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14. ABSTRACT

In collaboration with ARDEC Benet Labs, Rensselaer Polytechnic Institute (RPI), and Harvard University, we conducted a systematic investigation of sub-band gap optical response in hyper-doped silicon. Doping silicon with non-equilibrium concentrations of chalcogen atoms (i.e., hyperdoping) yields remarkably strong optical absorptance to wavelengths as long as 5 µm, and measureable photodiode response at wavelengths as long as 1.5 µm. Despite these remarkable properties, photodiode response remains weak at sub-band gap wavelengths shorter

15. SUBJECT TERMS

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Report Title

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ABSTRACT

In collaboration with ARDEC Benet Labs, Rensselaer Polytechnic Institute (RPI), and Harvard University, we conducted a systematic investigation of sub-band gap optical response in hyper-doped silicon. Doping silicon with non-equilibrium concentrations of chalcogen atoms (i.e., hyperdoping) yields remarkably strong optical absorptance to wavelengths as long as 5 µm, and measureable photodiode response at wavelengths as long as 1.5 µm. Despite these remarkable properties, photodiode response remains weak at sub-band gap wavelengths shorter than 1.5 µm, and negligible at longer wavelengths. We adopt a systematic approach to understand sub-band gap optical absorption in hyper-doped silicon. We provided a diagnosis of hyperdoped silicon's potential to achieve the Army's goal of 100% situational awareness, especially in the shortwave-infrared portion of the optical spectrum. Specifically, we performed multiple-wavelength spectroscopy to determine the location and bandwidth of states within hyperdoped silicon's band gap; contactless measurements of carrier concentration to determine whether sub-band gap photon absorption generates mobile carriers; and measurements of the photo-excited carriers transport properties. Using this knowledge, we provide an assessment for hyperdoped silicon as a potential sensor material at wavelengths important to specific Army operational goals, including eye-safe operation (?~1550 nm), replacement of InGaAs (?<1700 nm), and other applications (?>2000 nm).

This research generates a clearer picture of why hyperdoped silicon exhibits such strong sub-bandgap optical absorptance, yet low photoresponse: At very high dopant concentrations, a band crossing occurs, whereby the dopant band crosses the conduction band. This results in an insulator-to-metal transition. At these dopant concentrations, poor photoresponse is expected for traditional device geometries, as sub-bandgap photon absorption either results in "free-carrier absorption" (i.e., no new free carriers are generated) or produces a free carrier that rapidly decays into its original state. At slightly lower dopant concentrations (below the insulator-to-metal transition), there is promise for photodetector applications. However, the current photocarrier lifetime of the material is very low, estimated around or below one nanosecond. Assuming carrier lifetime can be improved to well above a nanosecond, either by defect engineering existing materials or by switching to alternative dopant species, there is promise for sub-bandgap photoresponse, given satisfactory electron mobility (> 10 cm2 V-1 s-1).

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>   <u>Paper</u>

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>   <u>Paper</u>

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

T. Buonassisi, M.T. Winkler et al., "Predictive Defect Engineering for Scalable Photovoltaics at $1/Wp," IBM T.J. Watson Research Center, Yorktown Heights, NY 1/28/2011

T. Buonassisi et al., "Predictive Defect Engineering for Scalable Photovoltaics at $1/Wp," Institute for Solar Energy, Polytechnic University of Madrid, Madrid, Spain 2/8/2011

T. Buonassisi et al., "Predictive Defect Engineering for Scalable Photovoltaics at $1/Wp," Caltech, Pasadena, CA 3/15/2011

B.K. Newman et al., "Sub-bandgap absorptance in chalcogenhyperdoped silicon," March American Physical Society Meeting, Dallas, TX 3/23/2011

M.T. Winkler et al., "Toward chalcogen:silicon intermediate band materials," Black Silicon All-Hands Meeting, Cambridge, MA 4/15/2011

T. Buonassisi et al., "Engineering Silicon Band Structure via Laser Hyperdoping," Night Vision and Electronic Sensors Directorate (US Army), Fort Belvoir, VA 4/29/2011

