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We report our results of a systematic computational investigation to reveal the origin of and limitations to the subband gap optical absorption of Au-hyperdoped silicon. Doping silicon with non-equilibrium concentrations of atoms (hyper-doping) yields strong optical absorption reaching out to wavelengths in the short and towards the mid infrared regime. Despite this, in gold-hyperdoped materials photodiode response is weak and device quantum efficiencies are low. First-principles density functional theory was used to determine realistic defect structures of silicon hyperdoped with gold, and establish how the electronic structure of the material evolves with increasing

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Report Title

Final Report: STIR: Rapid Identification of Optimal Dopants for Silicon Based Broadband Infrared Detectors via Quantum Mechanical Simulation

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We report our results of a systematic computational investigation to reveal the origin of and limitations to the subband gap optical absorption of Au-hyperdoped silicon. Doping silicon with non-equilibrium concentrations of atoms (hyper-doping) yields strong optical absorption reaching out to wavelengths in the short and towards the mid infrared regime. Despite this, in gold-hyperdoped materials photodiode response is weak and device quantum efficiencies are low. First-principles density functional theory was used to determine realistic defect structures of silicon hyperdoped with gold, and establish how the electronic structure of the material evolves with increasing defect concentration. The optical absorption of the material as a function of dopant concentration was be determined, and the reason for limited absorption identified as defect deactivation resulting from formation of defect clusters and precipitates. The proposed work complements currently on-going experimental efforts at ARDEC Benet Labs and U Dayton at synthesis and characterization of gold-hyperdoped silicon materials. The work will lay the foundation for further design and optimization of hyper-doped silicon materials as potential electronic sensors for the SWIR to the MWIR regime.

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Scientific Progress

See Attachment.

Technology Transfer

The proposed work complements currently on-going experimental efforts at ARDEC Benet Labs at synthesis and characterization of gold-hyperdoped silicon materials. We are regularly in contact with those researchers and intend to continue this work together.

STIR: Rapid Identification of Optimal Dopants for Silicon Based Broadband Infrared Detectors *via* Quantum Mechanical Simulation

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(1) FOREWARD

This document serves as our final report on our ARO STIR program, entitled "Rapid Identification of Optimal Dopants for Silicon Based Broadband Infrared Detectors *via* Quantum Mechanical Simulation". We summarize the objectives of the nine month research effort and the progress in achieving these objectives, as well as plans for continuation of the proposed work.

(2) TABLE OF CONTENTS

(3) LIST OF APPENDIXES, ILLUSTRATIONS, AND TABLES

(4) STATEMENT OF THE PROBLEM STUDIED

As outlined in our original proposal, the focus of this STIR has been to apply quantum mechanical modeling techniques to accelerate the identification of dopants that enhance infrared

sub band gap photoresponse in silicon-based photodetector materials. Hyperdoped silicon, and related materials, are those in which the presence of impurities at concentrations greatly exceeding the solid solubility limit, dramatically alter optical and electronic properties to achieve enhanced sub band gap photoresponse [1-13]. Hyperdoped silicon is typically fabricated using laser-based non-equilibrium synthesis techniques that incorporate large dopant concentrations exceeding the solid solubility limit in silicon by several orders of magnitude. Such materials have applicability to multiple areas related to soldier safety: for example imaging eye-safe lasers, hyper-spectral imaging, standoff explosive detection, and low-light night vision.

