Laser doping and texturing of silicon for advanced optoelectronic devices

FiO/LS Conference
Laser Material Processing
Rochester, NY, 18 October 2016
Laser doping and texturing of silicon for advanced optoelectronic devices

FiO/LS Conference
Laser Material Processing
Rochester, NY, 18 October 2016
and also....

Hemi Gandhi
Alexander Raymond
Marc Winkler
Eric Diebold
Haifei Albert Zhang
Dr. Brian Tull
Dr. Jim Carey (SiOnyx)
Prof. Tsing-Hua Her (UNC Charlotte)
Dr. Shrenik Deliwala
Dr. Richard Finlay
Dr. Michael Sheehy
Dr. Claudia Wu
Dr. Rebecca Younkin
Prof. Catherine Crouch (Swarthmore)
Prof. Mengyan Shen (Lowell U)
Prof. Li Zhao (Fudan U)

Prof. Alan Aspuru-Guzik
Prof. Michael Aziz
Prof. Michael Brenner
Prof. Cynthia Friend
Prof. Howard Stone

Dr. Martin Pralle (SiOnyx)
and everyone else at SiOnyx....

Prof. Tonio Buonassisi (MIT)
Prof. Silvija Gradecak (MIT)
Prof. Jeff Grossman (MIT)
Dr. Bonna Newman (MIT)
Joe Sullivan (MIT)
Matthew Smith (MIT)

Prof. Augustinus Asenbaum (Vienna)

Dr. François Génin (LLNL)
Mark Wall (LLNL)

Dr. Richard Farrell (RMD)
Dr. Arieh Karger (RMD)
Dr. Richard Meyers (RMD)

Dr. Pat Maloney (NVSED)

Dr. Jeffrey Warrander (ARDEC)
irradiate with 100-fs 10 kJ/m² pulses
“black silicon”
absorptance \((1 - R_{\text{int}} - T_{\text{int}})\)
absorptance \( (1 - R_{int} - T_{int}) \)

![Graph showing absorptance for black and crystalline silicon](image-url)

- **Absorptance**
- **wavelength (µm)**
- **Black Silicon**
- **Crystalline Silicon**
absorptance \( (1 - R_{int} - T_{int}) \)

![Graph of absorptance vs. wavelength for crystalline and black silicon.](attachment:image.png)
absorptance \((1 - R_{int} - T_{int})\)
absorptance \((1 - R_{int} - T_{int})\)
laser treatment causes:

- surface structuring
- inclusion of dopants
1. properties
2. intermediate band
1 properties  2 intermediate band  3 devices
properties
properties
cross-sectional Transmission Electron Microscopy
disordered surface layer
crystalline Si core
1 µm

properties
• 300-nm disordered surface layer

• undisturbed crystalline core

• surface layer: polycrystalline Si with 1.6% sulfur
two processes: melting and ablation
relevant time scales
relevant time scales
relevant time scales

- Carrier excitation
- Thermalization

Timescales:
- fs (femtoseconds)
- ps (picoseconds)
- ns (nanoseconds)
- μs (microseconds)
<table>
<thead>
<tr>
<th>Time Scale</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>fs</td>
<td>Carrier excitation</td>
</tr>
<tr>
<td>ps</td>
<td>Thermalization</td>
</tr>
<tr>
<td>ns</td>
<td>Ablation</td>
</tr>
</tbody>
</table>

# relevant time scales

- **fs**: femtoseconds
- **ps**: picoseconds
- **ns**: nanoseconds
- **µs**: microseconds

- **Cold**
- **Hot**
relevant time scales

- Carrier excitation
- Thermalization
- Ablation
- Thermal diffusion

Time scales:
- fs (femtoseconds)
- ps (picoseconds)
- ns (nanoseconds)
- µs (microseconds)
relevant time scales

carrier excitation

cold

hot

thermalization

ablation

thermal diffusion

resolidification
relevant time scales

- carrier excitation
- thermalization
- ablation
- thermal diffusion
- resolidification

relevant time scales

- room temperature lattice
- molten surface layer
- cooling material

Carrier excitation
Cold to hot thermalization
Ablation
Thermal diffusion
Resolidification

relevant time scales

different thresholds:

melting: 1.5 kJ/m²

ablation: 3.1 kJ/m²
decouple ablation from melting
decouple ablation from melting

doped
decouple ablation from melting

doped
decouple ablation from melting

doped
decouple ablation from melting

undoped

doped

properties
decouple ablation from melting
decouple ablation from melting
decouple ablation from melting
decouple ablation from melting
decouple ablation from melting

doped region

undoped region

10 nm
secondary ion mass spectrometry

![Graph showing depth vs. concentration]
Things to keep in mind

• near unit absorption extending into IR
• surface structure due to ablation
• hyperdoping due to rapid melting and resolidification
• can decouple both processes
Cu Ge Si ZnO

conductor semiconductor insulator

CB VB CB VB CB CB

0 2 4

$E_g$(eV)