T. Buonassisi et al., "Engineering Silicon Band Structure via Laser Hyperdoping," Office of Naval Research, Arlington, VA 5/2/2011

T. Buonassisi et al., "Predictive Defect Engineering for Scalable Photovoltaics at $1/Wp," University of Michigan, Ann Arbor, MI 4/22/2011

T. Buonassisi et al., "Engineering Silicon Band Structure via Laser Hyperdoping," DARPA, Arlington, VA 5/6/2011

T. Buonassisi et al., "Crystal Growth Engineering for High-Performance Earth-Abundant Photovoltaic Materials," 5th International Workshop on Crystal Growth Technology, Berlin, Germany 6/28/2011

T. Buonassisi et al., "Materials Challenges in Thin-Film Photovoltaics," Intersolar North America 7/13/2011

Number of Presentations: 11.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received   Paper

02/18/2013   1.00 Daniel Recht, Joseph T. Sullivan, Robert Reedy, Tonio Buonassisi, Michael J. Aziz. Controlling dopant
                    profiles in hyperdoped silicon by modifying dopant evaporation rates during pulsed laser melting,
                    Journal of Applied Physics (02 2012)

02/18/2013   2.00 Elif Ertekin, Mark T. Winkler, Daniel Recht, Aurore J. Said, Michael J. Aziz, Tonio Buonassisi, Jeffrey C.
                    Grossman. Insulator-to-Metal Transition in Selenium-Hyperdoped Silicon: Observation and Origin,
                    Physical Review Letters (10 2011)

TOTAL: **2**

Number of Manuscripts:

Books

Received   Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Joseph T. Sullivan	0.23	
FTE Equivalent:	**0.23**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Mark Winkler	0.67
Bonna Newman	0.15
FTE Equivalent:	**0.82**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics
This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME   PERCENT SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Report
Army Research Office Grant W911NF-10-1-0442
Period of Performance: 9/13/2010 to 9/12/2011

I. Abstract: In collaboration with ARDEC Benet Labs, Rensselaer Polytechnic Institute (RPI), and Harvard University, we conducted a systematic investigation of sub-band gap optical response in hyper-doped silicon. Doping silicon with non-equilibrium concentrations of chalcogen atoms (*i.e.*, hyperdoping) yields remarkably strong optical absorptance to wavelengths as long as 5 µm, and measureable photodiode response at wavelengths as long as 1.5 µm. Despite these remarkable properties, photodiode response remains weak at sub-band gap wavelengths shorter than 1.5 µm, and negligible at longer wavelengths. We adopt a systematic approach to understand sub-band gap optical absorption in hyper-doped silicon. We provided a diagnosis of hyperdoped silicon's potential to achieve the Army's goal of 100% situational awareness, especially in the shortwave-infrared portion of the optical spectrum. Specifically, we performed multiple-wavelength spectroscopy to determine the location and bandwidth of states within hyperdoped silicon's band gap; contactless measurements of carrier concentration to determine whether sub-band gap photon absorption generates mobile carriers; and measurements of the photo-excited carriers transport properties. Using this knowledge, we provide an assessment for hyperdoped silicon as a potential sensor material at wavelengths important to specific Army operational goals, including eye-safe operation (λ~1550 nm), replacement of InGaAs (λ<1700 nm), and other applications (λ>2000 nm).
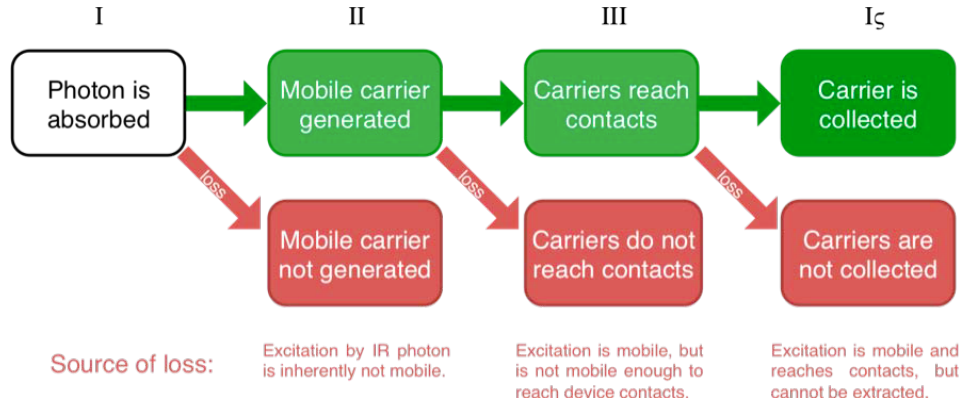
This research generates a clearer picture of why hyperdoped silicon exhibits such strong sub-bandgap optical absorptance, yet low photoresponse: At very high dopant concentrations, a band crossing occurs, whereby the dopant band crosses the conduction band. This results in an insulator-to-metal transition. At these dopant concentrations, poor photoresponse is expected for traditional device geometries, as sub-bandgap photon absorption either results in "free-carrier absorption" (*i.e.*, no new free carriers are generated) or produces a free carrier that rapidly decays into its original state. At slightly lower dopant concentrations (below the insulator-to-metal transition), there is promise for photodetector applications. However, the current photocarrier lifetime of the material is very low, estimated around or below one nanosecond. Assuming carrier lifetime can be improved to well above a nanosecond, either by defect engineering existing materials or by switching to alternative dopant species, there is promise for sub-bandgap photoresponse, given satisfactory electron mobility (> 10 cm^2 V^{-1} s^{-1}).