Prior work on hyperdoped silicon had largely focused on doping with chalcogens, but our earlier quantum mechanical simulations revealed fundamental limitations to enhanced sub band gap response using chalcogen dopants. First, the impurity bands that arise from the defects are completely filled. Second, these bands appear close to the conduction band maximum and broaden into the conduction band at high doping concentration, causing an undesirable insulator-to-metal transition. Based on these prior insights, we suggested pursuing transition metal dopant species which are more likely to produce the desired electronic structure for enhanced sub band gap photo response: a *mid-gap defect band* that is *partially filled*. Initial work based on these suggestions has focused on Au-doped silicon. However, while the Au-doped systems overcome these earlier limitations, to date they have exhibited far exhibit lower subband gap absorption. Despite the large incorporation of Au and the high crystalline quality of the synthesized systems, external quantum efficiencies (ratio of electrons of current produced per incident photon) are measured to be only 10^{-4} (**FIG. 5b**). The low EQEs suggest that only a small portion of the dopants are active for sub band gap absorption.

Accordingly, the purpose of this STIR was to reveal the reason for the low response measured in Si:Au and identify routes to overcoming the limitations. Our proposal outlined three primary tasks, the first two of which were to be carried out over the nine month STIR period and the third of which was established as a long-term goal for continuation of this effort. These are summarized in Table 1.

	Research Objective	Research Approach	Deliverable
1	(STIR) Prediction of Au concentration vs. optical absorption in Au-hyperdoped silicon photodetectors (Si:Au)	*Density functional theory; semiconductor physics; collaboration with experiment*	*Joint theory/experiment paper on Au dose vs. optical properties*
2	(STIR) Identification of optimal co-dopants to extend the optical response of Si:Au photodetectors	*Density functional theory; semiconductor physics.*	*Guidelines to achieve extended response for experimentalists.*
3	(Long term). Comprehensive assessment of dopants beyond Au for optimized photodetector response in hyperdoped silicon.	*Density functional theory; semiconductor physics; collaboration with experiment*	*Identification of optimal dopants for extending the optical response of hyperdoped silicon.*

Table 1. Description of Research Objectives. Items 1, 2 are research goals, approaches, and deliverables for 9-month STIR effort; Item 3 represents long-term vision.

Our proposed approach was to use first-principles density functional theory (DFT) to determine defect structures and energies, and to calculate the light absorption for a given defect composition in the Au-doped systems to identify the underlying reason for the limited optical response. We hypothesized that substitutional gold defects in silicon are ambipolar, and that the presence of ionized Au species could violate the design rules suggested above. To assess this hypothesis and to achieve the objectives in Table I, the tasks listed in Table 2 were outlined. The proposed computational work has been carried out in collaboration with with current, ongoing experimental efforts at ARDEC Benet Labs.

TASK A: Determine realistic defect composition including charged defect states (Au^{+1}, Au^{0}, Au^{-1}) as a function of total gold concentration in the sample.
TASK B: Given the defect composition, what is the light absorbing capacity of the material as a function of defect concentration? Identify key limiting features.
TASK C: Computational simulation and identification of most promising co-dopant species to recover subband gap absorption.

Table 2. Tasks proposed to be carried out for STIR funding period.

Primary deliverables at the conclusion of the funding period were identified to be a combined theoretical/experimental paper (or series of papers) on the effect of Au doping (concentration) on the optical properties of gold-hyperdoped silicon.

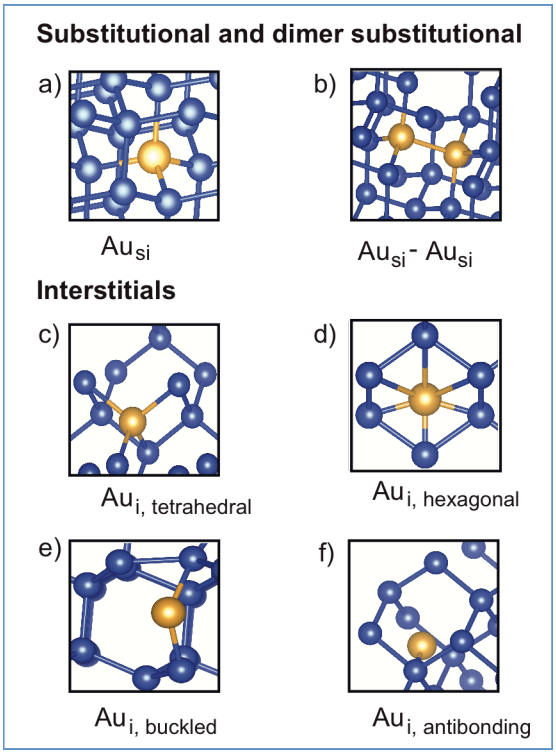

FIG 1. Substitutional and interstitial defect configurations for Au hyperdoped silicon that have been considered in this study.

