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de-NO$_x$ process if $\alpha = 0.35$. This is in agreement with the room-temperature determination presented in this paper, if one assumes that α is invariant with temperature. Using the information obtained from the reaction of NH_2 with NO, we can now simply describe the NO reduction mechanism.[6]

Conclusion

The rate of reaction for $NH_2 + NO$ can be represented by $k(\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) = [4.38 \times 10^{-5}]T^{-2.30} \exp(-1360\ \mathrm{cal\ mol^{-1}}/RT)$ over the temperature range 294–1215 K. The major products are $N_2 + H_2O$, but $N_2H + OH$ and/or $N_2 + H + OH$ are formed n 30–50% of all reactions. Although the analysis implies that $N_2H + OH$ is the radical product channel at room temperature, the relative importance of these two pathways is unclear at combustion temperatures. These measurements should help in elucidating the chemistry of NO in the polluted atmosphere, combustion flames, and combustor exhausts.

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Kinetics of the Dissociation of InP under Vacuum

P. K. Gallagher* and S. N. G. Chu

Bell Laboratories, Murray Hill, New Jersey 07974 *(Received: January 13, 1982; In Final Form: April 12, 1982)*

Mass-spectrographic evolved-gas analysis is used to study the rate of decomposition of InP at various linear heating rates under vacuum. Because of the high sensitivity of the technique, it is possible to evaluate the Arrhenius parameters at very low values of fraction reacted (α), $0.10 \geq \alpha \geq 0.0003$, by using the Ozawa method of data analysis. Derived values of the activation energy and log preexponential are 70.5 kcal mol^{-1} and 13.85 s^{-1}, respectively. These are consistent with the values calculated by using the Freeman and Carrol, Ozawa, and Kissinger methods in the more conventional range of $0.1 \leq \alpha \leq 0.9$. A composite of all of the calculated values shows a nearly linear relationship between activation energy and log preexponential resulting from the mathematical ill-conditioning of the Arrhenius equation. Some extrapolations are made to low temperatures as guidelines for those interested in the thermal processing of InP.

Introduction

The deterioration in the surface of polished InP substrate due to thermal decomposition is of concern in the preparation of a variety of optoelectronic and microwave devices by both vapor–phase epitaxial (VPE) and liquid-phase epitaxial (LPE) growth. The effect is significant at temperatures above 450 °C in a hydrogen ambient.[1-4] Above about 630 K InP vaporizes incongruently[5] giving rise to a pitted surface which is rich in In.[1] Typical VPE growth temperatures are around 700 °C.[6] The rate of this vaporization of phosphorus is therefore of considerable technological importance.

Because of the short time involved in heating the substrate to the growth temperature before VPE growth actually starts, it is the relatively early stage of the dissociation process which is of interest, and a highly sensitive technique is required. In addition, the reaction is expected to have a significant dependence upon the partial pressure of oxygen due to oxide formation on the surface. Both of these factors suggest that mass-spectrometric techniques in a moderate vacuum would be a suitable method to follow the vaporization process.

Dynamic kinetic studies have been made by using a mass-spectrometric evolved-gas analysis (EGA) approach.[7] Conventional methods of mathematical analysis of thermogravimetric data[8] can be readily adapted to this EGA technique. Of the methods designed to analyze the major portion of the reaction, i.e., from a fraction reacted (α) of 0.05 to 0.95, the Ozawa method[9] can also be used to measure the early stages of the reaction, $0.0001 \leq \alpha \leq 0.05$, thus taking advantage of the high sensitivity of the mass spectrometer.

In this work small samples of InP having a relatively high surface area are subjected to linear heating rates from 0.5 to 20 °C min^{-1} under vacuum while the relative intensity of phosphorus evolved is followed mass spectrometrically. A variety of mathematical methods are used to analyze the resulting data.

Experimental Procedures and Results

The sample material used in this study was an (001) InP substrate wafer cut from a single-crystal boule grown by the standard liquid encapsulated Czochralski (LEC) me-

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(1) W. Y. Lum and A. R. Clawson, *J. Appl. Phys.*, **50**, 5296 (1979).

(2) Y. Yamauchi and N. Susa, *J. Electrochem. Soc.*, **128**, 210 (1981).

(3) K. Pak and T. Nishinaga, *Jpn. J. Appl. Phys.*, **18**, 1859 (1979).