II. Work Products:
- a) Papers published in peer-reviewed journals: 2
  - E. Ertekin *et al*., "Insulator-to-Metal Transition in Selenium-Hyperdoped Silicon: Observation and Origin," *Physical Review Letters* **108**, 026401 (2012).
  - D. Recht *et al*., "Controlling dopant profiles in hyperdoped silicon by modifying dopant evaporation rates during pulsed laser melting," *Applied Physics Letters* **100**, 112112 (2012).
- b) Papers published in non-peer-reviewed journals: None
- c) Presentations
  - i. Presentations at meetings, but not published in Conference Proceedings:
    - a. T. Buonassisi, M.T. Winkler *et al*., "Predictive Defect Engineering for Scalable Photovoltaics at $1/Wp," IBM T.J. Watson Research Center, Yorktown Heights, NY 1/28/2011
    - b. T. Buonassisi *et al*., "Predictive Defect Engineering for Scalable Photovoltaics at $1/Wp," Institute for Solar Energy, Polytechnic University of Madrid, Madrid, Spain 2/8/2011
    - c. T. Buonassisi *et al*., "Predictive Defect Engineering for Scalable Photovoltaics at $1/Wp," Caltech, Pasadena, CA 3/15/2011
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    - e. M.T. Winkler *et al*., "Toward chalcogen:silicon intermediate band materials," Black Silicon All-Hands Meeting, Cambridge, MA 4/15/2011
    - f. T. Buonassisi *et al*., "Engineering Silicon Band Structure via Laser Hyperdoping," Night Vision and Electronic Sensors Directorate (US Army), Fort Belvoir, VA 4/29/2011
    - g. T. Buonassisi *et al*., "Engineering Silicon Band Structure via Laser Hyperdoping," Office of Naval Research, Arlington, VA 5/2/2011
    - h. T. Buonassisi *et al*., "Predictive Defect Engineering for Scalable Photovoltaics at $1/Wp," University of Michigan, Ann Arbor, MI 4/22/2011
    - i. T. Buonassisi *et al*., "Engineering Silicon Band Structure via Laser Hyperdoping," DARPA, Arlington, VA 5/6/2011
    - j. T. Buonassisi *et al*., "Crystal Growth Engineering for High-Performance Earth-Abundant Photovoltaic Materials," 5th International Workshop on Crystal Growth Technology, Berlin, Germany 6/28/2011
    - k. T. Buonassisi *et al*., "Materials Challenges in Thin-Film Photovoltaics," Intersolar North America 7/13/2011
  - ii. Non-Peer-Reviewed Conference Proceeding publications (other than abstracts): None
  - iii. Peer-Reviewed Conference Proceeding publications (other than abstracts): None
- d) Manuscripts: None
- e) Books: None
- f) Honors and Awards: None
- g) Title of patents disclosed during the reporting period: None
- h) Patents awarded during the reporting period: None

