

Final Technical Report

DOE Award DE-SC0013906

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Early Career: Mesoscale Fragments of Crystalline Silicon by Chemical Synthesis

Sponsoring Program Office:

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Executive Summary

Silicon has transformed the modern era, with applications in computing, solar cells, energy storage, and beyond. The traditional approach to making silicon is a high-temperature “top-down” process that affords only the most stable form of silicon, leaving hidden vast swathes of structure-function space. The goal of this program as originally proposed in “Early Career: Mesoscale Fragments of Crystalline Silicon by Chemical Synthesis” was to establish new bottom-up approaches to making silicon-based materials, allowing structural precision from the atomic level up to the bulk, and to understand how structure influences function.

Key results included the development of the cyclosilane building blocks and low-temperature methods for their polymerization, as well as new tools for spectroscopic characterization. Throughout, we coupled experimental work to computation in order to place our fundamental and applied insights on a solid theoretical foundation. A detailed description of research progress is provided below.

In addition to revealing new materials chemistry insights, in the five-year period covered by this award, this program resulted in 11 peer-reviewed publications in high impact factor journals and three graduate student theses. The PI received several awards in recognition of the creative and ground-breaking work performed under this DOE-supported project, including the American Association for the Advancement of Science (AAAS) Mason Award for Women in Chemistry (2017), the Sloan Research Fellowship (2017), and the American Chemical Society (ACS) Award in Pure Chemistry (2021).

Publications resulting from DE-SC0013906

1. Zhou, J.; Folster, C. P.; Surampudi, S. K.; Jimenez, D.; Klausen, R. S.; Bragg, A. E. “Asymmetric charge separation and recombination in symmetrically functionalized σ - π hybrid oligosilanes” *Dalton Trans.* **2017**, 46, 8716.
2. Press, E. M.; Marro, E. A.; Surampudi, S. K.; Siegler, M. A.; Klausen, R. S. “Synthesis of a Fragment of Crystalline Silicon: Poly(Cyclosilane)” *Angew. Chem. Int. Ed.* **2017**, 56, 568.
3. Marro, E. A.; Press, E. M.; Purkait, T. K.; Jimenez, D.; Siegler, M. A.; Klausen, R. S. “Cooperative Noncovalent Interactions Induce Ion Pair Separation in Diphenylsilanides” *Chem. Eur. J.* **2017**, 23, 15633.
4. Folster, C. P.; Klausen, R. S. “Metallocene Influence on Poly(cyclosilane) Structure and Properties” *Polym. Chem.* **2018**, 9, 1938.
5. Marro, E. A.; Press, E. M.; Siegler, M. A.; Klausen, R. S. “Directional Building Blocks Determine Linear and Cyclic Silane Architectures” *J. Am. Chem. Soc.* **2018**, 140, 5976.
6. Purkait, T. K.; Press, E. M.; Marro, E. A.; Siegler, M. A.; Klausen, R. S. “Low-Energy Electronic Transition in SiB Rings” *Organometallics* **2019**, 38, 1688.
7. Marro, E. A.; Klausen, R. S. “Conjugated Polymers Inspired by Crystalline Silicon” *Chem. Mater.* **2019**, 31, 2202.
8. Folster, C. P.; Nguyen, P. N.; Siegler, M. A.; Klausen, R. S. “Tunable SiN Hybrid Conjugated Materials” *Organometallics*, **2019**, 38, 29092.
9. Marro, E. A.; Folster, C. P.; Press, E. M.; Im, H.; Ferguson, J. T.; Siegler, M. A.; Klausen, R. S. “Stereocontrolled Syntheses of Functionalized *cis*- and *trans*-Siladecalins” *J. Am. Chem. Soc.* **2019**, 141, 17926.

10. Dorn, R. W.; Marro, E. A.; Hanrahan, M. P.; Klausen, R. S.; Rossini, A. J. "Investigating the Microstructure of Poly(cyclosilane) by ^{29}Si Solid-State NMR Spectroscopy and DFT Calculations" *Chem. Mater.* **2019**, *31*, 9168.
11. Folster, C. P.; Nguyen, P. N.; Klausen, R. S. "Reductive Halocyclosilazane Polymerization", *Dalton Trans.* **2020**, *49*, 16125.

Other Products from DE-SC0013906

During the period of this award, the PI and personnel supported by the award (postdoctoral scholars and graduate students) delivered invited and contributed oral presentations at national and international meetings and conferences, including the American Chemical Society National Meeting, the Canadian Chemistry Conference, the North American Silicon Symposium, the US-Japan Polymer Symposium, the US-Japan Meeting on Advances in Organic/Inorganic Hybrid Materials, the Polymeric Materials Fusion Conference, and the Reaction Mechanisms Conference. Rebekka Klausen (PI) delivered more than 40 invited seminars at university departments, conferences, meetings, and workshops. In addition, three graduate students completed graduate theses.

1. Press, E. M. 2018 "Expanding the Functionality of Organosilicon Compounds Through the Use of Unconventional Building Blocks", PhD Thesis, Johns Hopkins University, Baltimore, MD.
2. Marro, E. A. 2019 "Strategic Synthesis of Complex Silane Frameworks", Johns Hopkins University, Baltimore, MD.
3. Folster, C. P. 2019 "Synthesis and Properties of Functional Silanes", PhD Thesis, Johns Hopkins University, Baltimore, MD.