(4) K. Pak, T. Nishinaga, and S. Vehiyama, *Jpn. J. Appl. Phys.*, **14**, 1613 (1975).

(5) R. F. C. Farrow, *J. Phys. D*, **7**, 2436 (1974).

(6) W. D. Johnston, Jr., and K. E. Strege, IEEE 38th Device Research Conference, Ithaca, NY, (1980).

(7) D. Price, D. dollimore, N. S. Fatemi, and R. Whitehead, *Thermochim. Acta*, **42**, 323 (1980).

(8) D. W. Johnson, Jr., and P. K. Gallagher, *J. Phys. Chem.*, **76**, 1474 (1972).

(9) T. Ozawa, *J. Therm. Anal.*, **2**, 301 (1970).

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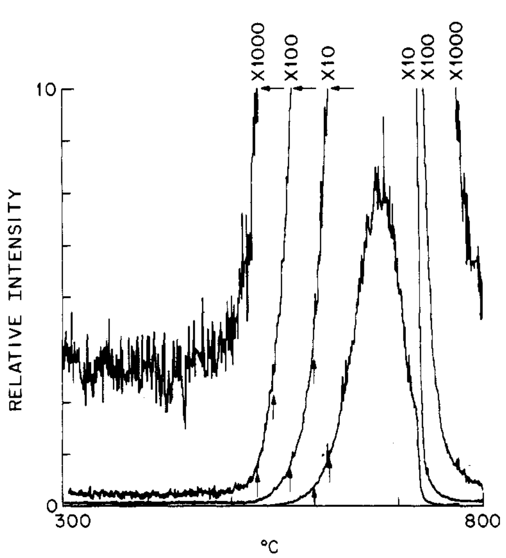

Figure 1. Relative intensity of P_2 as a function of temperature for 0.95 mg of InP heated at 20 °C min^{-1} under vacuum (5×10^{-8} torr). Arrows represent points of analysis (see text and Figure 3).

thod. The crystal was highly doped with sulfur (10^{18-19} atom cm^{-3}) to reduce the dislocation density. The edge of the wafer was cleaved away. This sample of InP was then ground and sieved to pass a 230 mesh screen, ≤36 μm. A surface area of 0.786 m^2 g^{-1} was measured by Kr adsorption (BET technique) using a Micrometrics Model Digisorb 2500.

Several modifications have been made in the EGA system since an earlier description.[10] The furnace controller is a Netzsch Model 411, and a UTI programmable peak selector Model 2054 is used to control the mass spectrometer and to collect and store the data in a digital manner. The analog output from a Fluke Model 2190A temperature digital thermometer was amplified (×10) by a Spectrum Model 1021 electronic filter amplifier and passed to channel one of the programmable peak selector. The background, predominantly water, is about 5×10^{-8} torr in the absence of sample outgassing.

Nominally 1.0-mg samples of InP were weighed and placed in an alumina crucible. The ionizing filaments and furnace controller were turned on when the vacuum was below about 5×10^{-6} torr. Five heating rates were used, 20, 10, 5, 1, and 0.5 °C min^{-1}. Parameters were set on the programmable peak selector to scan mass peak 62 amu (P_2) at four consecutive decades of amplification, 10^7–10^{10} at heating rates ≥5 °C min^{-1} and 10^8–10^{11} for slower heating rates. Mass 62 was selected because it was the most intense of the phosphorus-containing vapor species. The assumption is made that proportions of the various species do not change during the reaction.

The digitized data were transferred to a Honeywell 6000 computer. Programs were developed (1) to plot intensity vs. temperature and (2) to subtract background and integrate these curves to obtain a conventional sigmoidal curve analogous to a weight-loss curve. These latter curves were analyzed over the range $0.1 \leq \alpha \leq 0.9$ by methods previously devised for thermogravimetric data.[8] Figure 1 shows a typical set of the conventional EGA curves (type 1 plots). Figure 2 presents the complete series of integrated curves (type 2 plots). Table I summarizes the results of a Freeman and Carrol[8,11] type mathematical analysis of the curves in Figure 2. In this method the activation energy is derived from the slope and the order of the reaction from the intercept of a plot of d[log (dα/dT)/d[log (1 − α)] vs. d(1/T)/d[log (1 − α)]. The value of the preexponential term is subsequently determined from a separate relationship.