(5) SUMMARY OF MOST IMPORTANT RESULTS

5a. *Overall Summary and Progress Towards Deliverables.* **The analysis that we have carried out through this effort, in collaboration with closely related experimental work, has helped to identify a possible dominant underlying mechanism for the low sub band gap response in Au-hyperdoped silicon. These insights have further established new guidelines for identification of more highly absorbing defect species that will be considered in our future anlaysis.** Our STIR results are currently being summarized and prepared for two journal publications: (i) one paper of a two-part series (experiment/theory) focusing on identifying the configuration of gold defects in laser processed silicon, and (ii) a joint experiment/theory publication focusing on the concentration-

Configurations	Defect formation energy eV/Au atom
Isolated Substitutional	1.59
Dimer Substitutional	0.74
Tetrahedral Interstitial	2.60
Si-Au-Si Buckled Interstitial	2.91
Vacancy+2 opposite Interstitial Au	1.94

***Table 3**. Formation energies of various configurations of gold defects in silicon according to density functional theory. Simulation supercells containing 250 atoms in the computational domain were considered for this analysis; all defects here correspond to neutral (unionized) configurations.*

dependent optical response of the Au-hyperdoped material. Both of these will be prepared in collaboration with our experimental partners at ARDEC Benet Labs and the group of Prof. Jim Williams at the Australian National University.

Our quantum mechanical modeling indicates that the gold that is incorporated into silicon at ultra-high concentrations is largely accommodated by the lattice in the form of substitutional defects. This finding is in agreement with recent experimental results based on Secondary Ion Mass Spectroscopy (SIMS), which also suggest a substitutional nature of the incorporated Au. Further, we find that while the isolated substitutional defect state would be associated with the desired electronic structure (a partially filled mid-gap defect band) and reasonably large sub band gap absorption, there is a thermodynamic tendency for the substitutional Au to bind together into dimer substitutional pairs. Our results further show that the formation of these dimers is directly coupled to a disappearance of mid-gap defect levels, and a marked reduction in the desired sub band gap absorption. As recent experimental results in the group of Prof. Jim Williams suggest that large clusters of Au-rich regions form in the hyperdoped material upon annealing, and that the deactivation of optical absorption is highly correlated to the formation of these clusters, we suggest that the formation of dimers may occur as an early intermediate stage as the precipitates form during annealing.

The identification of a dominant mechanism for reduced sub band gap absorption now points to additional considerations that must taken into account in our future studies, towards the long term goal of identification of optimal dopants to enhance the optical response of silicon based photodetector materials. It will be important to limit the deactivation of optical absorption by defect clustering and precipitation of defect-rich regions. We note that such deactivation has been observed in the chalcogen doped systems as well. Limiting, minimizing, or otherwise slowing down the deactivation can be accomplished, in principle, either thermodynamically or kinetically:

- *Thermodynamics:* The identification of defects species for which there is a lower thermodynamic driving force for the formation of clusters.
- *Kinetics:* Identify species for which movement through the lattice is associated with larger energy barriers.

In addition to the design rules previously identified, our future work therefore will focus as well on these aspects.

5b. *Detailed Summary of Results.*

Task A. Our characterization of the most likely defect configurations associated with Au-hyperdoped silicon are summarized in Fig. 1 and Table 3. Our results suggest that substitutional Au defects are substantially more stable than interstitials since they have lower defect formation energy under the experimentally observed silicon-rich and gold-rich thermodynamic environment. Additionally, our simulations revealed a strong tendency for isolated substitutional defects to bind together to form substitutional dimers (associated with an energy recovery of around 1.7 eV per Au pair).