III. Technical Approach; Summary of Goals & Deliverables

From original proposal: Hyper-doped silicon's sub-band gap optical properties have been studied for potential applications for almost 10 years, and yet a complete understanding of the origins of its intriguing optical properties remains elusive. Previous research into hyper-doped silicon has successfully addressed the characterization of individual properties (*e.g.*, the absorption coefficient and dopant diffusion characteristics) or specific applications (*e.g.*, building a prototype detector). However, none of these efforts have produced a sufficiently general description of hyper-doped silicon as to understand the material's ultimate potential or limitations as a detector. Thus we begin by suggesting a new framework for answering these questions. Our framework considers the progression of physical phenomena necessary for the generation of a photocurrent in hyper-doped silicon – beginning with optical absorption and proceeding to carrier generation, transport, and collection. Our specific experimental approach flows examining this framework, and experimentally determining which stage is responsible for the loss of photocurrent that previous researchers have identified. We believe that the framework we are suggesting represents a novel, original approach to understanding hyper-doped silicon.


Research Goal	Experimental approach	Deliverable of proposed work
Determine the optical transition that gives rise to sub-bandgap absorption.	Multi-wavelength spectroscopy, photobleaching of IR absorption, pump-probe spectroscopy	Precise description of optical transition responsible for sub-bandgap absorption; bounds on the lifetime and dynamics of excitation
Identify performance-limiting processes in converting sub-band gap photons to current	Contactless measurements of free-carrier concentration following illumination; measurement of carrier transport parameters	Establishment of whether sub-band gap absorption yields mobile carriers; if so, determine transport limitation to photocurrent collection
Diagnose ultimate potential of hyper-doped silicon as SWIR detector	Modeling / simulation of previous results; optimization of device processing to improve performance	Definitive verdict of hyper-doped silicon's role as a infrared sensor for Army's needs

Table I. Goals and deliverables of the proposed work

IV. Summary of Research Outcomes

a) Multiple-wavelength spectroscopy to determine location and bandwidth of states within hyperdoped silicon's bandgap

At the onset of this project, we identified three possible configurations of the dopant-induced states, represented by the figure below:
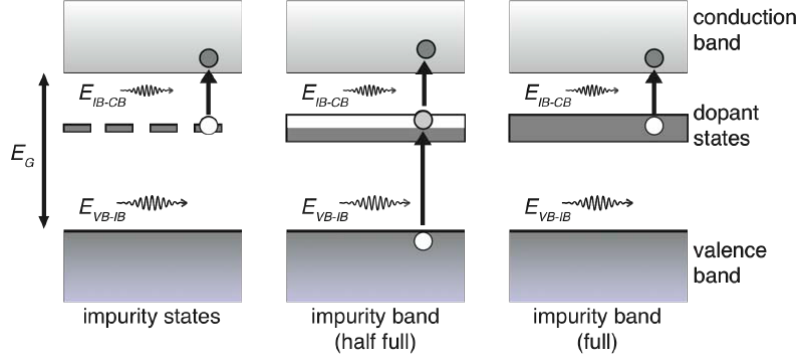

Figure 1. Possible electronic dopant states configurations hypothesized at the onset of the project. Depending on the density of sulfur dopants, the system may undergo a transition to metallic conduction in which the electronic states form a delocalized band. The exact nature of that band (full or partially full) depends on the detailed behavior of the sulfur in the silicon lattice