Cu Ge Si ZnO

1 properties 2 intermediate band
gap determines optical and electronic properties

Conductor: CB, VB
Semiconductor: CB, VB
Insulator: CB, VB

$E_g$ (eV)

Cu, Ge, Si, ZnO
shallow-level dopants control electronic properties

1 properties
2 intermediate band

conductor semiconductor insulator

CB VB CB VB CB

0 2 4 $E_g$ (eV)

Cu Ge Si ZnO
deep-level dopants typically avoided

properties

intermediate band
1 part in $10^6$ sulfur introduces donor states in gap

1 part in $10^6$ sulfur introduces donor states in gap

at high concentration states broaden into band
$10^{-6}$ sulfur doping

- **energy (eV)**
- **wavelength (µm)**
- **absorptance**

- **crystalline Si**
- **Si band edge**
- **sulfur impurity states**

1 properties
2 intermediate band
laser-doped S:Si

- **energy (eV)**
- **wavelength (µm)**
- **absorptance**

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Absorptance</th>
<th>Wavelength (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>1.5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>1.5</td>
<td>1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

- **crystalline Si**
- **laser-doped Si**
- **sulfur impurity states**
- **Si band edge**

**Properties**

1. **intermediate band**
laser-doped S:Si

Properties

- sulfur impurity states
- crystalline Si
- Si band edge
- multiple reflections

Intermediate band
laser-doped S:Si

![Graph showing absorptance vs energy and wavelength for laser-doped Si](graph.png)

- **laser-doped Si**
- **sulfur impurity band**
- **crystalline Si**
- **Si band edge**

**Properties**

1. intermediate band
isolate surface layer for Hall measurements

- device layer
- buried oxide
- silicon substrate
isolate surface layer for Hall measurements

device layer
buried oxide
silicon substrate

1 properties
2 intermediate band
isolate surface layer for Hall measurements

laser doped region
buried oxide
silicon substrate

1 properties
2 intermediate band
isolate surface layer for Hall measurements

- buried oxide
- silicon substrate

1 properties
2 intermediate band
isolate surface layer for Hall measurements

- buried oxide
- silicon substrate

1 properties
2 intermediate band
1 properties  
2 intermediate band
Hall measurements

1/\(T\) (mK\(^{-1}\))

Temperature (K)

\(N/N_{room}\)

n-doped 5000 \(\Omega\)-cm

properties

intermediate band
Hall measurements

\[ N^2 = C T^{-3} e^{-E_g/k_B T} \]

properties

intermediate band
Hall measurements

\[ E_G = 1.217 \, \text{eV} \]

n-doped 5000 \( \Omega \)-cm

\[ N^2 = C T^3 e^{-E_G/k_B T} \]

1. properties
2. intermediate band
Hall measurements

- n-doped 5000 Ω-cm
- p-doped 10 Ω-cm

Properties: intermediate band
Hall measurements

$E_d = 43 \text{ meV}$

- n-doped 5000 $\Omega$-cm
- p-doped 10 $\Omega$-cm

**properties**

**intermediate band**
Hall measurements

Properties

Intermediate band
Hall measurements

- n-doped 5000 Ω-cm
- p-doped 10 Ω-cm
- laser-doped

Temperature (K):

- n-doped 5000 Ω-cm: $E_d = 310$ meV
- p-doped 10 Ω-cm: $N = 10^{17}$ cm$^3$

The graph shows the relationship between temperature and the ratio of carrier density to room temperature carrier density ($N/N_{room}$) as a function of inverse temperature ($1/T$). The graph is useful for understanding properties in the intermediate band.
Hall measurements

- n-doped 5000 Ω-cm
- p-doped 10 Ω-cm
- laser-doped

**1 properties**  **2 intermediate band**
Hall measurements

- n-doped 5000 \( \Omega \)-cm
- p-doped 10 \( \Omega \)-cm
- laser-doped high concentration

