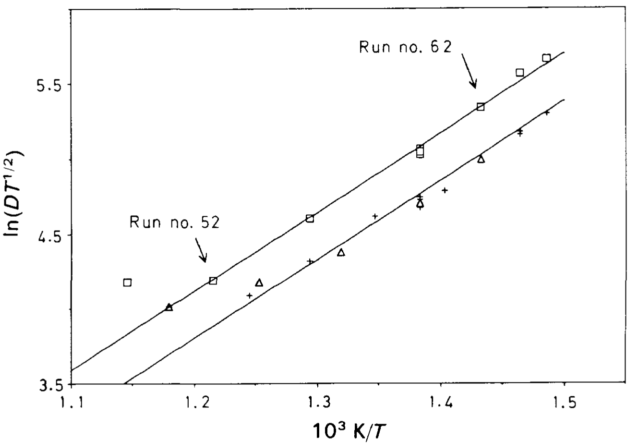

Fig. 8 Plot of $\ln(DT^{1/2})$ against $1/T$ with temperature corrected for illumination-dependent substrate heating. The lines represent the theoretical model from eqn. (10), normalized to runs 52 and 62. Points are the experimental data taken from Fig. 2

From *W*, the value of $\alpha\tau_0$ can be calculated *via* eqn. (7). Assuming the previously stated values of Z_0 and σ yields $\alpha\tau_0/s = 2.3 \times 10^{-15}$. Again, this is a plausible value which would not be unreasonable for τ_0 alone,[40] indicating that the absorption cross-section of GaI is not radically altered in going from the gaseous state to being adsorbed in the photoactive layer.

The surface coverage of the photoactive layer calculated from the deBoer equation, and assuming one monolayer contains 1.4×10^{19} molecule (GaI) m^{-2}, has a maximum value of approximately 0.3 of a monolayer. The non-incorporation of arsenic into the growing film suggests that the gallium surface is completely shielded from gas-phase arsenic molecules. It is postulated that photodeposition takes place from a submonolayer of GaI adsorbed onto a monolayer of GaI or I strongly bound to the gallium surface. Photodissociation from the first monolayer may be prevented by the close proximity of the first monolayer to the metal surface. This reduces the excited-state lifetime below the value required for separation of the atoms.[41,42] Alteration of the nature of the Ga—I bonding orbital in the first monolayer may also prevent photodissociation on interaction with photons from a mercury arc source.

This multilayer structure can be modelled using the simplified B.E.T. equation

$$\Theta = 1/[1 - (P/P_0)] \tag{11}$$

where P_0 is the saturated vapour pressure of the adsorbed species and *P* the actual pressure. P_0 was calculated by comparing the surface coverages of two samples (runs 52 and 62 from Fig. 2) calculated from both the deBoer and B.E.T. equations using the calculated heat of adsorption of the photoactive layer. This yields the relationship

$$D = 39.1(\Theta - 1) \tag{12}$$

The theoretical relationship (11) is compared with the experimental data from Fig. 2, *via* eqn. (12), in Fig. 9. Agreement between the two is reasonable, with some deviation at P/P_0 values <0.05. This may be due to preferential adsorption on a small number of 'active sites'.

The experimental results are consistent with deposition *via* the equilibrium thermal dissociation of GaI_3 to GaI, followed by the photodeposition of gallium from an adsorbed submonolayer of GaI, this process taking place on a gallium surface covered with a monolayer of chemisorbed iodine.

The proposed deposition mechanism is consistent with the adsorption/desorption work of Cox *et al.*[39] The simple experiments carried out here leave much to speculation. However, it would be of interest to carry out work on the surface science of the Ga–I system. This has a van der Waals to metallic atomic diameter of 1.53, suggesting similar behaviour to the Fe–Br : Cl, Cr–Cl : Br and W–Br : I systems.[43] Such work would provide basic information about the Ga–GaI–GaI_3 system studied here. This would shed more light on the potentially useful deposition mechanism investigated in this work.

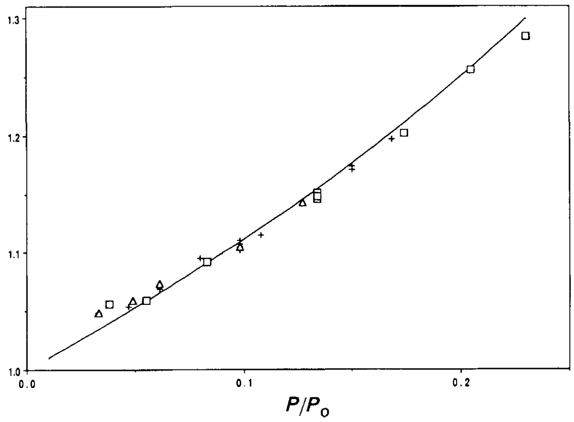

Fig. 9 Plot of surface coverage (Θ) against the ratio of actual and saturated (P/P_0) GaI vapour pressures over the substrate. The line represents eqn. (11) and the points are experimental data from Fig. 2 processed *via* eqn. (12)

Summary

The photodeposition of gallium from a GaI_3 vapour stream onto Si and GaAs substrates has been found to be consistent with photodeposition from a submonolayer of GaI, sourced from the equilibrium thermal decomposition of GaI_3, adsorbed onto a chemisorbed monolayer of iodine on the gallium surface. This monolayer prevented the reaction of deposited gallium with arsenic to form GaAs. The adsorbed phase photodecomposition of other metal iodides, especially from Group IIIb, by this method should be practical. The corrosive nature of halide species would require the use of substrates which are inert in the precursor atmosphere. This rules out deposition onto most metal and compound semiconductor surfaces, although deposition would take place in illuminated areas whilst the dark regions are etched. Deposition onto many oxide and refractory materials should prove possible. The domination of adsorbed phase photodeposition over the gas-phase process can be attributed to the high heat of adsorption of GaI into the photoactive layer and to the rapid recombination of any gas-phase photoproducts.