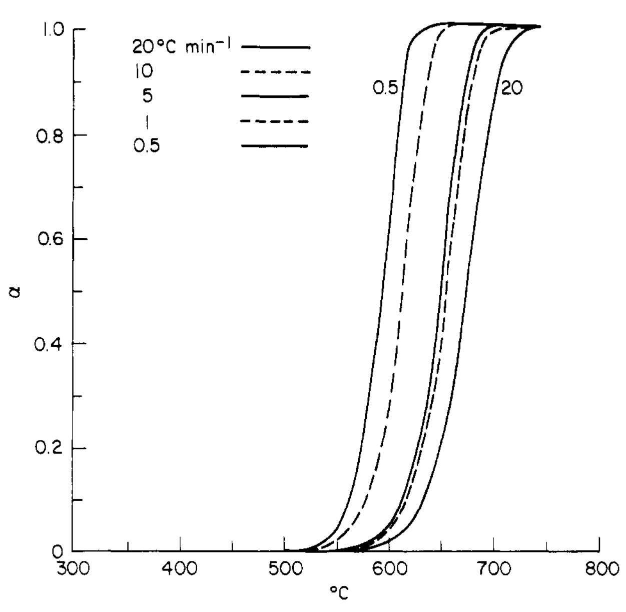

Figure 2. Normalized integrated intensity as a function of temperature for nominally 1-mg samples of InP heated at the indicates rates under vacuum (~5×10^{-8} torr).

TABLE I: Results of the Kinetic Analysis Based upon the Method of Freeman and Carrol,[17] $0.1 \leqslant \alpha \leqslant 0.9$

heating rate, °C min^{-1}	activation energy, kcal mol^{-1}	log pre-exponential, s^{-1}	reaction order
20	67.1	13.41	1.10
10	76.4	15.59	0.93
5	70.4	13.66	0.61
1	80.2	16.55	1.08
0.5	73.4	14.52	0.63

In order to obtain kinetic parameters for the earlier stages of the reaction ($\alpha < 0.1$), the method of analysis proposed by Ozawa[9] was applied to the curves prior to integration (type I). In this approach, the values of temperature at constant fractions reacted are determined for different heating rates. A plot of log heating rate vs. reciprocal temperature will have a slope proportional to the activation energy, E. This method is applicable for any choice of α. Because of the high inherent sensitivity of mass-spectrometric techniques, it was felt that values of α as low as 0.0003 could be utilized. A series of α values was established for use in this method: 0.10, 0.03, 0.01, 0.003, 0.001, and 0.0003.

Values of α were determined by comparison of the cumulative area at different temperatures with the total area using curves such as those in Figure 1. Values of area were normalized for heating rates and sample sizes by dividing the measured areas in ampere minutes by the sample weight in milligrams (A min mg^{-1}). Areas were measured manually by using a planimeter. Measurements were made in triplicate and averaged. It was considered impractical to iterate until the specified value of α was reached. Therefore, a number of measurements were made at convenient points and plotted. The temperature associated with the six specific values of α were then determined by interpolation. Figure 3 is such a plot of values derived from Figure 1. The arrows in Figure 1 indicate the points at which the cumulative areas were measured in order to

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(10) P. K. Gallagher, *Thermochim. Acta*, **23**, 175 (1978).
(11) E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).

TABLE II: Temperature as a Function of Fraction Reacted for Various Heating Rates and the Arrhenius Parameters Calculated by the Ozawa Method[9] (Manual Integration)

heating rate, °C min^{-1}	α =	temp, °C 0.10	0.03	0.01	0.003	0.001	0.0003	
20		632.0	610.2	591.2	570.2	555.1	530.0	
10		617.5	594.3	573.7	551.0	530.4	507.6	
5		615.2	593.7	573.5	553.5	534.0	513	
1		574.5	555.5	538.5	519.5	502.5	483.5	
0.5		559.5	540.5	523.8	504.5	487.5	468.7	
E, kcal mol^{-1}		70.6	70.9	71.6	70.3	70.3	69.6	70.5 av
log A, s^{-1}		14.03	14.03	14.16	13.56	13.76	13.58	13.85 av

