Silicon hydrides in RMG-Py

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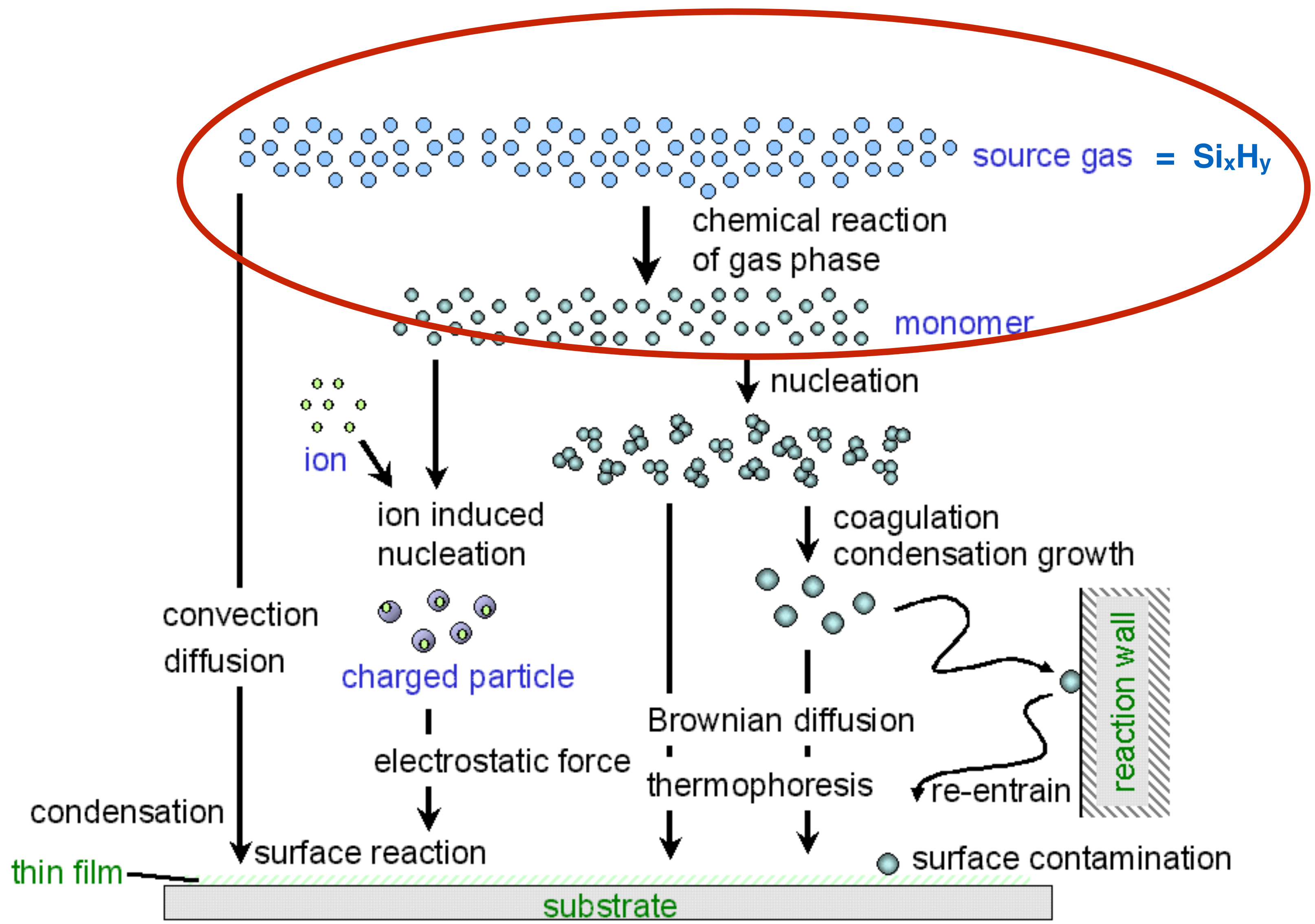
Purpose of today's study group

- 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: SiH_4, Si_2H_6
  - 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



http://aerosols.wustl.edu, “Generation Mechanism”

Thermochemistry of silicon hydrides

- Group additivity values (details in Swihart and Girshick, *J Phys. Chem. B* 1999)
    - 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

