Heterogeneous hydride pyrolysis in a chemical beam epitaxy cracker cell and growth of high quality InP

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The decomposition of phosphine and arsine in a chemical beam epitaxy cracker cell was investigated with a quadrupole mass spectrometer. We have determined the kinetical parameters for a unimolecular reaction of the first order, i.e. the activation energy and frequency factor, from the decomposition efficiency as a function of temperature. These results are compared with data from literature. We find the lowest activation energies ever reported for the hydride pyrolysis, namely 72 and 48 kJ/mol for phosphine and arsine, respectively. This is due to the heterogeneous decomposition on catalytic molybdenum baffles inside the cracker cell. Additionally, we have studied the impurity incorporation in epitaxially grown bulk InP layers in relation to the efficiency of this particular molybdenum containing cracker cell. Impurity levels were determined by fitting calculated Hall values to experimental data. The best quality is achieved for the cracker temperature at which the efficiency starts to saturate. At this cracker temperature, optimized mass flow rates resulted in InP layers with a maximum mobility of 186 000 cm^2/V s and impurity concentrations in the low 10^{14} cm^{-3} range. © *1997 American Vacuum Society.* [S0734-2101(97)00301-1]

I. INTRODUCTION

In the technique of chemical beam epitaxy (CBE) the ultrahigh vacuum (UHV) technology of molecular beam epitaxy (MBE) is combined with the starting materials of metalorganic vapor phase epitaxy (MOVPE). The metal organic group-III source materials and the group-V precursors are passed through separate injectors into the growth chamber. The injector of the metalorganics is kept at a constant temperature to avoid condensation of these materials. Their decomposition occurs on the heated substrate. In contrast herewith the group-V precursors, mostly the hydrides, phosphine and arsine, are pre-cracked in a high temperature (HT) injector. Their decomposition is thereby made independent of the substrate temperature. A number of studies has been devoted to the pyrolysis of phosphine and arsine under MOVPE conditions[1–3] as well as CBE conditions.[4–7] A thermodynamic analysis of the hydride pyrolysis was presented by Jordan and Robertson[8] and the calculation of unimolecular rate constants was performed by Buchan and Jasinski.[9]

The aim of this work is to add to the knowledge of the reaction kinetics and activation energies of the hydride pyrolysis. Therefore, in the first part of this study we analyze the arsine and phosphine decomposition in a CBE injector by measuring background mass spectrometric intensities of the various species involved in the pyrolysis.

The temperature of the HT injector is an important process parameter during CBE growth. This is demonstrated in the second part of this article where the electrical properties of bulk InP layers in relation to the cracker temperature are discussed. We compare these results with the performance of a hydride injector containing only pyrolytic boron nitride, as was used previously by us.

II. EXPERIMENT

For the growth of (Ga,In)(As,P) structures we use a Riber CBE 32P system. All gas flows are regulated by mass flow controllers. The group-III starting materials we use are trimethylindium (TMIn) and triethylgallium (TEGa). In previous work[10] the hydrides, phosphine (PH_3) and arsine (AsH_3), were injected via a high temperature injector (Riber, HTG 5) containing pyrolytic boron nitride (PBN) baffles requiring an operating temperature of 1373 K. Later, we replaced this item with a low pressure gas injector (Riber, HTI 432) where the hydrides flow through a Mo (molybdenum) tube into the high temperature zone. This zone contains three Mo baffles so that impingement and adsorption are ensured. It is known that Mo, as a transition metal, is an extremely effective catalyst for the heterogeneous decomposition of phosphine.[11] The kinetic studies reported here were performed by measuring the mass spectrometric intensities of the various chemical species inside the growth chamber, with dependence of the injector temperature, using a quadrupole mass spectrometer (VG, Sensorlab) with a mass range from 1 to 300 amu. In order to measure pressures below 10^{-10} mbar, we used the secondary electron multiplier (SEM). The mass spectrometer is not in line of sight of the group-V beam. It thus measures the steady state concentration of species in the growth chamber whereby all molecules have had at least one collision with the walls. Gas pulses with durations of approximately 60 s are introduced into the growth chamber. Within this time all measured intensities reach a constant value. The introduction of a second pulse, with the gas injector set to a new temperature, was postponed until all intensities had reached again their initial values. Typical on/off ratios for the unreacted hydrides at low cracker temperatures are on the order of 100. We assume that on their flight to the mass spectrometer, reaction products do not recombine and form

