

## MP24

### Low Pressure Pyrolysis of Alternative Phosphorous Precursors for Chemical Beam Epitaxial Growth Of InP and Related Compounds

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#### Introduction

The most widely used phosphorous source in chemical beam epitaxy (CBE) is phosphine ( $\text{PH}_3$ ). However, because it is highly toxic, alternatives to phosphine have been sought for the growth of phosphorous-containing compounds. We have investigated the pyrolysis rates and reaction products, in low pressure conditions, of three alternative phosphorous precursors: tertiarybutylphosphine (TBP), bisphosphinoethane (BPE) and trisdimethylaminophosphorous (TDMAP).

#### Experimental

The reactor used in the low pressure pyrolysis studies consists of a helical quartz tube uniformly heated inside a Thermolyne furnace. The tube has an inside diameter of 0.4 cm and the length of the heated region is 57 cm. Vacuum is produced by a diffusion pump with a pumping speed of 150 l/s and a mechanical roughing pump. The decomposition products were studied using a quadrupole mass spectrometer with an ionization energy of 70 eV. The source gasses were introduced via a leak valve and the pressure at the inlet end of the tube was measured with a Baratron capacitance manometer. No carrier gas was used in these experiments. The pressures at the inlet end of the tube were  $< 10$  mtorr for all experiments.

#### Results

Figure 1 shows the percent decomposition vs. temperature for the three sources studied.  $T_{50}$ , the temperature at which the source is 50% pyrolysed, is 475, 500 and 550 °C for TDMAP, BPE and TBP, respectively. All three sources are believed to decompose via first-order, homolytic reactions (see below). Thus, the variation in  $T_{50}$  between the three compounds reflects the differences in phosphorous-ligand bond strength.

#### TBP Pyrolysis

Previous studies of TBP pyrolysis have been conducted at atmospheric pressure [1]. In the low pressure conditions of CBE, heterogeneous reactions are expected to dominate the decomposition process and both the reaction rates and the products may differ significantly from those found at atmospheric pressure. The effect of the surface composition on the pyrolysis rate can be seen in figure 2, which shows the percent decomposition of TBP vs.

temperature for three different pyrolysis conditions. Curve A was calculated from the

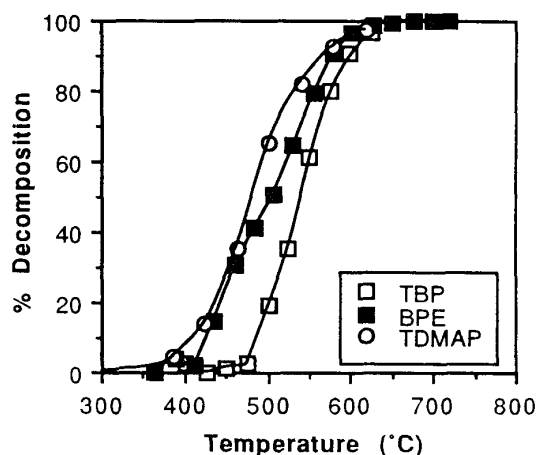


Figure 1. Temperature dependence of percent decomposition of phosphorous precursors at low pressure.

Arrhenius parameters for the first-order reaction at atmospheric pressure [1] using a residence time of 1.5 seconds, appropriate for the low pressure reactor. Curve B shows the experimental data for the low pressure reaction on a quartz surface. Curve C shows the results for low pressure pyrolysis on a deposited InP layer. As can be seen in the figure, pyrolysis on the InP surface occurred at about 100 °C lower temperatures than on the quartz surface.

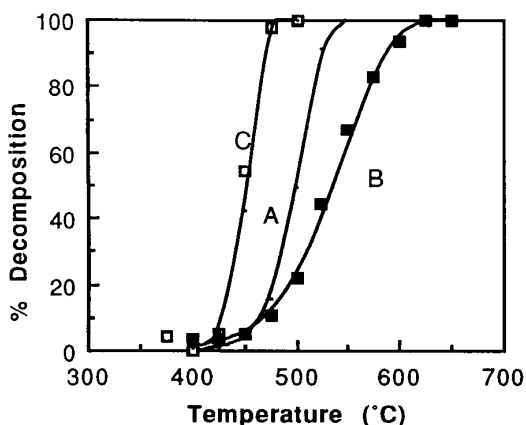


Figure 2. Percent decomposition of TBP for three different pyrolysis conditions.