TABLE III: Temperature as a Function of Fraction Reacted for Various Heating Rates and the Arrhenius Parameters Calculated by the Ozawa Method[9] (Computer Integration)

heating rate, °C min^{-1}	α =	temp, °C 0.90	0.70	0.50	0.30	0.10	0.03
20		709.2	689.9	675.5	659.7	633.5	610.5
10		679.5	665.0	654.1	640.6	616.6	595.6
5		672.5	659.6	649.9	637.6	614.3	592.2
1		647.9	618.1	613.7	600.9	584.2	556.3
E, kcal mol^{-1}		66.6	68.0	72.1	73.4	76.1	75.0
log A, s^{-1}		13.19	13.54	14.46	14.77	15.39	15.07

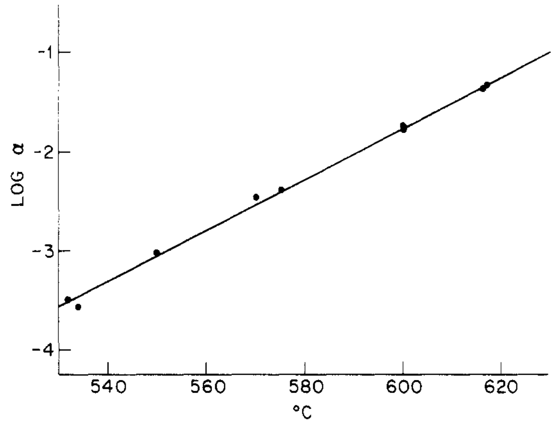

Figure 3. Values of log fraction reacted as a function of temperature for points indicated by arrows in Figure 1.

produce the points in Figure 3. Table II is a compilation of the temperatures determined at each heating rate for the desired values of α, interpolated from curves such as Figure 3.

The Ozawa method could also be used at the higher values of α where the Freeman and Carrol approach had been utilized. In this case, the values of temperature for each desired α could be read directly from the curves in Figure 2. Table III presents these results for α values of 0.03, 0.10, 0.30, 0.50, 0.70, and 0.90. The agreement in the region of overlap of Tables II and III is reasonable. Figure 4 shows typical Ozawa plots based upon a set of data from each of Tables II and III.

Kissinger[12] has developed a method based upon the variation of the temperature at maximum rate (maximum $d\alpha/dT$), T_m, as a function of heating rate. A plot of log (B/T_m^2), where B is the heating rate in °C min^{-1}, vs. T_m^{-1} (see Figure 5) should yield a straight line whose slope is proportional to the activation energy. Doyle[13] has shown

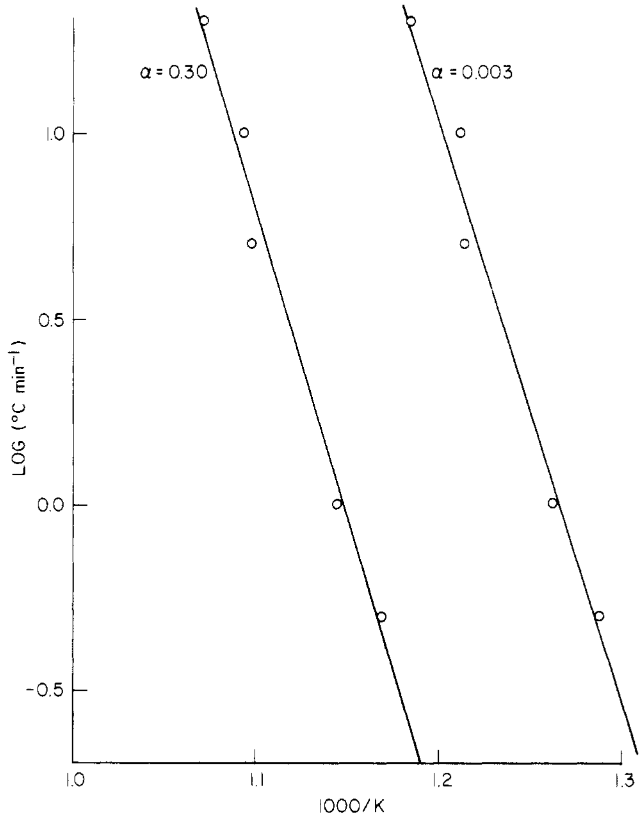

Figure 4. Ozawa-type plots of indicated experiments from Tables II (α = 0.003) and III (α = 0.3).

