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GAS PHASE REACTION BETWEEN MCl_4 AND NH_3 : MONOMERS OR OLIGOMERS?

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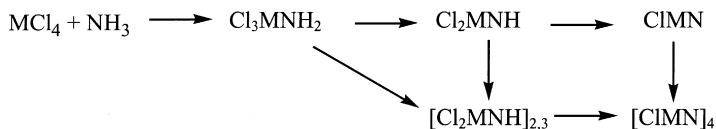
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The technology of nitride films production is based on the reaction of metal tetrachloride with ammonia at high temperatures. The knowledge of the mechanism of the CVD processes is crucial for optimizing experimental conditions to achieve high quality materials. Formation of polymer forms during SiCl_4 ammonolysis was observed experimentally by mass spectrometry.¹ In this work we theoretically investigate gas phase oligomer formation in course of MCl_4 ($\text{M} = \text{Si, Ge, Sn}$) ammonolysis. All calculations have been carried out using the GAUSSIAN 98 program package. The geometries of all compounds were optimized by B3LYP/DZP method and correspond to minima on the potential energy surface.

The following scheme shows possible pathways of gas phase reactions during MCl_4 ammonolysis at high temperatures:



Formation of $[\text{Cl}_2\text{MNH}]_{2,3}$ oligomers from Cl_3MNH_2 is endothermic, but favored by entropy. Therefore, the existence of these dimeric and

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trimeric forms in gas phase is probable only at very high temperatures (1700–3000 K). On the contrary, dimerization and trimerization processes of Cl_2MNH compounds are much more exothermic (by 100–180 kJ mol^{-1}). Formation of trimers is about 40 kJ mol^{-1} more exothermic compared to dimers. Due to highly unsaturated character of M and N in ClMN , formation of cubanes $[\text{ClMN}]_4$ is very favorable energetically ($\Delta G_{(1000)}^0$ is exothermic by 170–275 kJ mol^{-1}). Formation of tetramers according to the reaction $\text{MCl}_4 + \text{NH}_3 = \frac{1}{4} [\text{ClMN}]_4 + 3\text{HCl}$ is highly endothermic, but favored by entropy. Therefore, formation of $[\text{ClMN}]_4$ is feasible at temperatures higher than 1810, 2096 and 2612 K for Si, Ge and Sn, respectively. The analogous reaction for TiCl_4 is less endothermic, so the formation of $[\text{ClTiN}]_4$ is favorable at temperatures higher than 1650 K.²

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