Silicon hydrides in RMG-Py

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Purpose of today’s study group

- Explain the new capabilities in RMG for Si-H
- Serve as tutorial on how to add new chemistries to RMG
- Feedback / get ready for merging
Vision

• Chemical vapor deposition for semiconductor industry
  • Thin, high quality layer of metal (Si) on substrate
  • Common gases used: SiH₄, Si₂H₆
  • Moving towards chlorinated silanes, Si/Ge CVD
    • What is the detailed chemistry?
    • Want to maximize growth rate, purity of product layer and reduce particle formation
Chemical vapor deposition

$\text{source gas} = \text{Si}_x\text{H}_y$

http://aerosols.wustl.edu, "Generation Mechanism"
Thermochemistry of silicon hydrides

  - Based on ab initio calculations of Katzer et al., *J. Phys. Chem. A*, 1997
  - Same general methodology as Benson
  - Implemented in input/thermo/groups.py
  - Found thermo for some Si-H radicals using QM + CanTherm and put into libraries
Changes in CanTherm

- Si is a recognized element when a geometry is loaded
- Spin orbital coupling energy for Si
- Atomic energies for Si in CBS-QB3 and DFT-g03-B3LYP methods
- Experimental enthalpies of formation
Reaction libraries

• Giunta et al., J. Appl. Phys. 67, 1062 (1990): mechanism from several different CVD experiments of SiH$_4$ and Si$_2$H$_6$

• Dollet and de Persis, J. Anal. Appl. Pyrolysis 80, 460 (2007): pressure-dependent reaction rates from quantum calculations. Mainly focus on Si$_2$H$_4$ but with many other reactions relevant to CVD
Reaction families

• Silylene Insertion
  \[ \text{H}_2 + \text{SiH}_2 \leftrightarrow \text{SiH}_4 \]
  \[ \text{SiH}_4 + \text{SiH}_2 \leftrightarrow \text{Si}_2\text{H}_6 \]

• \( \text{H}_2 \) transfer
  \[ \text{SiH}_4 + \text{H}_3\text{Si-SiH} \leftrightarrow \text{SiH}_2 + \text{Si}_2\text{H}_6 \]

• Silylene-to-Silene isomerization
  \[ \text{H}_3\text{Si-SiH} \leftrightarrow \text{H}_2\text{Si}=\text{SiH}_2 \]

• Some groups and training data added for Hydrogen Abstraction
Experimental comparison

Shock tube data and modeling for high temperature SiH4 CVD
1000 ppm SiH4 in Ar

RMG generated model simulated in Cantera
A factor varied for reaction:
SiH4 $\rightleftharpoons$ SiH2 + H2

Conclusions

• RMG-Py has Si capability, applications in the microelectronics industry

• Additional analysis is needed to get reasonable comparisons with experiment

• I will rebase and make a pull request soon for comments, questions and additions