Using a combination of simulation and experiment, we are fairly confident that sulfur and selenium-hyperdoped silicon is best represented by a more nuanced energy-band diagram, which varies as a function of chalcogen concentration (*x*-axis):
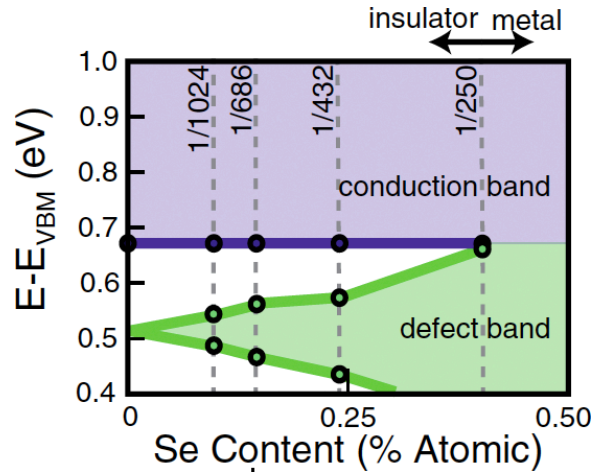
Figure 2. Energy band diagram of chalcogen-hyperdoped silicon, calculated using density-functional theory. From E. Ertekin *et al.*, "Insulator-to-Metal Transition in Selenium-Hyperdoped Silicon: Observation and Origin," *Physical Review Letters* **108**, 026401 (2012).

This energy band diagram is supported experimentally by temperature-dependent Hall-effect measurements on selenium-hyperdoped silicon, demonstrating an insulator-to-metal transition at approximately the chalcogen concentration predicted by theory.
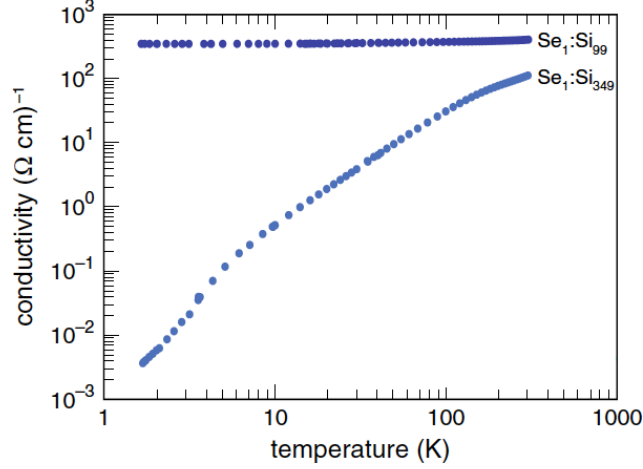
Figure 3. Temperature-dependent Hall effect measurements on selenium-hyperdoped silicon demonstrate an "insulator-to-metal" transition between 1 part per 350 and 1 part per 100 selenium concentration, as evidenced by a dramatic increase in low-temperature conductivity. From E. Ertekin *et al.*, "Insulator-to-Metal Transition in Selenium-Hyperdoped Silicon: Observation and Origin," *Physical Review Letters* **108**, 026401 (2012).

A consistent picture emerges of a system that undergoes an insulator-to-metal transition driven by an overlap of the defect band with the conduction band, resulting in a dramatic increase in low-temperature conductivity and corresponding optical sub-bandgap photoresponse. Thus, **at very high concentrations** (> 1 part per 100), **chalcogen-related states appear not to comprise an isolated deep band of states within the silicon bandgap**.