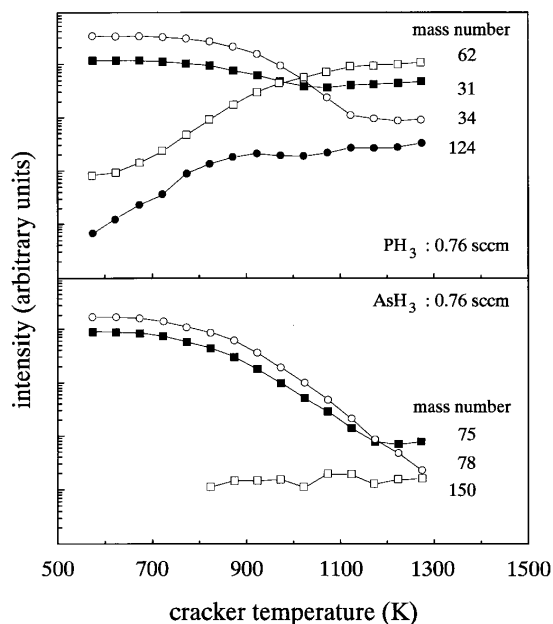[a]Electronic mail: tnnvrr@urc.tue.nl

FIG. 1. Mass spectrometric intensities of various masses as a function of cracker temperature for both phosphine and arsine.

FIG. 2. Relative amount C/C_0 [$C_0 = C(573$ K$)$] of unreacted phosphine and arsine as a function of the cracker temperature. The solid curves represent calculations according to first order kinetics. A typical error bar that is determined from the worst possible on/off ratio of about 40 for the measured intensities in Fig. 1 is indicated.

the original hydride molecules. In view of the low temperature of the walls and the long mean free path length at the pressures employed here, this is a reasonable assumption. Measurement of the steady state concentrations of the unreacted phosphine and arsine molecules as a function of temperature enables one to derive reaction rate equations for the heterogeneous decomposition of these hydrides on a Mo surface.

InP epitaxial layers have, in addition, been grown at various injector temperatures on semi-insulating (Fe-doped) InP(100) wafers misorientated 2° off to (110). The growth temperature was always 535 °C, as measured by optical pyrometry. Layer thicknesses were between 3 and 4 μm. The electrical properties of these layers were characterized by measuring the concentration of free carriers and their mobility in the temperature range from 20 to 300 K. These measurements were carried out using the van der Pauw configuration. The experimental data were used to derive the individual concentrations of shallow donors, deep donors and acceptors incorporated in the epitaxial InP layers.

III. RESULTS AND DISCUSSION

A. Hydride pyrolysis

For both arsine and phosphine, with a constant flow rate of 0.76 sccm, mass spectra were measured for gas pulses injected at cracker temperatures between 573 and 1273 K. In Fig. 1 the dominant intensities are shown. These are found at mass numbers corresponding to the unreacted hydrides (34 and 78 amu), as well as monomers (31 and 75 amu), dimers (62 and 150) and tetramers (124) of phosphorus and arsenic, respectively. A quantitative analysis on reaction products cannot be carried out in our system. At the injector tempera-
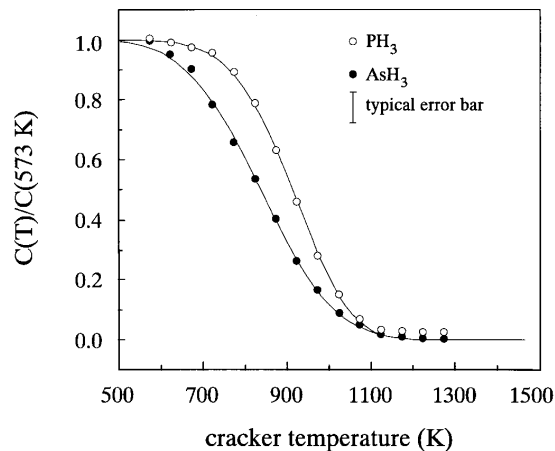
tures required here for pyrolysis of phosphine and arsine, the reaction products are most likely As and P dimers.[2,4,6,8] Actually our method to determine the uncracked fraction of the starting compounds is very similar to the studies described in Refs. 2 and 3 using mass spectrometry[2] and infrared spectroscopy[3] to investigate the role of various surfaces on the hydride decomposition rate. From Fig. 1 we conclude that no decomposition occurs at 573 K. Consequently, the relative amount (C/C_0) of unreacted hydride molecules at a specific temperature is equivalent to the measured intensity at this temperature normalized to the intensity at 573 K. These values are shown in Fig. 2. As can be seen, an almost complete decomposition occurs above about 1100 K. The maximum cracking efficiencies for phosphine and arsine are 97.5% and 99.5%, respectively.