TABLE IV: Rate Parameters and Results[a] Based upon the Analysis of Kissinger[12]

heating rate, °C min^{-1}	T_m,[b] °C	α_m[c]	reaction order
20	681	0.573	1.36
10	661	0.623	1.05
5	656	0.621	1.06
1	620	0.621	1.06
0.5	600	0.660	0.86

[a] Arrhenius parameters are E = 73.3 kcal mol^{-1} and log A = 14.98 s^{-1}. [b] Temperatures at maximum rate of decomposition. [c] Fraction reacted at T_m.

TABLE V: Some Calculated Kinetic Values for the Decomposition of InP

temp, °C	first-order rate constant, s^{-1}	time to α = 0.9, h	α after 1 h	molecules decomposed per mg after 1 h
350	1.53×10^{-11}	4.18×10^{7}	5.51×10^{-8}	2.28×10^{11}
400	1.04×10^{-9}	6.16×10^{5}	3.74×10^{-6}	1.55×10^{13}
450	3.94×10^{-8}	1.62×10^{4}	1.42×10^{-4}	5.87×10^{14}
500	9.34×10^{-7}	6.85×10^{2}	3.35×10^{-3}	1.38×10^{16}
550	1.51×10^{-5}	4.25×10^{1}	5.28×10^{-2}	2.18×10^{17}
600	1.77×10^{-4}	3.62×10^{0}	4.70×10^{-1}	1.94×10^{18}

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(12) H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).

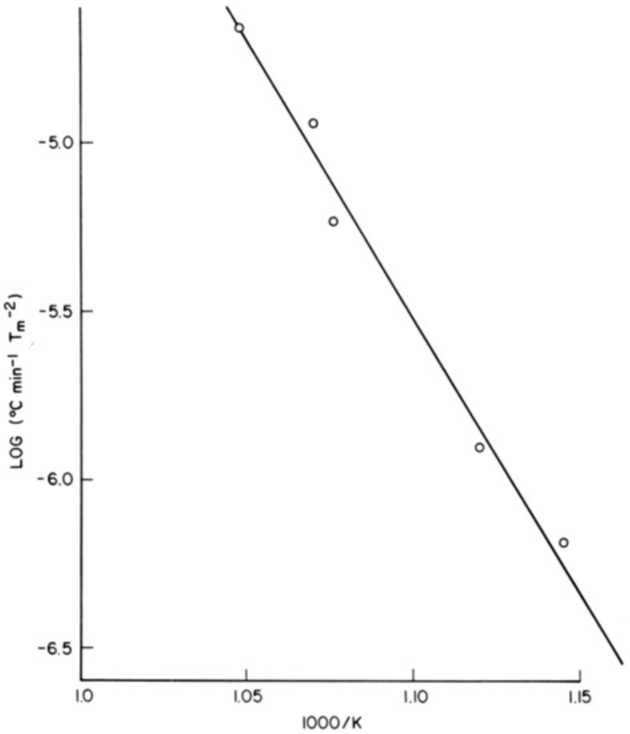

Figure 5. Plots of Kissenger-type analysis for the decomposition of InP at different heating rates (see Table IV).

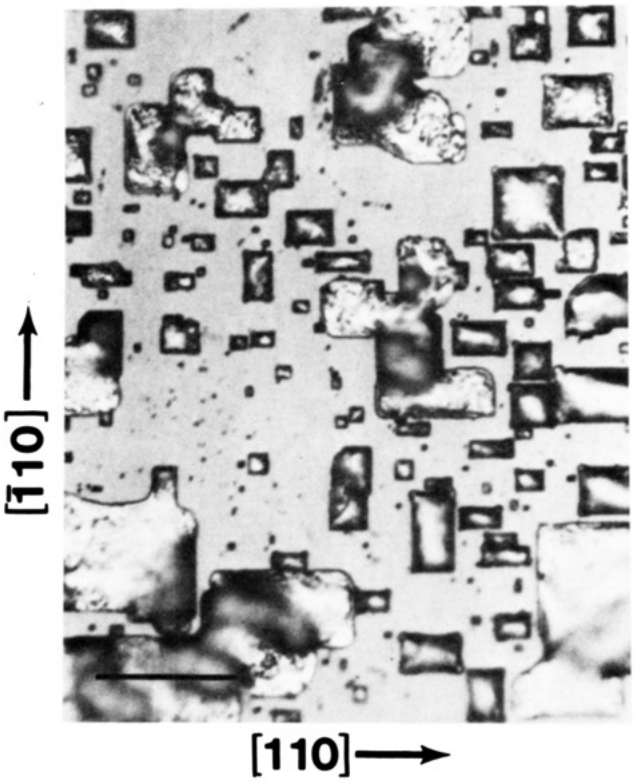

Figure 6. Optical micrograph of previously polished surface after some decomposition (α = 0.01). Marker represents 50 μm.

