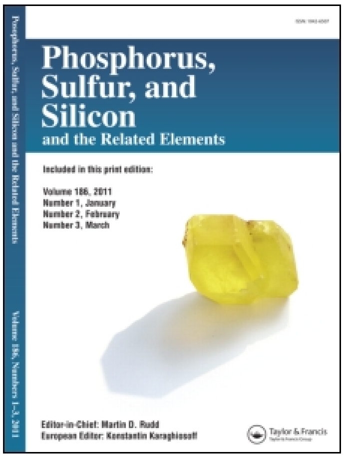

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INORGANIC RINGS AND CLUSTERS AS SINGLE-SOURCE PRECURSORS TOWARD STOICHIOMETRY CONTROLLED SYNTHESIS OF MATERIALS: GAS PHASE CHEMISTRY IN COMMAND

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Potential of the inorganic rings and clusters as single-source precursors to 13–15 binary materials and composites is examined employing quantum-chemical methods. Importance of the gas phase association reactions during MOCVD processes from organometallic and hydride precursors is emphasized. Generation of the gas phase $[HMYH]_n$ *clusters (M = Al,Ga,In; Y = N,P,As) with large oligomerization degree* ($n \geq 30$) *is thermodynamically favorable even at high temperature conditions (1000 K) for all M,Y pairs. High stability of the N-containing clusters makes mixed metal oligomer imidometallanes excellent single-source precursors for the stoichiometry-controlled MOCVD of 13–15 composites.*

Keywords: Gas phase thermochemistry; inorganic rings and clusters; single-source precursors; theoretical study

Processes of the chemical vapor deposition (CVD) are widely used for the production of 13–15 composite materials (such as $Al_xGa_yIn_{1-x-y}N$) for microelectronics (reaction 1):

$$AlMe_3 + GaMe_3 + InMe_3 + NH_3 = Al_xGa_yIn_{1-x-y}N + 3CH_4 \qquad (1)$$

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However, achieving the stoichiometry control (desired Al:Ga:In ratio) in such reactions is still a considerable task. Use of single-source precursors (SSP) that already possess different metal atoms in a desired stoichiometric ratio is expected to solve this problem. Inorganc ring and cluster compounds $[RMYR']_n$ are the most promising candidates. In the present report results of the extensive theoretical studies[1–9] of the model group 13–15 ring and cluster compounds $[HMYH]_n$ (M = Al,Ga,In; Y = N,P,As; $n = 1$–16) are summarized.

RESULTS AND DISCUSSION

Structural and thermodynamic properties of compounds have been predicted at the B3LYP/LANL2DZ(d,p) level of theory. Initial gas-phase reactions between MX_3 and NH_3 (donor-acceptor complex formation, HX elimination processes, formation of dimeric amidometallanes $[X_2MYH_2]_2$) have been considered.[4] It was shown that HX elimination reactions are highly unfavorable for halide substituents, and very favorable in the case of X = H,CH_3. It also was concluded, that hydrogen is a satisfactory model for the methyl group.[9,10] Process of cluster generation starting from group 13 and 15 hydrides (Eq. 2) is highly favorable thermodynamically.[1] Even at 1000 K, Gibbs energies of the process (2) are exothermic for all M,Y pairs.

$$H_3M + YH_3 = {}^1/_n[HMYH]_n + 2H_2 \tag{2}$$

At standard conditions, the most stable clusters are those with $n = 12$ (Y = N), $n = 13$ (Y = P) and $n = 14$ (Y = As).[1] As the temperature increases, hexamers forms in the case of Y = N and trimeric rings in the case of Y = P, As became the most stable.

Analysis of the thermodynamic parameters of the process of cluster oligomerization (reaction 3) reveals, that with increase of the oligomerization degree n, standard enthalpy is approximately constant for $n = 10$–16, while standard entropy linearly decreases after $n = 9$.

$$HMYH = {}^1/_n[HMYH]_n \tag{3}$$

Due to the entropy factor, stability of the oligomers linearly decreases with an increase of the oligomerization degree. It is expected, that higher oligomers will follow the same trend. Therefore, it is possible to estimate the upper values of the oligomerization degree, for which formation of $[HMYH]_n$ clusters will be still thermodynamically favorable. Figure 1 presents trends in Gibbs energy of the process (2) at 1000 K as a function of oligomerization degree n. Nitrogen-containing clusters (especially in the case of Al) exhibit remarkable stability. Note that for

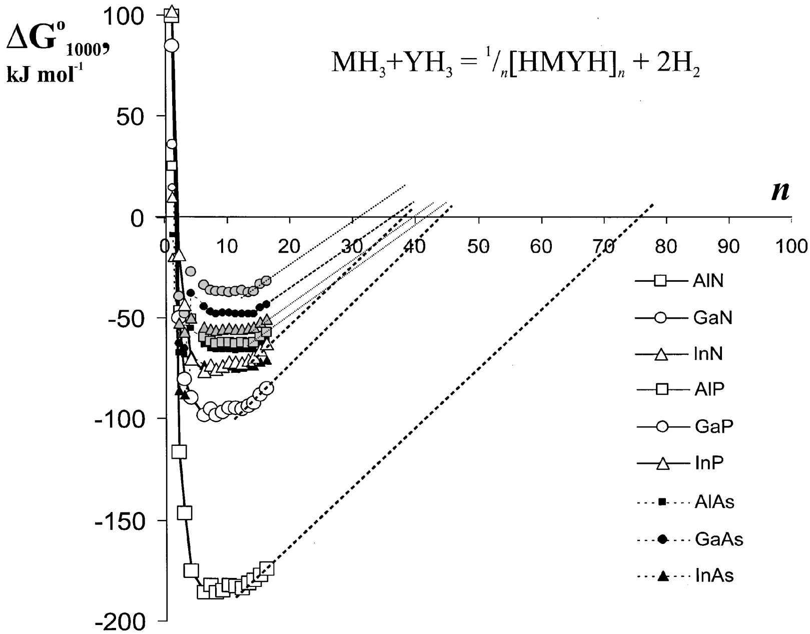

FIGURE 1 Gibbs energy at 1000 K for the reaction (2) (ΔG^o_{1000}, kJ mol^{-1}) versus the oligomerization degree n, and estimation of the highest oligomerization degree, for which formation of clusters is still favorable thermodynamically.

the last members of the oligomer series Gibbs energy increases consistently and monotonically. Assuming that higher oligomers will follow the same trend, one can estimate the highest oligomerization degree for a given M,Y pair by extrapolating (dashed lines, Figure 1) to the point when it cross the x-axis. Values of n, for which formation of oligomer is still favored thermodynamically (compared to MH_3 and YH_3), are maximal for nitrogen-containing clusters ($n = 75, 44, 38$ for M = Al, Ga, and In respectively) and range from 32 to 42 for P-As containing species. Of course, linear extrapolation is only a first, very crude approximation. Nevertheless, it suggests that gas phase generation of high ($n > 30$) oligomers is viable for the all M,Y pairs even at the high temperature conditions. As the temperature decreases, the entropy factor becomes less important, favoring even higher oligomerization degrees. Mixed metal/mixed pnictogen rings and clusters have been studied in case of trimers/hexamers[2] and tetramers,[5] their synthesis also is expected to be viable. Obtained results suggest, that mixed metal nitrogen-containing clusters will be excellent SSP for the production of 13–15 composite nitrides with a desired stoichiometry.

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