The flow in the hydride cell is molecular and therefore the cracking process is dominated by the interaction between the gas and Mo baffles. The kinetics for this heterogeneous reaction can be described by

$$\frac{dC}{dt} = -k \times C^n, \tag{1}$$

where C is the concentration of the reactant (arsine or phosphine), k the rate constant and n the reaction order. The rate constant can be written as

$$k = A \exp(-E_a/RT), \tag{2}$$

where A is the frequency factor for the reaction and E_a is the activation energy for the hydride decomposition. By substitution of Eq. (2) in Eq. (1) and integration of Eq. (1) from 0 to τ, the residence time of the hydride molecule in the cracker hot zone, we find the functional dependence of C/C_0 on the absolute temperature T for a reaction of order n. This relation can be fitted to the measured values of C/C_0 using $A \times \tau$ and E_a as fitting parameters. For a decomposition process of order 0, 1, and 2 this was carried out. The most

TABLE I. Compilation of kinetic constants. References are indicated, in some cases the values have been calculated using decomposition data found in literature.

Reaction conditions	PH₃		AsH₃	
	E_a (kJ/mol)	log(A/s⁻¹)	E_a (kJ/mol)	log(A/s⁻¹)
Homogeneous, high pressure limit calculated[a]	345	15.7	314	15.7
Homogeneous, (0.1–1) mbar				
T>1170 K[b]	290	15.9		
T>890 K[c]			251	14.0
Heterogeneous, (0.1–1) mbar				
on glass[d]	185	...		
on quartz[c]			142	6.8
Heterogeneous, (0.1–1) mbar				
on InP[e]	151	...		
on GaAs[c]			75	3.8
Heterogeneous, 10⁻³ mbar				
on Mo[f]	72	6.9	48	5.8

[a]Reference 9.
[b]Reference 1.
[c]Reference 3.
[d]Reference 12.
[e]Reference 2.
[f]This work.

accurate description is obtained for a first order reaction. The result of this first order fit is also shown in Fig. 2. As can be seen, the calculated curve describes the experimental data very well. We have also verified that at a temperature of 1173 K the cracking efficiency is virtually independent of the hydride flow rate for values up to 11 sccm. Explicitly, the cracking efficiency is constant for phosphine (about 97.5%) and changes from 99.5% at a flow rate of 0.76 sccm to 98.0% at 11 sccm for arsine. This observation is consistent with the proposed first order kinetics.

In order to obtain more insight in the rate limiting step in the overall decomposition we compare our results with literature. Hereto, an estimation of the residence time τ is required in order to calculate the frequency factor A. Based on the assumption that the particle flow through the entire hydride line (MFC—gas tube—HT cell) must be constant and that the pressure inside the cracker cell is typically in the order of 1 mbar, we estimate a value of 1 ms for the residence time. The same order of magnitude for the residence time in a CBE injector was used in Ref. 8.

In Table I we compare our values for activation energies and frequency factors with data from literature. The energy required to break the first H bond of the hydride molecule in the homogeneous case is 345 kJ/mol for phosphine and 314 kJ/mol for arsine.[8,9] It is assumed that the removal of the first H atom is the rate limiting process in the overall decomposition:[2,8,9]

$$PH_3^{ads} \rightarrow PH_2^{ads} + H^{ads}, \tag{3a}$$

$$AsH_3^{ads} \rightarrow AsH_2^{ads} + H^{ads}. \tag{3b}$$

The activation energies for both reactions are lowered in the presence of surfaces. Thus the adsorption of the hydride on the surface leads to a significant weakening of the H–PH₂, respectively the H–AsH₂ bond. For heterogeneous reactions in the low pressure regime, the apparent activation energy E_a in Eq. (2) is actually given by $E_a - Q_{ads}$: the "true" activation energy reduced by the heat of adsorption of the reactant.[13] Our study gives values for this "reduced" activation energy of 72 kJ/mol for phosphine and 48 kJ/mol for arsine, significantly lower than those reported in literature (Table I). Therefore, we conclude that Mo as transition metal element is indeed an active catalyst for the decomposition of phosphine and arsine compared to glass and InP, respectively, GaAs surfaces.