Next, we attempted a two-photon pump-probe experiment to directly measure the energy position and width of the dopant-induced states within the bandgap. The essence of the experiment is shown below:
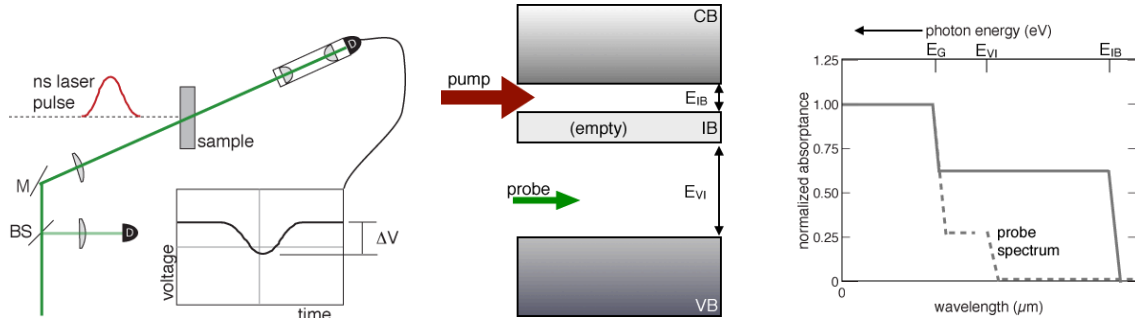
Figure 4. (Left) Schematic of the two-wavelength pump-probe experiment. (Middle) Energy band diagram schematic of the experiment: A pump beam empties the dopant-induced states, and a probe beam promotes electrons from the valence band to the dopant band, measuring the density and energy-width of the dopant band. (Right) A schematic of the expected normalized absorptance spectrum before (solid) and after (dashed) the pump beam. From M.T. Winkler *et al.*, under preparation.

In the subsequent figures, background-subtracted pump-probe measurements ("after" minus "before" the arrival of the pump pulse) are shown at chalcogen doses below and above the insulator-to-metal transition. These results are preliminary and subject to further analysis, yet a few salient points emerge: (1) a clear sub-bandgap signal is observed; (2) It appears that the pump beam is of insufficient brightness to promote all carriers from the intermediate band to the conduction band. While the laser is capable of outputting more power, the sample is irreversibly

5

damaged when increasing incident pump laser power. This result suggests a **very short lifetime of photoexcited carriers from the dopant band into the conduction band**.
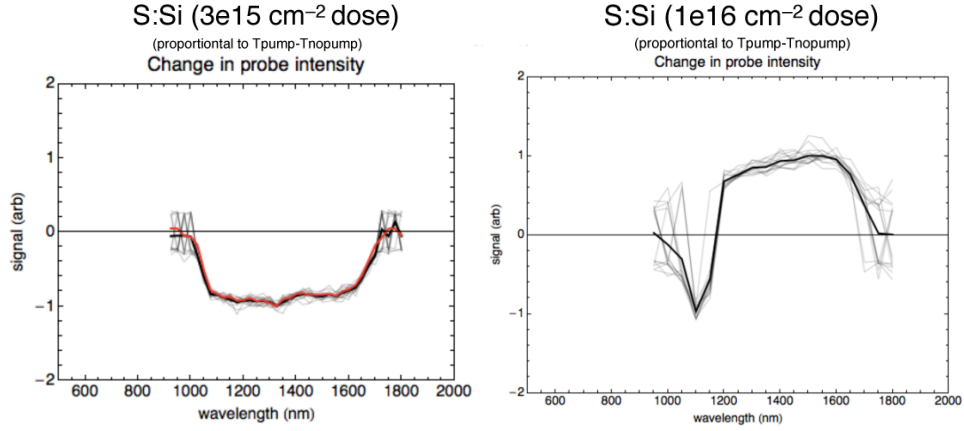
Figure 5. Background-subtracted (after – before) pump-probe spectroscopy measurements of sulfur-hyperdoped silicon. A clear sub-bandgap signal is observed during pump-probe experiments, suggesting the existence of unique defect-induced states within the silicon bandgap. Quantification of such states was impeded by the short minority-carrier lifetime of free carriers, coupled to the finite damage threshold of the material. From M.T. Winkler *et al.*, under preparation.

