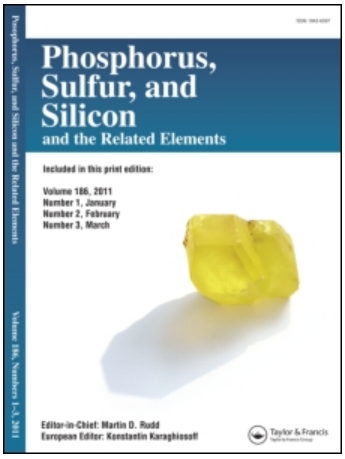

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Online publication date: 12 August 2010

To cite this Article Davydova, E. I. , Timoshkin, A. Y. , Sevastianova, T. N. , Suvorov, A. V. and Frenking, G.(2004) 'GAS PHASE REACTION BETWEEN MCl_4 AND NH_3: MONOMERS OR OLIGOMERS?', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 953 — 954
To link to this Article: DOI: 10.1080/10426500490429013
URL: http://dx.doi.org/10.1080/10426500490429013

Phosphorus, Sulfur, and Silicon, 179:953–954, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490429013

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

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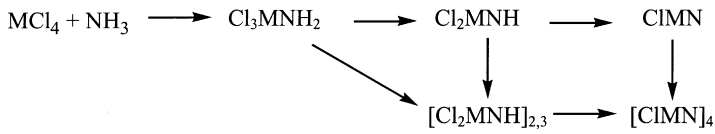
(Received August 17, 2003; accepted October 3, 2003)

Keywords: Cl_2SiNH oligomers; nitride films; DFT calculations

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 observeded experimentally by mass spectrometry.[1] In this work we theoretically investigate gas phase oligomer formation in course of MCl_4 (M = 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 $[Cl_2MNH]_{2,3}$ oligomers from Cl_3MNH_2 is endothermic, but favored by entropy. Therefore, the existence of these dimeric and

This work was supported by the Russian Foundation for Basic Research, grants 01-03-06085 and 00-03-32566. AYT is grateful to the Alexander-von-Humboldt Foundation for a return fellowship and to the St. Petersburg Center for Natural Science for grant PD03-1.3-117. EID is grateful to DAAD for the sponsorship of her research stay in Germany.

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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 $[ClMN]_4$ is very favorable energetically ($\Delta G^0_{(1000)}$ is exothermic by 170–275 kJ mol^{-1}). Formation of tetramers according to the reaction $MCl_4 + NH_3 = {}^1/_4\,[ClMN]_4 + 3HCl$ is highly endothermic, but favored by entropy. Therefore, formation of $[ClMN]_4$ 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 $[ClTiN]_4$ is favorable at temperatures higher than 1650 K.[2]

REFERENCES

[1] S.-S. Lin, *J. Electrochem. Soc.*, **125,** 1877 (1978).
[2] A. Y. Timoshkin, M. Siodmiak, A. A. Korkin, and G. Frenking, *Computional Materials Science*, **27,** 109 (2003).