Additionally, the frequency factors found here are lower. Our values (low pressure, Mo surface) are typically a factor of 10⁸–10⁹ lower than those for the homogeneous pyrolysis. From the thermodynamic approach of rate theory it is known that the rate constant k can be written as

$$k = (k_B T/h)\exp(\Delta S/R)\exp(-\Delta H/RT), \tag{4}$$

where k_B is the Boltzmann constant, h the Planck constant, ΔS the entropy change and ΔH the enthalpy change going from the initial to the activated state.[13] By comparing Eq. (4) with Eq. (1) it follows that the frequency factor is given by

$$A = (k_B T/h)\exp(\Delta S/R). \tag{5}$$

In the temperature range of interest (573–1273 K), the pre-exponential term should have a value of approximately 10^{13} s⁻¹. For the homogeneous pyrolysis the frequency factor is larger (10^{14}–10^{16} s⁻¹), indicating that the transition to the activated state is accompanied by an entropy increase. This can, for instance, be explained by a less rigid activated complex. A heterogeneous reaction shows in general a decrease in entropy when going to the activated state. This can be understood on the basis of the fact that, upon absorption, the molecule loses at least one (translational) degree of freedom. All experimental results on the heterogeneous reactions show frequency factors that are low indeed. This is thus consistent with the requirement that adsorption (and subsequent loss of degrees of freedom) occurs prior to reaction.

B. Growth of InP

In addition to the analysis of chemical kinetics in the hydride pyrolysis, we studied the performance of this HT cracker in relation to the impurity incorporation in bulk InP. Therefore, layers have been grown at various injector temperatures. In Fig. 3 the mobility and free carrier concentration of a particular sample are shown as a function of temperature. This InP layer was grown at a cracker temperature of 1123 K, and the TMIn and phosphine flow rate were 3.2 and 12.2 sccm, respectively. As can be seen, the fit to these data, allowing for the determination of impurity concentrations as discussed previously,[10] describes the experimental values well. For this sample a shallow donor concentration
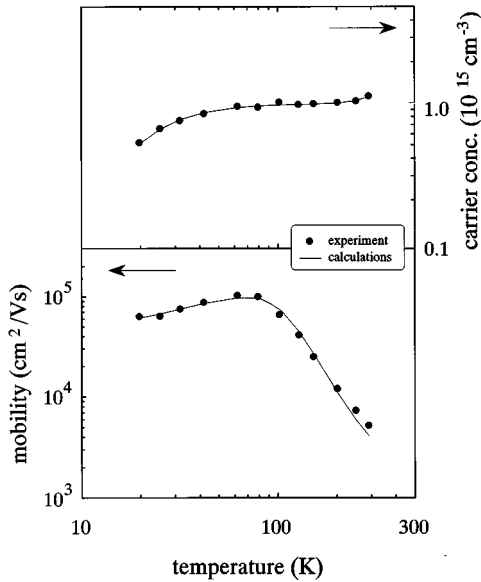
FIG. 3. Mobility and carrier concentration as functions of temperature for an InP layer grown with a cracker temperature of 1123 K; shown are experimental data and calculated curves. The impurity concentrations are 1×10^{14}, 8×10^{14}, and 1×10^{15} cm^{-3} for n_A, n_{DD}, and n_{SD}, respectively.

n_{SD} is found equal to 1×10^{15} cm^{-3}. The concentration of deep donors n_{DD} is 8×10^{14} cm^{-3}, whereas the acceptor concentration n_A is 1×10^{14} cm^{-3}. At low temperatures (T<50 K) the mobility is limited by ionized impurity scattering as a result of partly compensated donors by acceptors in the layer. The deep donors act as neutral scatterers around 77 K and their thermal activation starts at about 150 K. Scattering by polar optical phonons limits the mobility above 150 K.

In Fig. 4, the impurity concentrations depending on injector temperature are shown. The samples considered here have also been grown with a TMIn flow rate of 3.2 sccm,
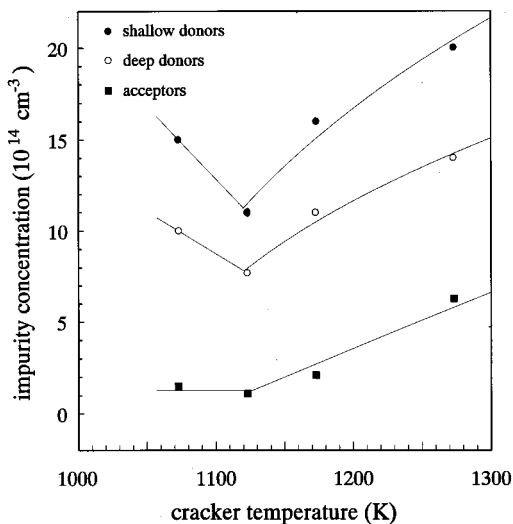

FIG. 4. Impurity concentrations in InP layers as a function of cracker temperature. Material flow rates are those as given for the sample shown in Fig. 3. The solid lines are guides to the eye.