More recent measurements, outside the scope of this grant, indicate variations in sub-bandgap photoresponse can be observed for varying concentrations of dopant. Of particular interest is the apparent increase in sub-bandgap photocarrier decay time (indicating decreased trapping rate) at dopant concentrations straddling the insulator-to-metal threshold, which indicate an apparent increase of photocarrier decay time.
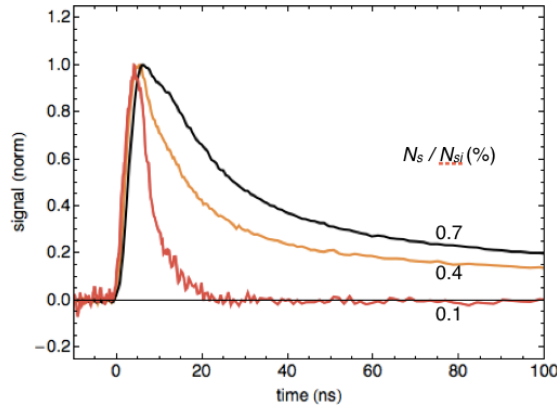
Figure 6. Pump-probe spectroscopy measurements of sulfur-hyperdoped silicon at concentrations crossing the insulator-to-metal threshold, indicating an increase of photocarrier decay time constant with increasing dopant concentration. From M.T. Winkler *et al.*, under preparation.

b) *Contactless measurements of carrier concentration to determine whether sub-bandgap photon absorption generates mobile carriers*

Contactless microwave photoconductivity decay (μ-PCD) measurements were performed at RPI to determine whether free carriers are generated during photoexcitation. It was observed that above the insulator-to-metal transition (after band crossing has already occurred), the background free-carrier concentration is generally too high to measure photoinduced changes of carrier concentration. (Detector fabrication would not be optimized in this regime.) These results were reported elsewhere (D. Recht *et al.*, "Contactless Microwave Measurements of Photoconductivity in Silicon Hyperdoped with Chalcogens," *Applied Physics Express* **5**, 041301, 2012).
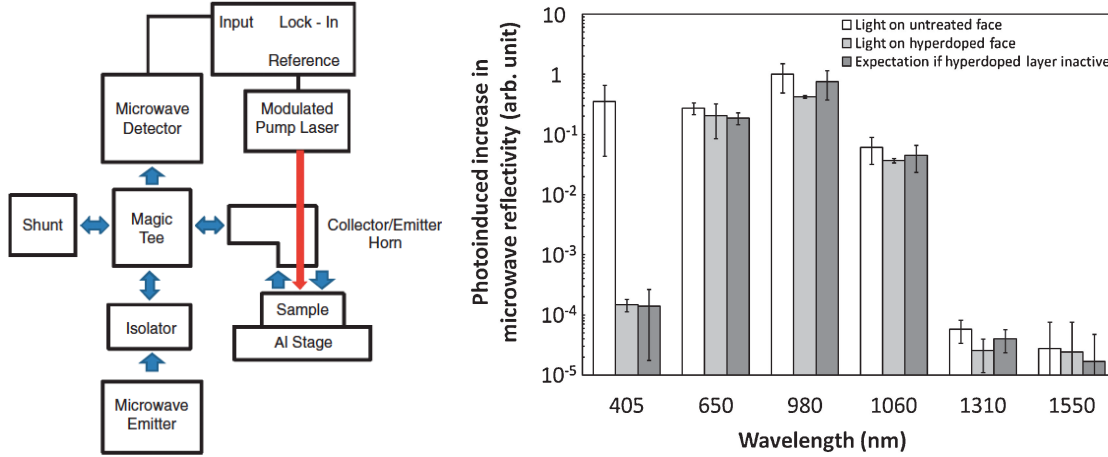
Figure 7. (Left) Schematic of microwave photoconductivity decay (μ-PCD) measurements of chalcogen-hyperdoped silicon. (Right) Results indicating undetectable photogenerated free-carrier concentrations in silicon hperdoped with sulfur and selenium at high [(2–3)×10²⁰ cm⁻³] doses. Figures from D. Recht *et al.*, "Contactless Microwave Measurements of Photoconductivity in Silicon Hyperdoped with Chalcogens," *Applied Physics Express* **5**, 041301, 2012.

