Introduction

1. Chemical vapor deposition (CVD) of SiC film and gas phase pyrolysis of silanes.

Pyrolyzing silanes was a critical step in the SiC film production using CVD. Therefore, studying its gas phase pyrolysis mechanism is important.

2. 1,1,2,2-tetramethyldisilane pyrolysis:
   (1) is a potential precursor for the SiC thin film productions.
   (2) might be a good candidate to study the sp²-hybridized Si by producing tetramethyldisilane (Me₃Si=SiMe₃) in situ.

Question:
What’s the role of tetramethyldisilane (Me₃Si=SiMe₃) in the 1,1,2,2-tetramethyldisilane pyrolysis?

Key:
Determining the existence of Me₃Si=CH₂ under unimolecular reaction conditions.

3. Approach:
   (1) Vacuum ultraviolet photoionization mass spectrometry coupled with flash pyrolysis: Unimolecular reactions were predominant!
   (2) Quantum chemistry calculations on the energetics of the decomposition pathways.

Experimental and computational method

1. Vacuum ultraviolet mass spectrometry (VUV-MS) coupled with flash pyrolysis microreactor:

   Advantages:
   1. Mainly unimolecular reactions
   2. Short reaction time (< 100 µs)
   3. Detection of reactive intermediates (supersonic cooling)
   4. Soft ionization (10.45 eV photon)

2. Reaction energetics calculations:
   (1) Geometry optimization and frequency calculations and single point energy calculations: UB3LYP/6-311++G(d,p).
   (2) Transition states verified using intrinsic coordinate (IRC) calculations: UB3LYP/6-311++G(d,p).

3. Quantum calculations suggest that reaction (1) and (2) are the most energetically favorable pathways.

Conclusions

1. Three major initiation pathways for 1,1,2,2-tetramethyldisilane (reaction 1)-(3).

2. Tetramethyldisilane was found to be produced in the pyrolysis of 1,1,2,2-tetramethyldisilane in situ for the first time. The signal of Me₃Si=CH₂ and SiCH₄ were observed as evidence.

3. Possible isomerization and decomposition pathways were examined theoretically.

4. The overall decomposition mechanism was summarized in the Scheme on the right.

Acknowledgement