- \( \frac{N}{N_{\text{room}}} \) properties
- Intermediate band

Graph:
- Temperature (K)
- \( \frac{N}{N_{\text{room}}} \) vs. \( \frac{1}{T} \) (mK\(^{-1}\))
- n-doped 5000 \( \Omega \)-cm
- high concentration laser-doped
- p-doped 10 \( \Omega \)-cm
impurity (donor) band centered at 310 meV

1 properties
2 intermediate band
Hyperdoping has emerged as a promising method for designing semiconductors with unique optical and electronic properties, although such properties currently lack a clear microscopic explanation. Combining computational and experimental evidence, we probe the origin of sub-band-gap optical absorption and metallicity in Se-hyperdoped Si. We show that sub-band-gap absorption arises from direct defect-to-conduction-band transitions rather than free carrier absorption. Density functional theory predicts the Se-induced insulator-to-metal transition arises from merging of defect and conduction bands, at a concentration in excellent agreement with experiment. Quantum Monte Carlo calculations confirm the critical concentration, demonstrate that correlation is important to describing the transition accurately, and suggest that it is a classic impurity-driven Mott transition.

DOI: 10.1103/PhysRevLett.108.026401
Insulator-to-Metal Transition in Selenium-Hyperdoped Silicon: Observation and Origin

Elif Ertekin, 1,* Mark T. Winkler, 1,‡ Tonio Buonassisi, 1,‡ Aurore J. Said, 3 Michael J. Aziz, 3

1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge Massachusetts 02139, USA
2Department of Materials Science and Engineering, Harvard School of Engineering and Applied Sciences, Cambridge Massachusetts 02138, USA
3Department of Materials Science and Engineering, University of Chicago, Chicago Illinois 60637, USA

(Received 14 October 2011; published 11 January 2012)

DFT calculations

Emergence of very broad infrared absorption band by hyperdoping of silicon with chalcogens

Ikurou Umezu, Jeffrey M. Warrender, Supakit Charnvanichborkarn, Atsushi Kohno, James S. Williams, Malek Tabbai, Dimitris G. Papazoglou, Xi-Cheng Zhang, and Michael J. Aziz

Department of Physics, Konan University, Kobe 658-8501, Japan

U.S. Army ARDEC–Benét Laboratories, Watervliet, New York 12189, USA

Research School of Physics and Engineering, The Australian National University, Canberra, ACT 0200, Australia

Department of Applied Physics, Fukuoka University, Fukuoka 814-0180, Japan

Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, P.O. Box 1527, Heraklion, Greece

Materials Science and Technology Department, University of Crete, P.O. Box 2208, 71003 Heraklion, Greece

Department of Physics, American University of Beirut, Beirut 1107 2020, Lebanon

Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

(Received 9 September 2012; accepted 29 April 2013; published online 3 June 2013)

We report the near through mid-infrared (MIR) optical absorption spectra, over the range 0.05–1.3 eV, of monocrystalline silicon layers hyperdoped with chalcogen atoms synthesized by ion implantation followed by pulsed laser melting, a broad mid-infrared optical absorption band emerges, peaking near 0.5 eV for sulfur and selenium and 0.3 eV for tellurium hyperdoped samples. Its strength and width increase with impurity concentration. Its strength decreases markedly with subsequent thermal annealing. The emergence of a broad MIR absorption band is consistent with the formation of an impurity band from isolated deep donor levels as the concentration of chalcogen atoms in metastable local configurations increases.

I. INTRODUCTION

Silicon hyperdoped with chalcogens can be synthesized by pulsed laser irradiation in a sulfur-bearing atmosphere, ion implantation followed by pulsed laser melting, or pulsed laser mixing. This material has attracted interest because of its sub band gap absorption and has been studied as a candidate for infrared (IR) photodetectors and efficient solar cells. In addition, observations of carrier lifetime recovery for sufficiently high concentrations of chalcogen atoms have shown interest in this material.