Defects in the ionized state were also considered, and consistent with our expectations we find that substitutional Au has an ambipolar nature and can act as a compensating defect: it will become positively ionized (a donor) in p-type material, and it will become negatively ionized (an acceptor) in n-type material. The net concentration of neutral, positively ionized, and negatively ionized species, as determined self-consistently from charge neutrality and mass action. When implanted in an n-type Si substrate (as in Ref. [1]), some of the Au atoms will serve as compensating acceptors, and appear in the negatively ionized state. The doped region will largely be depleted of carriers, and largely intrinsic. However, most of the Au atoms are simply present in the neutral state. Therefore, our original hypothesis for the low sub band gap absorption is likely not applicable to this system, since the defect band is partially filled. Instead, the low sub band gap absorption is, as described above, likely related to dissolution of Au from silicon and the formation of large Au-rich precipitate

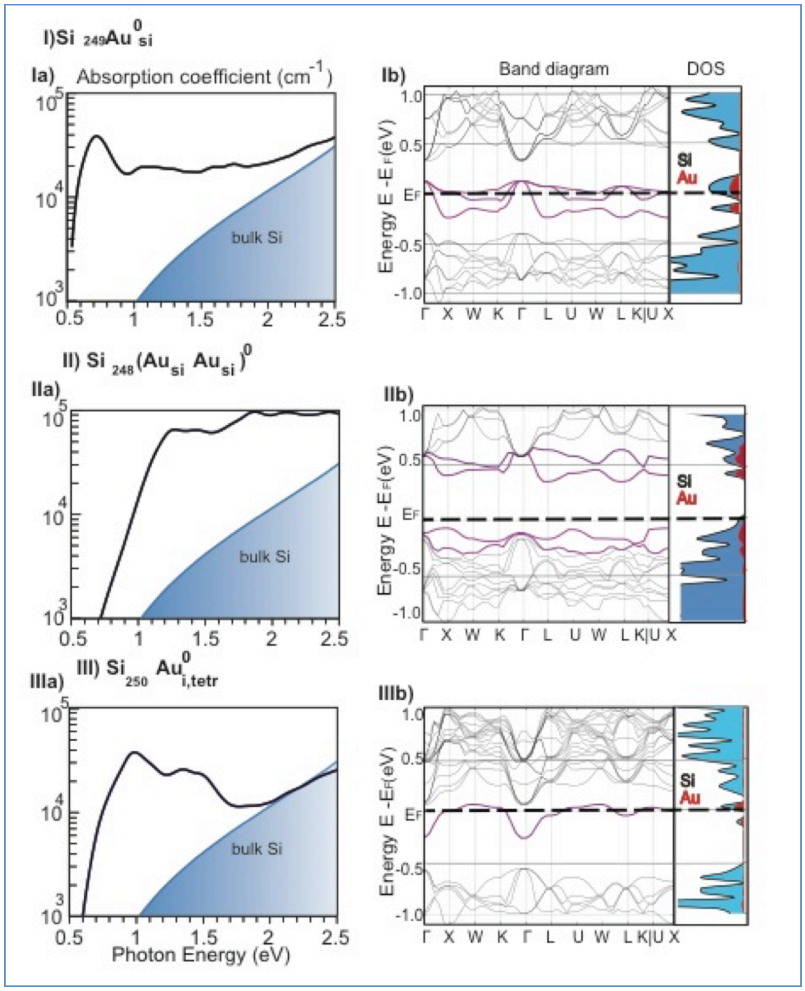

FIG. 2. Calculated absorption coefficient and electronic band structure for substitutional, dimer substitutional, and interstitial Au in silicon. The absorption is large for isolated substitutional Au, consistent with the partially filled mid-gap defect level. The formation of a substitutional dimer, which is energetically favorable, is associated with the disappearance in the mid-gap defect levels and a corresponding reduction in absorption.