Personnel Funded by DE-SC0013906

Over the course of this award (07/15/2015 – 07/14/2020), the PI (Rebekka Klausen), 3 postdoctoral scholars, and 7 graduate students were supported in part or in full by these DOE funds. Three are employed in the chemical industry, one is employed at a US government laboratory, one is pursuing postdoctoral research in academia, and the remainder continue as graduate students. The PI has earned tenure and her DOE-supported work has been recognized with several awards, including the American Association for the Advancement of Science (AAAS) Mason Award for Women in Chemistry (2017), the Sloan Research Fellowship (2017), and the American Chemical Society (ACS) Award in Pure Chemistry (2021).

Review of Technical Achievements

The goal of the research proposed in "Early Career: Mesoscale Fragments of Crystalline Silicon by Chemical Synthesis" was to identify the "bottom-up" synthetic principles that could afford well-defined silicon materials across multiple length scales. Silicon is a ubiquitous semiconductor and energy-relevant material, appearing in computer chips, silicon-lithium batteries, and many other applications. New precursors and new preparative methods have the potential to uncover structure-dependent properties inaccessible by traditional approaches that are limited to the most thermodynamically stable forms of silicon. The originally articulated Specific Aims included: (1) develop innovative cyclosilane building blocks inspired by fragments of the crystalline silicon lattice; (2) identify approaches to modulating band gap/HOMO-LUMO gap through polymerization (especially length-controlled) and/or heteroatom-incorporation; and (3) elucidate structure-dependent properties. Over the course of the award period, the PI systematically investigated all of these specific aims. In particular, the project focused on the development of novel silicon-based

precursors, methods for their polymerization to higher-order materials, and elucidation of unusual structure-dependent physical and optoelectronic properties. We also focused on developing a suite of spectroscopic tools for proof of structure, which included liquid- and solid-state NMR spectroscopy.

Initial work focused on identifying a scalable synthesis of the novel cyclosilane building block **1,4Si₆** (*Angew. Chem. Int. Ed.* **2017**). In the course of this work, we came to appreciate the utility of silane dianions (*Chem. Eur. J.* **2017**), which have proven to be versatile intermediates in the synthesis of several new cyclosilanes, including the isomeric cyclosilane **1,3Si₆** (*J. Am. Chem. Soc.* **2018**), boron-functionalized cyclosilanes (*Organometallics* **2019**), and a dimensionally expanded bicyclic silane (*J. Am. Chem. Soc.* **2019**). Our research under this award has now firmly established general synthetic principles that yield novel functional cyclic building blocks.

Having in hand a family of functional atomically-defined cyclosilanes, we sought to stitch these building blocks together to make well-defined polymeric materials (synthetic control from the atomic to the nanoscale). Catalytic dehydropolymerization proved particularly useful and we demonstrated the ability to control silicon nanomaterial shape (linear vs. cyclic) through the use of either **1,4Si₆** or **1,3Si₆** (*Angew. Chem. Int. Ed.* **2017**; *J. Am. Chem. Soc.* **2018**). We also found that tuning of the catalyst structure could provide linear or branched poly(**1,4Si₆**) (*Polym. Chem.* **2018**). Recently, we also investigated reductive polymerization to obtain nitrogen-functionalized polysilanes (*Dalton Trans.* **2020**).

The pursuit of novel forms of this essential semiconductor requires in parallel development of new approaches to structural characterization that validate the synthetic control. We reported solution-phase ¹H and ²⁹Si NMR spectroscopic characterization that proved poly(cyclosilane)s are precisely and regularly decorated with silicon hydride functional groups. In a subsequent collaboration initiated at a DOE PI meeting (2018) with Prof. Aaron Rossini (Iowa State and Ames Laboratory), we demonstrated the promise of a combined experimental and theoretical approach (*Chem. Mater.* **2019**) employing solid-state NMR spectroscopy. In this work, we identified spectral signatures consistent with poly(**1,4Si₆**) tacticity and assigned diastereomeric relationships on the basis of DFT calculated models and simulated spectra. We have further reported the use of simulated infrared (IR) spectra to support structural assignments (*J. Am. Chem. Soc.* **2018**).

Our synthetic achievements were coupled to property characterization. An early report (*Dalton Trans.* **2017**) using transient spectroscopy and ultrafast time-resolved Raman measurements found that silanes act as electron donors. This work also investigated length-dependent properties arising from increased conjugation in the silane chains. This initial study focused on electron transfer to organic acceptors. Inspired by doping in silicon semiconductors, we also sought to understand the influence of group 13 and 15 substituents. In subsequent studies, we showed that boron can act as an inorganic acceptor (Purkait et al. *Organometallics* **2019**) and that nitrogen can bridge inorganic and organic conjugated systems (Folster et al. *Organometallics* **2019**). Comparison of linear and cyclic polycyclosilanes found not only intriguing optical differences, but also pointed to new ways for architecture to influence materials function. Macrocyclic silanes orient polarized, hydridic groups towards a central pore with promise for ion transport applications (*J. Am. Chem. Soc.* **2018**).

From this summary and the detailed annual reports, this highly productive project yielded major new insights into the construction of new forms of silicon and understanding of how structural-tuning can influence the emergence of desirable new properties in an earth-abundant semiconductor. Research was published in high-impact factor journals. Results were

DOE-JHU-13906

disseminated through presentations by the PI and funded graduate students and postdoctoral scholars.