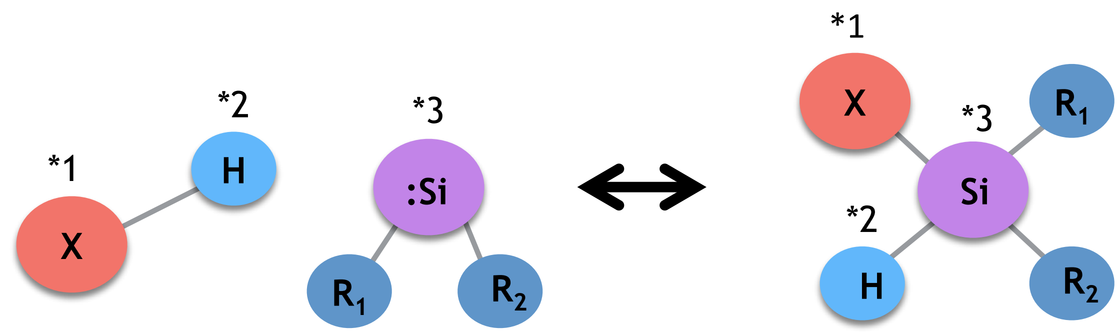
- Giunta et al., J. Appl. Phys. 67, 1062 (1990): mechanism from several different CVD experiments of SiH_4 and Si_2H_6
- Dollet and de Persis, J. Anal. Appl. Pyrolysis 80, 460 (2007): pressure-dependent reaction rates from quantum calculations. Mainly focus on Si_2H_4 but with many other reactions relevant to CVD

Reaction families

- Silylene Insertion

  $H_2 + SiH_2$ <—> SiH_4

  $SiH_4 + SiH_2$ <—> Si_2H_6



Recipe:
- Break bond {*1, S, *2}
- Lose pair {*3, 1}
- Form bond {*1, S, *3}
- Form bond {*2, S, *3}

- H_2 transfer

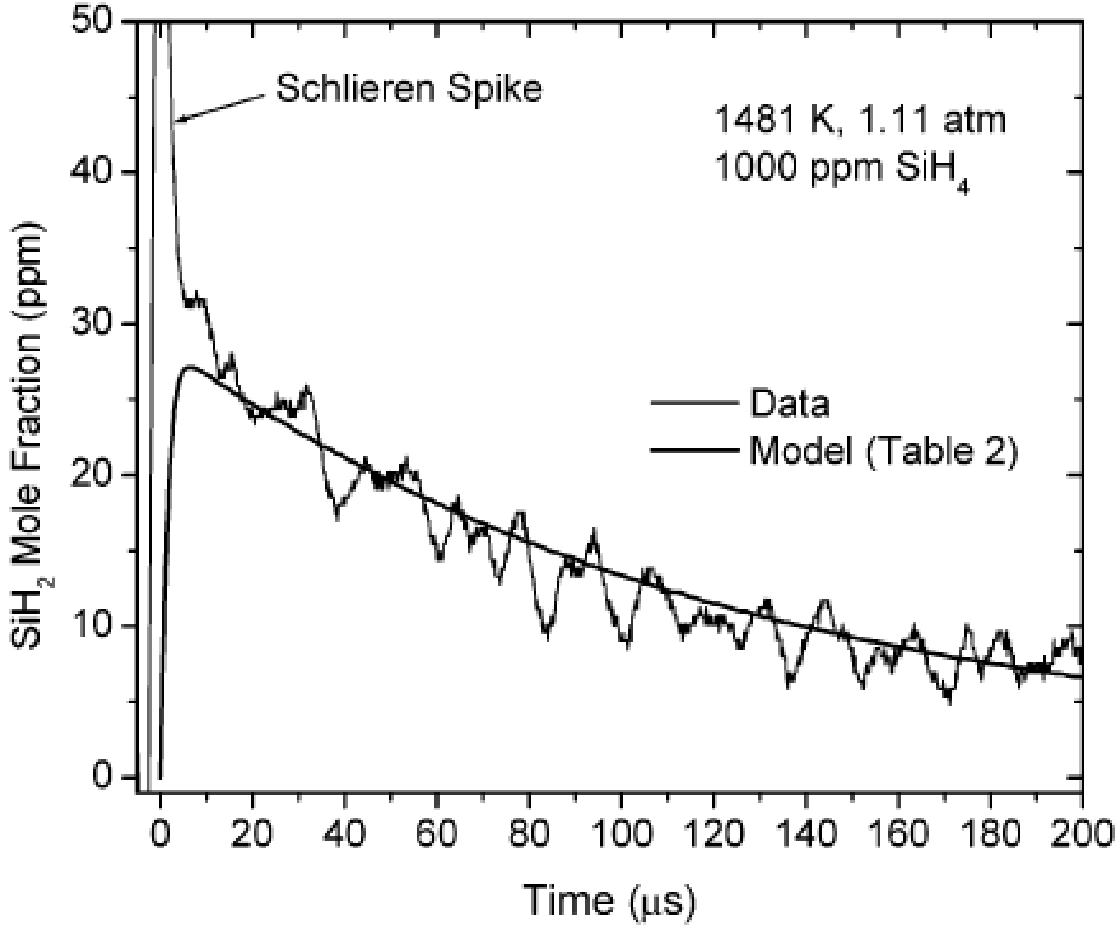
  $SiH_4 + H_3Si\text{-}SiH$ <—> $SiH_2 + Si_2H_6$