For the pyrolysis of TBP on a quartz surface, the major products observed were  $\text{PH}_3$ , isobutene ( $\text{C}_4\text{H}_8$ ) and  $\text{H}_2$ . Figure 3 shows the mass spectrum of TBP pyrolysis products at 625 °C. These products are consistent with those observed in previous atmospheric pressure studies [1], in which the input partial pressure of TBP was less than 2.0 torr.

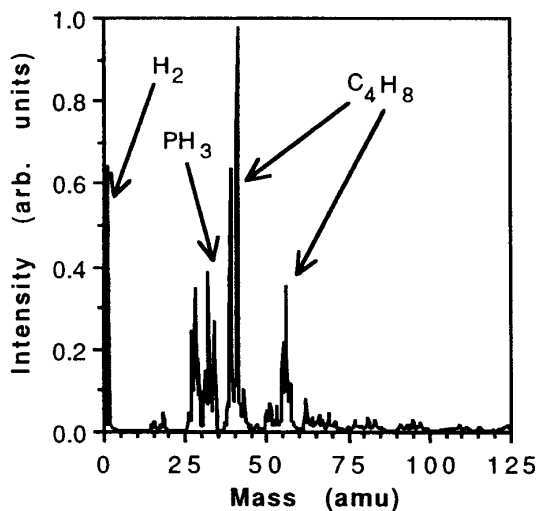


Figure 3. Mass spectrum of TBP pyrolysis products at 625 °C.

The products can be accounted for by the following mechanism:



Reaction 1, homolysis of the TBP molecule, is the rate limiting step. An alternative mechanism, postulated for the decomposition of tertiarybutylarsine at atmospheric pressure [2], is the  $\beta$ -hydrogen elimination reaction:



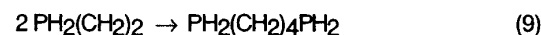
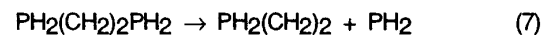
However, this reaction does not account for the presence of  $\text{H}_2$  in the low pressure pyrolysis products.

No significant amount of  $\text{P}_2$  or  $\text{P}_4$  was detected during TBP pyrolysis, even at temperatures high enough to decompose the  $\text{PH}_3$ . This absence is believed to be due to the formation of a phosphorous-containing polymer on the cool quartz surfaces adjacent to the heated portion of the tube. A yellow-brown deposit was observed in these areas.

#### BPE Pyrolysis

Two phosphorous-containing compounds were produced during pyrolysis of BPE. These are shown in figure 4. One of the compounds,  $\text{PH}_3$  was generated over the same temperature range as with TBP. The similarity is reasonable since they both contain  $\text{PH}_2$  fragments. The recombination of  $\text{PH}_2$  radicals is presumably the source of the  $\text{PH}_3$ . As with TBP, no significant amount of  $\text{P}_2$  or  $\text{P}_4$  was detected.

The other phosphorous-containing product, bis-phosphinobutane, has a mass of 122 amu. It's occurrence can be accounted for by the recombination of  $\text{PH}_2(\text{CH}_2)_2$  radicals. We believe that the low pressure pyrolysis of BPE occurs via the reactions:



The high molecular weight product formed in reaction 9, bis-phosphinobutane, is considerably

more stable than BPE, and is not completely decomposed until the temperature is in excess of 750°C.

