Automated Pathway Exploration of Gas-Phase Reaction in AlN Metalorganic Vapor Phase Epitaxy – Initial Decomposition Process of Trimethylaluminum

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Introduction

Accurate modeling of gas-phase reactions in chemical vapor deposition (CVD) is essential for predicting concentrations of precursors and impurity species that reach the substate, as well as for understanding and controlling harmful processes such as particle formation. *Ab initio* calculations can yield thermodynamic stabilities and activation barriers for individual elementary reactions. However, fully elucidating the multi-step reaction pathways—the complete reaction network—requires an empirically constructed reaction model and analyzing each elementary step—a challenging manual task when the network is complex.

Calculation Methods

To address this, we adopted an automated reaction path exploration method (AFIR)[1] and applied it to the AlN metalorganic vapor phase epitaxy (MOVPE) system. The AFIR method induces reactions between the fragment pair using artificial forces iteratively, by applying the AFIR method to the automatically selected them iteratively, reaction pathways are automatically obtained using *ab initio* calculations. This enables systematic acquisition of the reaction network without human intervention. Density functional theory (DFT) calculations were performed using Gaussian16 at the B3LYP/6-31G(d,p) level.

Results and Discussion

Figure 1 shows the reaction pathway network automatically explored from starting systems consisting of trimethylaluminum (TMAl) and ammonia, as well as dimethylaluminum amide ($DMAlNH_2$) and ammonia. In this network, nodes represent numerous intermediate and product species and are color-coded according to the number of carbon atoms bonded to the aluminum atom. Edges connecting the nodes correspond to elementary reactions between those species. Although not shown here, the (approximate) transition states and activation barriers for each elementary step were also automatically obtained. In this way, a systematic investigation of the reaction mechanism—which has traditionally required tremendous effort and has been practically extremely difficult—was successfully achieved in an automated manner. In this presentation, we will describe intermediate species identified by this approach—some of which were not included in conventional AlN MOVPE models—and consider their possible roles and potential impact on growth.

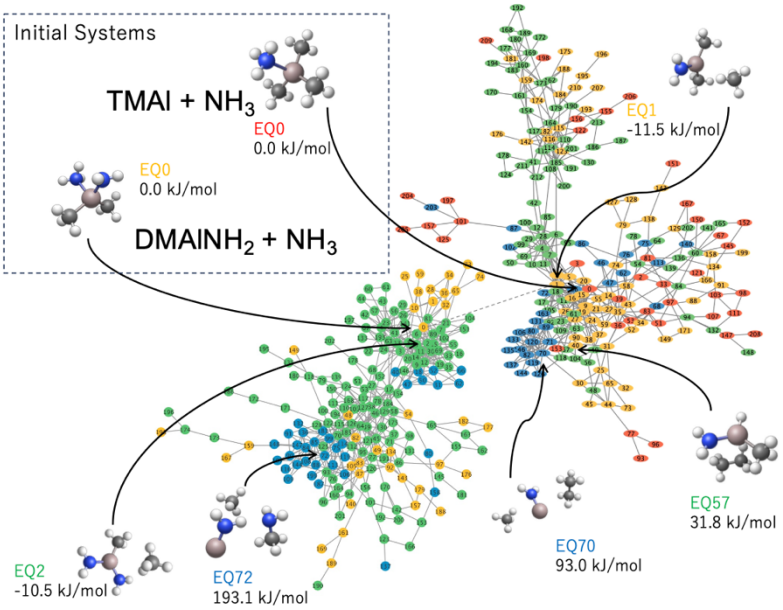

Figure 1. Reaction pathway networks started from TMAl + NH_3 and $DMAlNH_2$ + NH_3 systems.

References

[1] S. Maeda et al., *J. Comput. Chem.* **39**, 233-250 (2018).