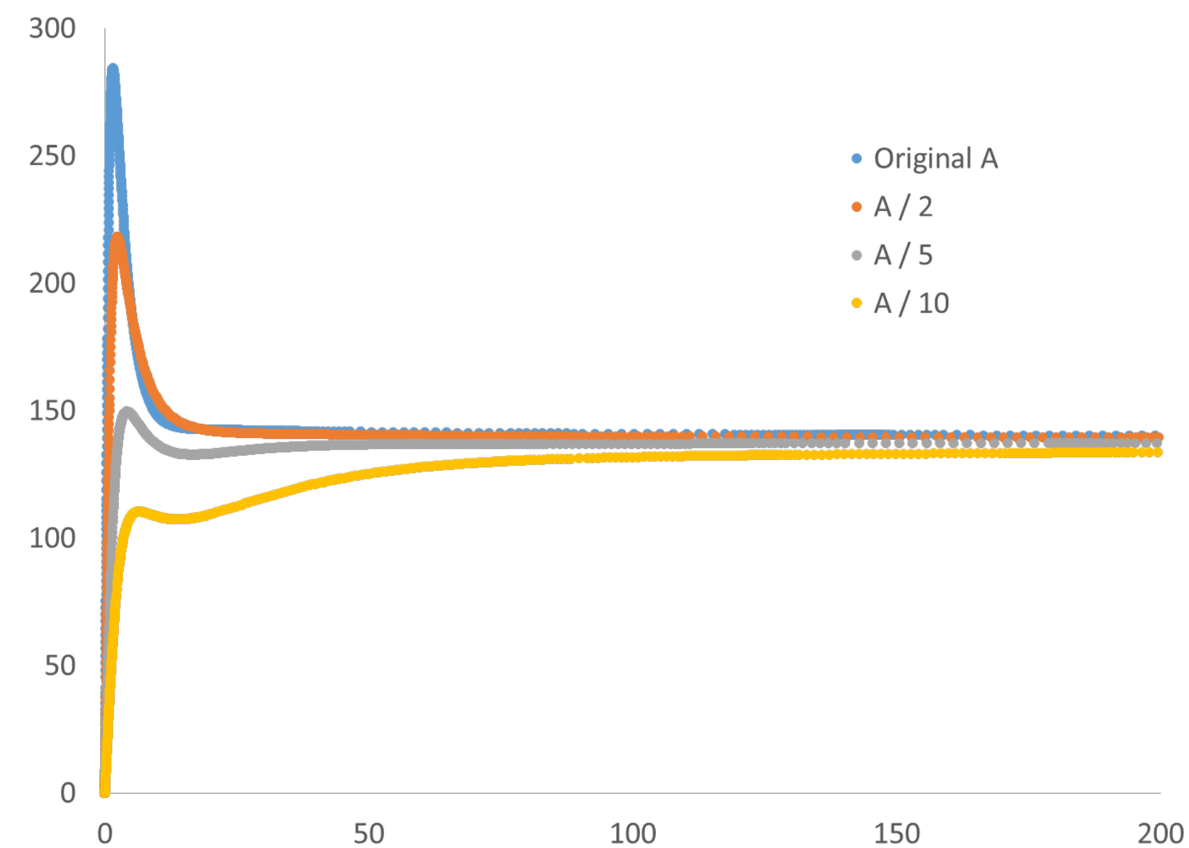
- Silylene-to-Silene isomerization

  $H_3Si\text{-}SiH$ <—> $H_2Si{=}SiH_2$

- 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 <—> SiH2 + H2

Petersen, E.L. and Crofton, M.W. J. Phys. Chem. A 2003, 107, 10988-10995

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