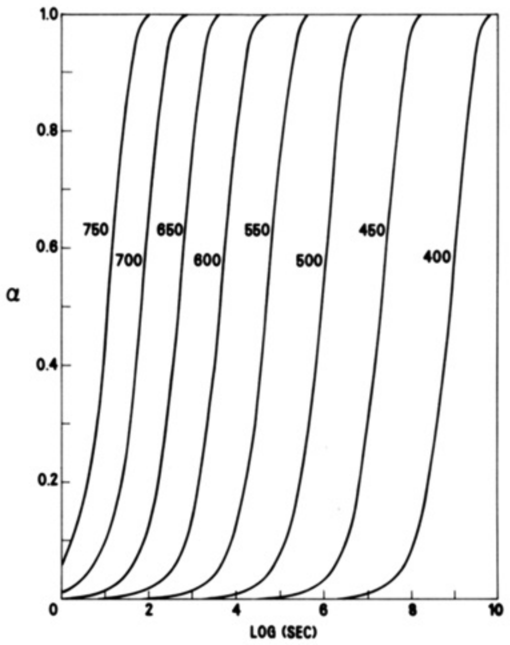

Figure 7. Calculated isothermal decomposition curves for InP.

that the order of the reaction, n (other than precisely unity), can be obtained from the value of $\alpha(\alpha_m)$ at T_m. Values of T_m and α_m are given in Table IV along with the values of E and n derived therefrom. An experiment using a small polished disk was stopped after reaching $\alpha = 0.01$ and the sample examined by Nomarski interference-contrast microscope. Figure 6 shows the surface after this decomposition. Some calculated kinetic values for the decomposition of InP are listed in Table V.

Discussion

Arriving at accurate kinetic parameters for solid-state reactions has always been a matter of concern. The temperature dependence of the reaction rate is generally described by the Arrhenius equation (eq 1), where k is the

$$k = Ae\ -E/RT \qquad (1)$$

rate constant, E the activation energy, and A the preexponential term. The wide spread in reported values of activation energy and preexponential term for the same reaction studied by various investigators is well-known.[14] It has been noted that there is frequently a relationship between the reported values of E and A for the same reaction. This relationship, eq 2, where a and b are con-

$$\log A = aE + b \qquad (2)$$

stants, has been referred to as "the kinetic compensation effect" and extensively discussed.[15-17] Recently, Arnold[18] et al. and Sestak[19] have shown that this relationship arises, at least partially, from the mathematically ill-conditioned nature of the Arrhenius equation (eq 1). Very accurate data are required to obtain unique values for A and E.[18] Less precise data yield a zone of probable values which approximate that defined by eq 2. This ill-conditioning has a major impact if unique values of A and E are required for mechanistic evaluation and/or chemical implications. If, however, the purpose is to determine rate

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(13) C. D. Doyle in "Techniques and Methods of Polymer Evaluation", Vol. 1, P. E. Slade and L. T. Jenkins, Eds., Arnold, London, 1966, p 113.

(14) P. K. Gallagher and D. W. Johnson, Jr., *Thermochim. Acta*, **6**, 67 (1973).

(15) J. Zasko, E. Kekedy, and C. Varhelyi in "Proceedings of the III International Conference of Thermal Analysis, Pavos, Switzerland, Aug 1971", H. G. Wiedermann, Ed., Birkhauser Verlag, Basel, 1972, p 487.

(16) P. D. Garn, *J. Therm. Anal.*, **7**, 475 (1975).

(17) P. K. Gallagher and D. W. Johnson, Jr., *Thermochim. Acta*, **14**, 255 (1976).

(18) M. Arnold, G. E. Versess, J. Paulik, and F. Paulik in "Thermal Analysis", Vol. 18 H. G. Wiedemann, Ed., Birkhauser Verlag, Basel, 1980, p 69.

(19) J. Sestak, in "Thermal Analysis", Vol. 1, H. G. Wiedemann, Ed., Birkhauser Verlag, Basel, 1980, p 29.