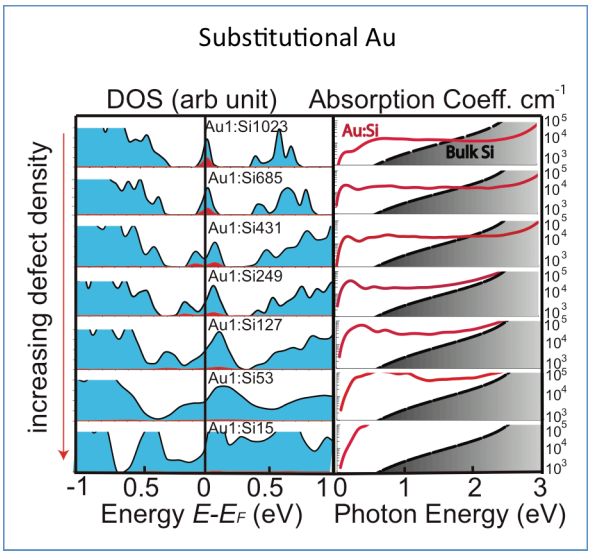

FIG. 3. Calculated variation in the electronic density of states and the absorption coefficient of Au-hyperdoped silicon for the case of isolated substitutional Au defects.

regions in the laser-processed material.

Task B. We considered the electronic band structure and the optical absorption for the most favorable defect configurations: these are the isolated substitutional, the dimer substitutional, and the tetrahedral interstitial. Despite its larger formation energy, the latter was also considered as a point of comparison. The electronic band structure, density of states, and the optical absorption is shown for each of these in FIG. 2. Optical absorption is estimated from direct (vertical) transition only, by direct calculation of matrix transition elements. Partially filled midgap defect states are observed for the isolated substitutional, confirming that this configuration satisfies the dopant design rules. Accordingly the calculated sub band gap absorption is significant. FIG. 3 further shows the evolution of the absorption coefficient as the isolated substitutional defect concentration increases, showing that large enhancement in principle is possible. However, the mid gap states are not present for the dimer substitutional, and the onset of sub band gap absorption is markedly reduced. We have been able to identify a reason for the disappearance of the mid-gap states upon binding of two isolated substitutional Au based on molecular orbital theory, in which the defects are considered to be well-described by states of isolated gold atoms interacting with the states of silicon mono and di –vacancies (not shown here explicitly). The interstitial defect, although not expected to form in appreciable quantities, also introduces a mid-gap defect state.

Task C. This task was not relevant to our analysis, since our original hypothesis for the low sub band gap absorption proved to be incorrect and a different mechanism has been determined.

5c. *Conclusions and Future Directions.*

- Our first-principles quantum mechanical modeling indicates that Au-hyperdoped Si satisfies both key design rules, both a *mid-gap* and a *partially-filled* defect band, for obtaining enhanced sub band gap absorption.
- We predict that Au appears in the form of substitutional defects in the silicon lattice, which are associated with a large sub band gap absorption. These predictions are in good agreement with recent measurements from SIMS.
- We attribute the the relatively low absorption, and further drop in absorption observed upon annealing, to the dissolution of Au from Si and the formation of Au-rich precipitates in Si. Quantum mechanical modeling results show a strong thermodynamic driving force for the

formation of Au-dimers, which we suggest may form during the initial stages of annealing as an early intermediate stage before preciptation occurs. The formation of these

- Our findings suggest that future considerations for optimal dopant species should consider mechanisms to limit or sufficiently slow down the growth of precipitates in the hyperdoped materials. In principle this can be accomplished either by kinetics or thermodynamics.

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(7) APPENDIXES

N/A.