The conclusion of these measurements is that while free carriers are generated by incident light, the relative (%) change in free-carrier concentration is too low to be detected. This is due to the **high background carrier concentration, coupled to the short lifetime of photoexcited carriers**.

More recent measurements (outside the scope of this grant) at lower doses of specific dopants suggest that a photoresponse may be detectable at certain wavelengths. Measurements are ongoing.

c) Measurements of the photo-excited carrier transport properties.

Hall-effect measurements were employed to determine temperature-dependent mobilities (carrier transport properties) in hyperdoped silicon materials. Electron mobility measurements suggest a smooth evolution from conduction-band mobility at low doses, to a more complex mobility behavior at higher doses. While electron mobility remains large, the character of transport changes. While mobility appears limited at higher temperatures by ionized impurity scattering (not surprising, given the high carrier concentrations in this material), the temperature dependence suggests carrier transport in the conduction band. Combined with the results reported in Section (a) (DFT and T-dependent conductivity measurements indicating dopant band crossing with the conduction band), a picture emerges of ionized dopants donating their free carriers to the conduction band, where transport is limited at room temperature by ionized impurity scattering. **Carrier mobility is nevertheless high >10 cm^2 V^{-1} s^{-1}, sufficient for most photodetector applications.**
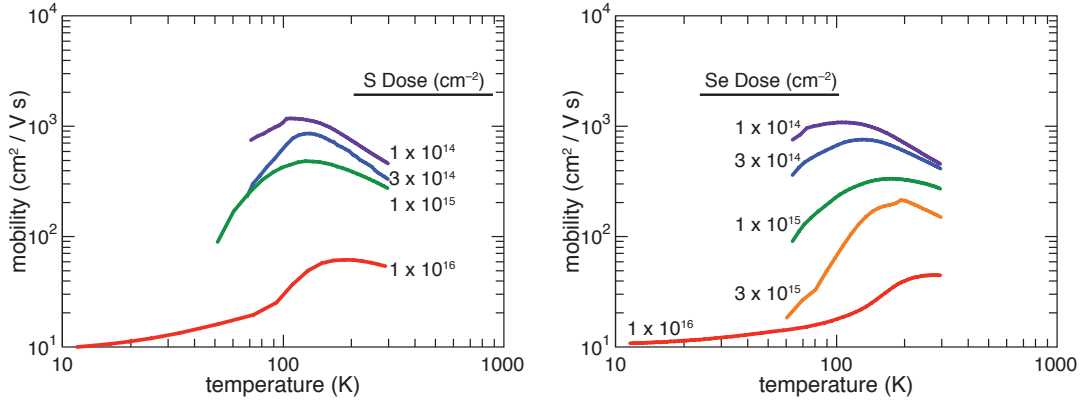
Figure 8. Temperature-dependent mobility measurements for chalcogen-hyperdoped silicon (varying doses) between 60 K and 300 K. From M.T. Winkler *et al*., under preparation.

d) ***Assessment for hyper-doped silicon as a potential sensor material at wavelengths important to specific Army operational goals, including eye-safe operation (λ~1550 nm), replacement of InGaAs (λ<1700 nm), and other applications (λ>2000 nm)***

This research generates a clearer picture of why hyperdoped silicon exhibits such strong sub-bandgap optical absorptance, yet low photoresponse: At very high dopant concentrations, a band crossing occurs, whereby the dopant band crosses the conduction band. This results in an insulator-to-metal transition. At these dopant concentrations, poor photoresponse is expected for traditional device geometries, as sub-bandgap photon absorption either results in "free-carrier absorption" (*i.e.*, no new free carriers are generated) or produces a free carrier that rapidly decays into its original state. At slightly lower dopant concentrations (below the insulator-to-metal transition), there is promise for photodetector applications. However, the current photocarrier lifetime of the material is very low, estimated around or below one nanosecond. Assuming carrier lifetime can be improved to well above a nanosecond, either by defect engineering existing materials or by switching to alternative dopant species, there is promise for sub-bandgap photoresponse, given satisfactory electron mobility ($> 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).