Photodeposition from the adsorbed state offers the prospect of depositing films with accurately controlled dimensions over large areas if required.

S.J.L. thanks the SERC and ICI Wafer Technology for funding throughout this project.

References

1 G. Herzberg, *Molecular Spectra and Molecular Structure*, Van Nostrand, Princeton, NJ, 1945 and 1966, vols. I and II.
2 J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1966.
3 I. W. Boyd, *Laser Processing of Thin Films and Microstructures*, Springer, Berlin, 1987.
4 D. Bauerle, *Chemical Processing with Lasers*, Springer, Berlin, 1986.
5 J. Y. Tsao, H. J. Zeigler and D. J. Ehrlich, *Surf. Sci.*, 1985, **160**, 419.
6 J. R. Creighton, *J. Appl. Phys.*, 1986, **59**, 410.
7 N. Bottka, P. J. Walsh and R. Z. Dalbey, *J. Appl. Phys.*, 1983, **54**, 1104.
8 N. S. Gluck, Z. Ying, C. E. Bartosch and W. Ho, *J. Chem. Phys.*, 1987, **86**, 4957.
9 D. B. Geohegan and J. G. Eden, *Appl. Phys. Lett.*, 1984, **45**, 1146.
10 E. von Miescher, *Helv. Phys. Acta*, 1935, **8**, 279.
11 E. von Miescher, *Helv. Phys. Acta*, 1936, **9**, 693.
12 W. Halg, *Helv. Phys. Acta*, 1943, **16**, 371.
13 R. F. Barrow, *Trans. Faraday Soc.*, 1960, **56**, 952.
14 E. Martin and R. F. Barrow, *Phys. Scr.*, 1978, **17**, 501.
15 E. von Miescher and M. Wehrli, *Helv. Phys. Acta*, 1934, **7**, 331.
16 Y. Kuniya, Y. Tanizawa and M. Hosaka, *Denki Kagaka*, 1973, **41**, 108.
17 D. Richman, *RCA Rev.* 1963, **596**.
18 G. Lakshminarayana and A. Sethumadhavan, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **23**, 343.
19 P. Davidovits and J. A. Bellisio, *J. Chem. Phys.*, 1969, **50**, 3560.
20 A. Terenin, *Phys. Z. Sowjetunion*, 1932, **2**, 377.
21 D. B. Geohegan, A. W. McCown and J. G. Eden, *J. Phys. Chem.*, 1984, **81**, 5336.

22 D. J. Ehrlich and R. M. Osgood, *J. Quantum. Electron.*, 1980, **16**, 257.

23 H. Hemmati and G. J. Collins, *Appl. Phys. Lett.*, 1979, **34**, 844.

24 T. F. Deutsch, D. J. Ehrlich and R. M. Osgood, *Op. Lett.*, 1979, **4**, 378.

25 W. Luthy, *Appl. Phys. B*, 1986, **40**, 121.

26 M. Ettenberg, A. G. Sigai, A. Dreeben and S. L. Gilbert, *J. Electrochem. Soc.*, 1971, **118**, 1355.

27 Y. Kuniya and T. Chino, *Denki Kagaka*, 1972, **40**, 858.

28 R. F. Lever, *J. Phys. Chem. Solids*, 1965, **26**, 1629.

29 N. W. Gregory, *J. Phys. Chem.*, 1977, **81**, 1854.

30 Ya. Kh. Grinberg, V. A. Boryakova, V. F. Shevel'kov and Z. S. Medvedeva, *Inorg. Mater.*, 1972, **8**, 55.

31 A. P. C. Reed, R. M. Lambert and J. S. Foord, *Surf. Sci.*, 1983, **134**, 689.

32 K. Jacobi, G. Steinert and W. Ranke, *Surf. Sci.*, 1976, **57**, 571.

33 R. R. Krchnavek, H. H. Gilgen, J. C. Chen, P. S. Shaw, T. J. Licata and R. M. Osgood, Jr., *J. Vac. Sci. Technol. B*, 1987, **5**, 20.

34 C. J. Chen and R. M. Osgood, *Chem. Phys. Lett.*, 1983, **98**, 363.

35 D. J. Ehrlich and R. M. Osgood, *Chem. Phys. Lett.*, 1981, **72**, 381.

36 V. R. McCrary and V. M. Donnelly, *J. Cryst. Growth*, 1987, **84**, 253.

37 J. H. DeBoer, *The Dynamical Character of Adsorption*, Oxford University Press, Oxford, 1968.

38 G. A. Zaidlova, A. A. Kuliev and S. M. Gadzhiev, *Uch. Zap., Azerb. Univ., Ser. Khim. Nauk.*, 1972, **2**, 55.

39 M. P. Cox, J. S. Foord and R. M. Lambert, *Surf. Sci.*, 1983, **129**, 375.

40 P. Jewsbury, *J. Phys. C*, 1977, **10**, 671.

41 D. H. Walpeck, A. P. Alivisatos and C. B. Harris, *Surf. Sci.*, 1985, **158**, 103.

42 P. Avouris and B. N. J. Persson, *J. Phys. Chem.*, 1984, **88**, 837.

43 J. S. Foord and R. M. Lambert, *Surf. Sci.*, 1984, **138**, 258.

Paper 0/04095I; *Received 7th September*, 1990