II. EXPERIMENT

Double side polished p type (001) Si wafers, resistivity of 5–25 Ω cm, were ion implanted at room temperature with either 95 keV $^{32}\text{S}^+$, 176 keV $^{80}\text{Se}^+$, or 245 keV $^{130}\text{Te}^+$ to doses of $1 \times 10^{16}$ ions/cm$^2$ and pre-amorphized by 32S$^+$ doses of $3 \times 10^{15}$ ions/cm$^2$. Pulsed laser melting was performed using a XeCl excimer laser beam (308 nm, 25 ns FWHM, 50 ns total duration). Each sample received three laser shots at 1.7 J/cm$^2$, followed by a fourth laser shot at 1.8 J/cm$^2$. Time-resolved reflectivity of a laser shot at 1.8 J/cm$^2$.
Emergence of very broad infrared absorption band by hyperdoping of silicon with chalcogens

Ikurou Umezu, Jeffrey M. Williams, and Michael J. Aziz

1Department of Physics, Konan University, Kobe 658-8501, Japan
2U.S. Army ARDEC–Ben Research School of Physics and Engineering, The Australian National University, Canberra, ACT 0200, Australia
3Department of Applied Physics, Fukuoka University, Fukuoka 814-0180, Japan
4Department of Physics, American University of Beirut, Beirut 1107 2020, Lebanon
5Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, P.O. Box 1527, 71110 Heraklion, Greece
6Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180, USA
7Harvard School of Engineering and Applied Sciences, Cambridge, Massachusetts 02138, USA

(Received 9 September 2012; accepted 29 April 2013; published online 3 June 2013)

I. INTRODUCTION

Silicon has aroused similar interest in this material. Chalcogen hyperdoping has been shown to cause an insulator-to-metal transition and has been proposed to form an intermediate band in the silicon band gap. We also report the effects of impurity dose and depth profiles of chalcogen atoms observed by secondary ion mass spectrometry (SIMS) are reported elsewhere.

II. EXPERIMENT

Silicon laser irradiation was performed using a XeCl excimer laser beam. The laser fluence was calibrated by comparing the melt duration with numerical solutions to the one-dimensional heat equation. The laser fluence was calibrated by comparing the melt duration with numerical solutions to the one-dimensional heat equation. The details of the sample preparation method are provided elsewhere.

We report measurements of the optical absorption coefficient over a broad range of photon energies for thermal and implanted, ion implanted, and laser melted samples. The optical absorption of chalcogen hyperdopants, particularly sulfur, has been reported previously. However, the band gap of chalcogens is in the near IR (NIR) region, or to photon energies above the con band gap. The laser fluence was calibrated by comparing the melt duration with numerical solutions to the one-dimensional heat equation.

The laser fluence was calibrated by comparing the melt duration with numerical solutions to the one-dimensional heat equation.
Abstract

This thesis explores the electronic structure, optical properties, and carrier lifetimes in silicon that is doped with sulfur beyond the equilibrium solid solubility limit, with a focus on applications as an absorber layer for an impurity-band photovoltaic device. The concept of an impurity-band material envisions the creation of a band of electronic states by incorporating high concentrations of deep-level dopants, which enable the generation of free carriers using photons with energy less than that of the band gap of the host semiconductor. The investigations reported in this thesis provide a framework for the appropriate selection of impurity-band candidate materials.

The thesis is divided into three primary sections, one for each of three experimental techniques, respectively. First, the electronic band structure is studied using synchrotron-based x-ray emission spectroscopy. These spectra provide the first insights into how the electronic structure changes as the sulfur concentration is increased across the metal-insulator transition, and how the electronic structure is linked to the anomalously high sub-band gap absorption. A discrete change in local electronic structure is seen that corresponds to the macroscopic change in electronic behavior. Additionally, a direct correlation is seen between sulfur-induced states and the sub-band gap absorption.

Next, the optical properties are studied using Fourier transform infrared spectroscopy. Extraction of the complex index of refraction is performed using numerical models that simulate both the transmission and reflection measurements. Analysis of the optical properties are studied using Fourier transform infrared spectroscopy. The position of the sulfur-induced states within the band gap of the host semiconductor is determined for different sulfur concentrations and in the metal-insulator transition, which enables the determination of different intermediate band properties.

Third, low-temperature photoconductivity experiments determine the mobility-lifetime product for carriers generated via sub-band gap photons. Combining both the FTIR optical results with the mobility-lifetime product measured from photoconductivity experiments, a comprehensive understanding of the electronic and optical properties of sulfur-doped silicon is achieved.
Understanding the Viability of Impurity-Band Photovoltaics: A Case Study of S-doped Si

by

Joseph Timothy Sullivan

Submitted to the Department of Mechanical Engineering on May 18, 2013, in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Abstract

This thesis explores the electronic structure, optical properties, and carrier lifetimes in silicon that is doped with sulfur beyond the equilibrium solid solubility limit, with a focus on applications as an absorber layer for an impurity-band photovoltaic device. The concept of an impurity-band material envisions the creation of a band of electronic states by incorporating high concentrations of deep-level dopants, which enable the generation of free carriers using photons with energy less than that of the band gap of the host semiconductor. The investigations reported in this thesis provide a framework for the appropriate selection of impurity-band candidate materials.