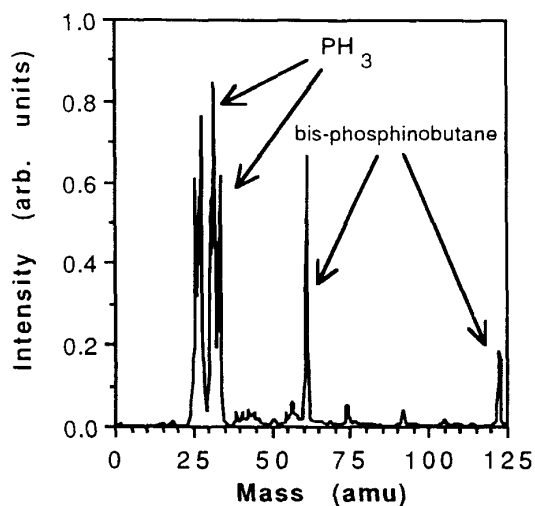
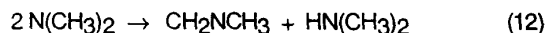
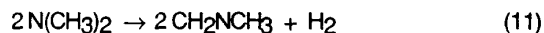
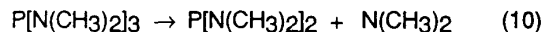


Figure 4. Mass spectrum of BPE pyrolysis products at 650 °C.

#### TDMAP Pyrolysis

The pyrolysis of TDMAP occurs at a slightly lower temperature than TBP or BPE.  $T_{50}$  is 475°C, about 75 °C lower than the  $T_{50}$  of TBP. There were no phosphorous-containing products detected during our pyrolysis studies of TDMAP. As with the other compounds studied, we believe this is because of a polymerization reaction in the cold regions of the pyrolysis tube. The principle peaks in the high temperature mass spectrum of TDMAP (figure 5) occur at 42 and 43 amu.

A mass of 43 amu corresponds to the formula  $\text{CH}_2\text{NCH}_3$ . This could be due to disproportionation reactions 11 or 12 [3,4] between dimethylamine radicals which come from homolysis of the parent molecule (reaction 10),



However, the peak in the mass spectrum at 45 amu, corresponding to the formula  $\text{HN}(\text{CH}_3)_2$ , did not change significantly in height during pyrolysis, indicating that reaction 12 was not significant.

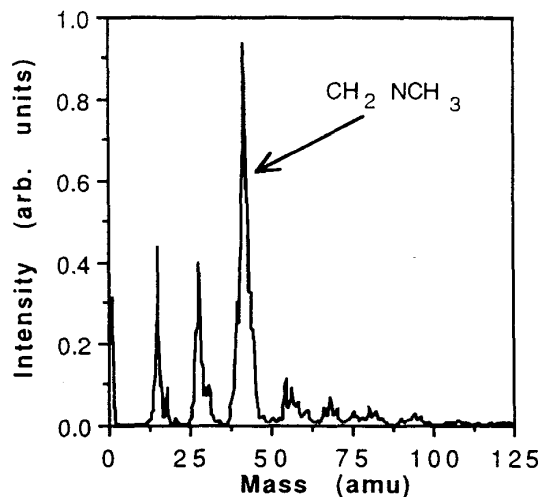


Figure 5. Mass spectrum of TDMAP pyrolysis products at 619 °C.

#### Conclusions

A mass spectrometric investigation of the pyrolysis of three alternative phosphorous sources for CBE has been presented. All three are believed to decompose via homolysis of the parent molecule. In the case of TBP, the major phosphorous-containing species produced under these conditions is  $\text{PH}_3$ . In the case of BPE,  $\text{PH}_3$  and bisphosphinobutane were produced. TDMAP pyrolysis produced no phosphorous-containing species.

#### Acknowledgment

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#### References

- [1] S. H. Li, C. A. Larsen, N. I. Buchan and G. B. Stringfellow, "Pyrolysis of Tertiarybutylphosphine" *J. Electron. Mater.*, Vol. 18, pp. 457-463, 1989.
- [2] C. A. Larsen, N. I. Buchan, S. H. Li and G. B. Stringfellow, "Decomposition Mechanisms of Tertiarybutylarsine", *J. Cryst. Growth*, Vol. 94, pp. 663-672, 1989.
- [3] P. W. Jones and H. D. Gesser, "Reactions of Alkylamino-radicals. Part I. Photolysis of Dialkylamino-compounds", *J. Chem. Soc. (B)*, pp. 1873-1876, 1971.
- [4] W. C. Danen and F. A. Neugebauer, "Aminyl Free Radicals", *Angew. Chem. Internat. Edit.*, Vol. 14, pp. 783-789, 1975.