i.e., a growth rate of 1.1 μm/h, and a phosphine flow rate of 12.2 sccm. As mentioned previously, the growth temperature was 535 °C. The lowest impurity levels are obtained with an injector temperature of 1123 K. Remarkably, this is the temperature at which the cracking efficiency of the injector saturates, as shown in Fig. 2. Increasing the hydride cell temperature above 1123 K leads to an enhanced desorption of species from the high temperature zone.[14,15] At cracker temperatures below 1123 K, for which the pyrolysis efficiency decreases, the acceptor concentration is approximately constant, whereas the shallow and deep donor concentrations are increasing. Therefore we can conclude that acceptors are related to the TMIn used in our system, whereas the shallow and deep donor incorporation is affected by the phosphine.

While maintaining the hydride injector temperature at 1123 K, we have further optimized the quality of the InP layers by adjusting the source material flow rates. With a TMIn flow rate of 1.6 sccm and a phosphine flow rate of 4.6 sccm material was obtained with a mobility of 186 000 cm^2/V s at a temperature of 60 K and impurity concentrations of 8×10^{13}, 4×10^{14}, and 4×10^{14} cm^{-3} for n_A, n_{DD}, and n_{SD}, respectively.

IV. CONCLUSIONS

The temperature dependent cracking efficiency in a low pressure CBE gas injector with Mo baffles was studied between 573 and 1273 K. Activation energies of 72 and 48 kJ/mol with frequency factors of 10^7 and 10^6 s^{-1} are determined for the first order heterogeneous decomposition of phosphine and arsine, respectively. The kinetic data are consistent with previously reported results on homogeneous and heterogeneous reaction rates and prove the catalytic nature of the Mo surface for hydride decomposition. The study by means of mass spectrometry reveals that the phosphine and arsine decompositions saturate to values of 97.5% and 99.5%, respectively at a temperature of 1123 K. When the hydride gas injector is operated at the lowest possible operating temperature ensuring maximum decomposition, this results in the lowest level of background impurities in epitaxial layers. Too high temperatures lead to excessive impurity incorporation. A catalytically active surface inside the injector by which the operating temperature can be reduced is thus beneficial for the growth of high quality epitaxial layers. By further optimization of, most notably, the material flow rates high quality InP layers with a maximum mobility of 186 000 cm^2/V s (60 K) and impurity concentrations in the low 10^{14} cm^{-3} range were grown.

[1] C.A. Larsen and G.B. Stringfellow, J. Cryst. Growth **75**, 247 (1986).

[2] C.A. Larsen, N.I. Buchan, and G.B. Stringfellow, J. Cryst. Growth **85**, 148 (1987).

[3] S.P. DenBaars, B.Y. Maa, P.D. Dapkus, A.D. Danner, and H.C. Lee, J. Cryst. Growth **77**, 188 (1986).

[4] R. Chow and Y.G. Chai, J. Vac. Sci. Technol. A **1**, 49 (1983).

[5] D. Huet, M. Lambert, D. Bonnevie, and D. Dufresne, J. Vac. Sci. Technol. B **3**, 823 (1985).

[6] M.B. Panish and R.A. Hamm, J. Cryst. Growth **78**, 445 (1986).

[7] M.J. Hafich, H.Y. Lee, P. Silvestre, and G.Y. Robinson, J. Cryst. Growth **111**, 507 (1991).

[8] A.S. Jordan and A. Robertson, J. Vac. Sci. Technol. A **12**, 204 (1994).

[9] N.I. Buchan and J.M. Jasinski, J. Cryst. Growth **106**, 227 (1990).

[10] R.T.H. Rongen, M.R. Leys, P.J. van Hall, C.M. van Es, H. Vonk, and J.H. Wolter, J. Electron. Mater. **24**, 1391 (1995).

[11] H.W. Melville and H.L. Roxburgh, J. Chem. Soc. 586 (1933).

[12] G.G. Devyatykh, V.M. Kedyarkin, and A.D. Zorin, Russ. J. Inorg. Chem. **14**, 1055 (1969).

[13] K.J. Laidler, *Chemical Kinetics,* 3rd ed. (Harper & Row, New York, 1987).

[14] J.L. Benchimol, F. Alaoui, Y. Gao, G. Le Roux, E.V.K. Rao, and F. Alexandre, J. Cryst. Growth **105**, 135 (1990).

[15] T. Sudersena Rao, C. Lacelle, M. Davies, R. Barber, P. Chow-Chong, J. McCaffery, S.J. Rolfe, A.P. Roth, B. Benyon, and B. Foster, J. Cryst. Growth **136**, 179 (1994).