The thesis is divided into three primary sections, one for each of three experimental techniques, respectively. First, the electronic band structure is studied using synchrotron-based x-ray emission spectroscopy. These spectra provide the first insights into how the electronic structure changes as the sulfur concentration is increased across the metal-insulator transition, and how the electronic structure is linked to the anomalously high sub-band gap absorption. A discrete change in local electronic structure is seen that corresponds to the macroscopic change in electronic behavior. Additionally, a direct correlation is seen between sulfur-induced states and the sub-band gap absorption.

Next, the optical properties are studied using Fourier transform infrared spectroscopy. Extraction of the complex index of refraction is performed using numerical models that simulate both the transmission and reflection measurements. Analysis of the absorption coefficient determines the position of the sulfur-induced states within the band gap and their optical cross section for different sulfur concentrations and annealing conditions. At sulfur concentrations above the metal-insulator transition, the sulfur states become degenerate or near-degenerate with the conduction band, and such high concentrations are deemed to have an electronic structure unsuitable for an impurity-band photovoltaic material.

Third, low-temperature photoconductivity experiments determine the mobility-lifetime product for carriers generated via sub-band gap photons. Combining both the FTIR optical results with the mobility-lifetime product measured from photoconductivity experiments provides a comprehensive understanding of the sulfur-doped silicon material properties.

Understanding the Viability of Impurity-Band Photovoltaics: A Case Study of S-doped Si

Joseph Timothy Sullivan

Submitted to the Department of Mechanical Engineering on May 18, 2013, in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Abstract

This thesis explores the electronic structure, optical properties, and carrier lifetimes in silicon that is doped with sulfur beyond the equilibrium solid solubility limit, with a focus on applications as an absorber layer for an impurity-band photovoltaic device. The concept of an impurity-band material envisions the creation of a band of electronic states by incorporating high concentrations of deep-level dopants, which enable the generation of free carriers using photons with energy less than that of the band gap of the host semiconductor. The investigations reported in this thesis provide a framework for the appropriate selection of impurity-band candidate materials.

The thesis is divided into three primary sections, one for each of three experimental techniques, respectively. First, the electronic band structure is studied using synchrotron-based x-ray emission spectroscopy. These spectra provide the first insights into how the electronic structure changes as the sulfur concentration is increased across the metal-insulator transition, and how the electronic structure is linked to the anomalously high sub-band gap absorption. A discrete change in local electronic structure is seen that corresponds to the macroscopic change in electronic behavior. Additionally, a direct correlation is seen between sulfur-induced states and the sub-band gap absorption.

Next, the optical properties are studied using Fourier transform infrared spectroscopy. Extraction of the complex index of refraction is performed using numerical models that simulate both the transmission and reflection measurements. Analysis of the absorption coefficient determines the position of the sulfur-induced states within the band gap and their optical cross section for different sulfur concentrations and annealing conditions. At sulfur concentrations above the metal-insulator transition, the sulfur states become degenerate or near-degenerate with the conduction band, and such high concentrations are deemed to have an electronic structure unsuitable for an impurity-band photovoltaic material.

Third, low-temperature photoconductivity experiments determine the mobility-lifetime product for carriers generated via sub-band gap photons. Combining both the FTIR optical results with the mobility-lifetime product measured from photoconductivity experiments.

Understanding the Viability of Impurity-Band Photovoltaics: A Case Study of S-doped Si

by Joseph Timothy Sullivan

Submitted to the Department of Mechanical Engineering on May 18, 2013, in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Abstract

This thesis explores the electronic structure, optical properties, and carrier lifetimes in silicon that is doped with sulfur beyond the equilibrium solid solubility limit, with a focus on applications as an absorber layer for an impurity-band photovoltaic device. The concept of an impurity-band material envisions the creation of a band of electronic states by incorporating high concentrations of deep-level dopants, which enable the generation of free carriers using photons with energy less than that of the band gap of the host semiconductor. The investigations reported in this thesis provide a framework for the appropriate selection of impurity-band candidate materials.