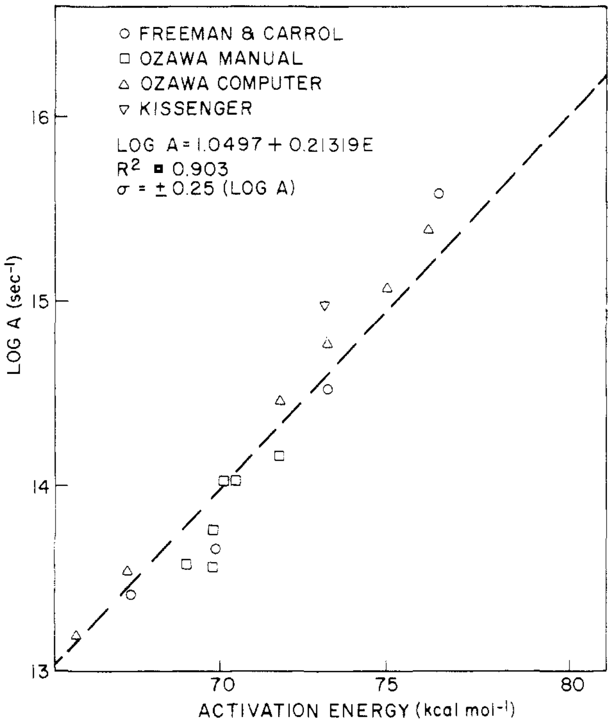

Figure 8. Kinetic compensation effect plot of the Arrhenious parameters.

constants at other temperatures, not far from the experimental range, then the ill-conditioning is not a factor.

The data in Tables I–IV have been plotted in Figure 7 according to eq 2. Clearly the data herein basically conform to the kinetic compensation effect. The line in Figure 6 corresponds to the least-squares fit to the 18 points, and the resulting values of a and b are given. Values derived from application of the Ozawa method with the manual integration of type I curves (Table II) gave the most internally consistent values. In addition, these values were derived from data during the early stages of the reaction. Hence, the average values of E and log A, 70.5 kcal mol^{-1} and 13.85 s^{-1}, respectively, from Table II are used in the subsequent discussion. Values for the order of the reaction (see Tables I and IV) clustered around unity. Consequently, pseudo-first-order kinetics (i.e., the rate of decomposition is proportional to the amount of unreacted material remaining (eq 3) is also assumed.

$$kt = \ln (1 - \alpha) \qquad (3)$$

Using the sample weight, surface area, and density of InP, one can equate the powdered samples in this study to a wafer approximately 2 cm square and 0.5 μm thick if exposed on both sides or 2.8 cm square and 0.25 μm thick if only one surface is considered. The extent of isothermal decomposition under vacuum can be calculated from the combination of eq 1 and 3 using the average values of E and A from Table II. Some selected examples are shown in Figure 8. These plots are based upon several assumptions, e.g., that the mechanism does not change, that a vacuum is present, that there are no significant orientational effects, that the sample was representative, etc. These uncertainties coupled with the ill-conditioned nature of the Arrhenius equation make the plots presented in Figure 8 approximations. They should, however, offer guidelines for those concerned with the processing of InP.

To have an idea of the decomposition rate at the typical VPE growth temperature, which is 700 °C, Figure 8 shows a 10% loss of phosphorous in a period of 10 s. In converting into atoms cm^{-2}, it corresponds to 90 monolayers on (100) surface of 30 monolayers cm^{-2} on (111) surface which were decomposed, assuming homogeneous decomposition. Therefore, the surface decomposition at VPE growth temperature is indeed a serious problem. The indium metal which is left on the surface will be trapped at the interface when the growth commences and cause interfacial problems.

At 400 °C, annealing for 1 h only decomposes 10 ppm of a monolayer per cm^2, which is consistent with the surface morphology studies[1] where no sign of decomposition was observed.

Comparing to the annealing studies in the H_2 ambient, Lum et al.[1] showed that, for Fe-doped InP substrate annealed at 700 °C for 30 min, rectangular pits with aspect ratio of 2 were formed on (100) surface. The density of the pits is approximately 10^5 cm^{-2} with an estimated average size of 20 × 10 μm^2 and ~10 μm deep. The estimated number of pits using the average Arrhenius parameters under vacuum is of the same order of magnitude. However, the pits observed in Figure 6 show elongation in both [110] directions in contrast to the previous work.[1] Accumulation of In in the pits is obvious.

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