III-V Cluster Compounds

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The most common semiconductor is *silicon*, which forms a *diamond* lattice.
Semiconductors based in III-V combinations (Al/Ga/In with N/P/As) are becoming more popular because of some special properties:

- fast switching (GaAs)
- blue-light LEDs (Al/Ga N)
III-V Semiconductor Synthesis

Typically made by epitaxial growth from the gas phase:

\[ MR_3 + EH_3 \xrightarrow{\Delta} \frac{\Delta}{-3\text{ RH}} ME \]

This reaction happens in steps:

\[ MR_3 + EH_3 \rightarrow R_3M\cdotEH_3 \]

\[ R_3M\cdotEH_3 \xrightarrow{\Delta}{-\text{ RH}} [R_2MEH_2] \rightarrow (R_2MEH_2)_n \]

\[ (R_2MEH_2)_n \xrightarrow{\Delta}{-\text{ RH}} \text{(RMEH)}_n \]

\[ \text{(RMEH)}_n \xrightarrow{\Delta}{-\text{ RH}} \text{(ME)}_n \]
III-V Semiconductor Synthesis

- The first "acid-base reaction" is fast in solution, not so fast in the gas phase.
- Subsequent steps are slow in any phase.
- High temperatures are required (600-1200°C for nitrides!).

- The product needs to be crystalline. But often bonds initially formed to the surface do not correspond to the ideal diamond lattice. High temperatures are also required for equilibration to the desired structure.

- If the temperature gets too high, some III/V compounds decompose.
III-V Semiconductor Synthesis

- Extreme purity is essential. This means less than 1 ppm of common contaminants in the reactants!

- Metal precursors are typically methyl or hydride derivatives. Larger organic groups often result in incorporation of carbon in the product.

- The group III precursors are pyrophoric, the group V hydrides (except for NH₃) are extremely toxic.
Model compounds for epitaxial growth

- Reaction of $R_3M$ with $R_2NH$ or $RNH_2$ have been used to study models of possible intermediate stages of the condensation.

- The geometries observed are governed mainly by the steric requirements of the substituents.

- The ideal diamond lattice contains only 6-membered $(ME)_3$ rings, but many model compounds contain 4-membered $(ME)_2$ rings.

- Compounds containing 3-coordinate $M$ are probably important intermediates, but most isolated clusters have only 4-coordinate $M$ atoms.
Cyclohexane
Adamantane
Diamantane
Hexagonal prism
Ladder
Failed prism
Fused prisms
Capped prism
Cube
Ladder+