The thesis is divided into three primary sections, one for each of three experimental techniques, respectively. First, the electronic band structure is studied using synchrotron-based x-ray emission spectroscopy. These spectra provide the first insights into how the electronic structure changes as the sulfur concentration is increased across the metal-insulator transition, and how the electronic structure is linked to the anomalously high sub-band gap absorption. A discrete change in local electronic structure is seen that corresponds to the macroscopic change in electronic behavior. Additionally, a direct correlation is seen between sulfur-induced states and the sub-band gap absorption.

Next, the optical properties are studied using Fourier transform infrared spectroscopy. Extraction of the complex index of refraction is performed using numerical models that simulate both the transmission and reflection measurements. Analysis of the absorption coefficient determines the position of the sulfur-induced states within the band gap and their optical cross section for different sulfur concentrations and annealing conditions. At sulfur concentrations above the metal-insulator transition, the sulfur states become degenerate or near-degenerate with the conduction band, and such high concentrations are deemed to have an electronic structure unsuitable for an impurity-band photovoltaic material.

Third, low-temperature photoconductivity experiments determine the mobility-lifetime product for carriers generated via sub-band gap photons. Combining both the FTIR optical results with the mobility-lifetime product measured from photoconductivity experiments provides a comprehensive understanding of the material's photovoltaic properties.

Understanding the Viability of Impurity-Band Photovoltaics: A Case Study of S-doped Si

by Joseph Timothy Sullivan

Submitted to the Department of Mechanical Engineering on May 18, 2013, in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Abstract

This thesis explores the electronic structure, optical properties, and carrier lifetimes in silicon that is doped with sulfur beyond the equilibrium solid solubility limit, with a focus on applications as an absorber layer for an impurity-band photovoltaic device. The concept of an impurity-band material envisions the creation of a band of electronic states by incorporating high concentrations of deep-level dopants, which enable the generation of free carriers using photons with energy less than that of the band gap of the host semiconductor. The investigations reported in this thesis provide a framework for the appropriate selection of impurity-band candidate materials.

The thesis is divided into three primary sections, one for each of three experimental techniques, respectively. First, the electronic band structure is studied using synchrotron-based x-ray emission spectroscopy. These spectra provide the first insights into how the electronic structure changes as the sulfur concentration is increased across the metal-insulator transition, and how the electronic structure is linked to the anomalously high sub-band gap absorption. A discrete change in local electronic structure is seen that corresponds to the macroscopic change in electronic behavior. Additionally, a direct correlation is seen between sulfur-induced states and the sub-band gap absorption.

Next, the optical properties are studied using Fourier transform infrared spectroscopy. Extraction of the complex index of refraction is performed using numerical models that simulate both the transmission and reflection measurements. Analysis of the absorption coefficient determines the position of the sulfur-induced states within the band gap and their optical cross section for different sulfur concentrations and annealing conditions. At sulfur concentrations above the metal-insulator transition, the sulfur states become degenerate or near-degenerate with the conduction band, and such high concentrations are deemed to have an electronic structure unsuitable for an impurity-band photovoltaic material.

Third, low-temperature photoconductivity experiments determine the mobility-lifetime product for carriers generated via sub-band gap photons. Combining both the FTIR optical results with the mobility-lifetime product measured from photoconductivity experiments provides a comprehensive understanding of the electronic and optical properties of S-doped Si.

Understanding the Viability of Impurity-Band Photovoltaics: A Case Study of S-doped Si

Joseph Timothy Sullivan

Submitted to the Department of Mechanical Engineering on May 18, 2013, in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Abstract

This thesis explores the electronic structure, optical properties, and carrier lifetimes in silicon that is doped with sulfur beyond the equilibrium solid solubility limit, with a focus on applications as an absorber layer for an impurity-band photovoltaic device. The concept of an impurity-band material envisions the creation of a band of electronic states by incorporating high concentrations of deep-level dopants, which enable the generation of free carriers using photons with energy less than that of the band gap of the host semiconductor. The investigations reported in this thesis provide a framework for the appropriate selection of impurity-band candidate materials.

The thesis is divided into three primary sections, one for each of three experimental techniques, respectively. First, the electronic band structure is studied using synchrotron-based x-ray emission spectroscopy. These spectra provide the first insights into how the electronic structure changes as the sulfur concentration is increased across the metal-insulator transition, and how the electronic structure is linked to the anomalously high sub-band gap absorption. A discrete change in local electronic structure is seen that corresponds to the macroscopic change in electronic behavior. Additionally, a direct correlation is seen between sulfur-induced states and the sub-band gap absorption.

Next, the optical properties are studied using Fourier transform infrared spectroscopy. Extraction of the complex index of refraction is performed using numerical models that simulate both the transmission and reflection measurements. Analysis of the absorption coefficient determines the position of the sulfur-induced states within the band gap and their optical cross section for different sulfur concentrations and annealing conditions. At sulfur concentrations above the metal-insulator transition, the sulfur states become degenerate or near-degenerate with the conduction band, and such high concentrations are deemed to have an electronic structure unsuitable for an impurity-band photovoltaic material.

Third, low-temperature photoconductivity experiments determine the mobility-lifetime product for carriers generated via sub-band gap photons. Combining both the FTIR optical results with the mobility-lifetime product measured from photoconductivity experiments, the appropriate selection of impurity-band candidate materials is discussed.

Things to keep in mind

- IR absorption rolls off around 8 µm
- Consistent evidence of intermediate band formation
- IB forms at 0.1% at. doping, broadens at higher doping
- IB merges with CB at 0.4% at. yielding metallic behavior
1 properties
2 intermediate band
3 devices
should have shallow junction below surface

sulfur-doped layer

p-doped substrate
excellent rectification (after annealing)

[Graph showing current density against bias]

- Current density (A/m²)
- Bias (V)

1. properties
2. intermediate band
3. devices
responsivity

Responsivity vs. Wavelength (nm)

- Si PIN

Properties
- Intermediate band

Devices
responsivity

![Graph showing responsivity vs. wavelength for Si PIN and InGaAs, Ge.](image)

1. properties
2. intermediate band
3. devices
responsivity

![Graph showing responsivity vs. wavelength for different materials: Si, S:Si, Si PIN, and InGaAs, Ge. The x-axis represents wavelength in nm, and the y-axis represents responsivity in A/W. The graph indicates the spectral response of these materials.]
Responsivity

Responsivity (A/W)

Wavelength (nm)

Si PIN
InGaAs, Ge

S:Si

100% QE

Properties
Intermediate band
Devices
responsivity

- S:Si
- NIR APD > 100 V bias
- 100% QE
- Si PIN
- InGaAs, Ge

1 properties  2 intermediate band  3 devices
• enhanced sensitivity

• extended IR response
www.sionyx.com

1 properties
2 intermediate band
3 devices
Combine state-of-the-art low-noise CMOS image sensor design with enhanced quantum efficiency.
US Patents: US 8,058,615; US 7,928,355; US 7,968,834
<table>
<thead>
<tr>
<th>Resolution</th>
<th>pixel (µm)</th>
<th>noise (e/pix)</th>
<th>$I_{\text{dark}}$ (e/pix/s)</th>
<th>$P$ (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>872 x 654</td>
<td>5.6</td>
<td>2.1</td>
<td>24</td>
<td>300</td>
</tr>
<tr>
<td>1280 x 720</td>
<td>5.6</td>
<td>2.1</td>
<td>24</td>
<td>360</td>
</tr>
<tr>
<td>1280 x 1024</td>
<td>10</td>
<td>2.6</td>
<td>83</td>
<td>400</td>
</tr>
</tbody>
</table>

8” CIS process flow
4T pixel architecture
Si CCD

Quantum efficiency vs. wavelength (µm)
Si CCD

G3 image intensifier

quantum efficiency

wavelength (µm)

Si CCD

G3 image intensifier
Things to keep in mind

- can turn b:Si absorption into carrier generation
Things to keep in mind

• can turn b:Si absorption into carrier generation

• very high responsivity in VIS and NIR
Things to keep in mind

- can turn b:Si absorption into carrier generation
- very high responsivity in VIS and NIR
- disruptive improvement in Si imaging
Things to keep in mind

• can turn b:Si absorption into carrier generation

• very high responsivity in VIS and NIR

• disruptive improvement in Si imaging

• potential benefits in solar energy harvesting
Summary

- new doping process
- new class of material
- new types of devices

1 properties  2 intermediate band  3 devices
What is different about this process?

1. properties
2. intermediate band
3. devices
Compare femtosecond laser doping to:

- inclusion during growth
- thermal diffusion
- ion implantation