Black silicon and the quest for intermediate band semiconductors

Siam Physics Congress & ARPU Annual Symposium
Krabi, Thailand, 21 May 2015
Black silicon and the quest for intermediate band semiconductors

Siam Physics Congress & ARPU Annual Symposium
Krabi, Thailand, 21 May 2015
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 Deliwalta
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
absorptance \( (1 - R_{\text{int}} - T_{\text{int}}) \)
absorptance \( (1 - R_{int} - T_{int}) \)
absorptance \( (1 - R_{\text{int}} - T_{\text{int}}) \)
absorptance \((1 - R_{int} - T_{int})\)
absorptance \((1 - R_{int} - T_{int})\)
laser treatment causes:

• surface structuring

• inclusion of dopants
properties
cross-sectional Transmission Electron Microscopy
disordered surface layer
crystalline Si core

1 µm

properties
electron diffraction

1 µm

electron diffraction

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

carrier excitation
relevant time scales

carrier excitation

cold  hot

properties
relevant time scales

- fs
- ps
- ns
- μs

- carrier excitation
- thermalization
- cold
- hot
- ablation
relevant time scales

carrier excitation

cold

hot

thermalization

ablation

thermal diffusion
relevant time scales

carrier excitation

thermalization

cold hot

ablation

thermal diffusion

resolidification

properties
relevant time scales

relevant time scales

- Room temperature lattice
- Molten surface layer
- Cooling material

- Carrier excitation
- Thermalization
- Ablation
- Thermal diffusion
- Resolidification

- Carrier excitation
- Thermalization
- Ablation
- Thermal diffusion
- Resolidification

relevant time scales

- Carrier excitation
- Thermalization
- Ablation
- Thermal diffusion
- Resolidification

Room temperature lattice

Inclusion of dopants

Molten surface layer

Cooling material

0.1 fs 1 ps 10 ns 1 µs
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
decouple ablation from melting
decouple ablation from melting

epoxy

laser affected region

substrate

100 nm
decouple ablation from melting
decouple ablation from melting
decouple ablation from melting

doped region

undoped region

10 nm
secondary ion mass spectrometry

![Graph showing concentration vs depth](image-url)
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
properties

intermediate band
gap determines optical and electronic properties

Cu Ge Si ZnO

1 properties
2 intermediate band
shallow-level dopants control electronic properties

- conductor
- semiconductor
- insulator

**Diagram:**

- CB
- VB

**Axes:**

- $E_g$ (eV)
- Cu, Ge, Si, ZnO

**Labels:**

- properties
- intermediate band
deep-level dopants typically avoided

- conductor
- semiconductor
- insulator

Properties

- Cu
- Ge
- Si
- ZnO

Intermediate band

$E_g$ (eV)
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

![Graph showing absorptance vs. energy and wavelength](image)

- Absorptance vs. energy (eV) and wavelength (µm)
- Energy levels:
  - Crystalline Si
  - Sulfur impurity states
  - Si band edge

Properties:

1. properties
2. intermediate band
laser-doped S:Si

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

properties  intermediate band
laser-doped S:Si

![Graph showing absorptance vs energy and wavelength for laser-doped Si and crystalline Si. The graph highlights sulfur impurity states and Si band edge, with multiple reflections indicated.]

1 properties
2 intermediate band
laser-doped S:Si

energy (eV)  wavelength (µm)

0  0.5  1.0

absorptance

1.0

16 8 4 2 1

laser-doped Si

sulfur impurity band

Si band edge

crystalline Si

properties  intermediate band
isolate surface layer for Hall measurements

- silicon substrate
- buried oxide
- device layer

1 properties
2 intermediate band
isolate surface layer for Hall measurements

1 properties
2 intermediate band
isolate surface layer for Hall measurements

- laser doped region
- buried oxide
- silicon substrate
isolate surface layer for Hall measurements

- buried oxide
- silicon substrate

1 properties
2 intermediate band
isolate surface layer for Hall measurements

1 properties
2 intermediate band
Hall measurements

![Graph showing temperature dependence of N/N_room for n-doped 5000 Ω-cm material.](graph)

- **properties**: intermediate band
n-doped 5000 $\Omega$-cm

$$N^2 = C T^3 e^{-E_g/k_B T}$$
Hall measurements

$n$-doped 5000 \Omega\text{-cm}

$E_G = 1.217 \text{ eV}$

$N^2 = C T^3 e^{-E_G/k_B T}$
Hall measurements

![Graph showing Hall measurements for n-doped 5000 \(\Omega\)-cm and p-doped 10 \(\Omega\)-cm materials. The graph plots temperature (K) on the x-axis and \(N/N_{\text{room}}\) on the y-axis. The graph includes curves for both n-doped and p-doped materials.](image)

1. Properties
2. Intermediate band
Hall measurements

\[ E_d = 43 \text{ meV} \]

- n-doped 5000 Ω-cm
- p-doped 10 Ω-cm

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

\(N/N_{\text{room}}\)

\(500, 200, 100, 50\)

100

10

1

0.1

0.01

0.001

0

5

10

15

20

100

50
Hall measurements

![Graph showing the temperature dependence of N/N_\text{room} for different doping types.]

- n-doped 5000 \( \Omega \)-cm
- p-doped 10 \( \Omega \)-cm
- Laser-doped

1. properties
2. intermediate band
Hall measurements

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

Temperature (K) vs. $N/N_{\text{room}}$ vs. $1/T$ (mK$^{-1}$)

- $E_d = 310$ meV
- $N = 10^{17}$ cm$^3$

Properties of intermediate band
Hall measurements

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

Temperature (K)

$N/N_{\text{room}}$ vs. $1/T$ (mK$^{-1}$)

1. properties
2. intermediate band
Hall measurements

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

Graph showing the ratio \( N/N_{\text{room}} \) vs. temperature (K) and inverse temperature \( 1/T \) (mK\(^{-1}\)).

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

1 properties

2 intermediate band
majority carrier mobility

Caughey et al., Proc. IEEE 55, 2192 (1967)
majority carrier mobility

Caughey et al., Proc. IEEE 55, 2192 (1967)

properties

intermediate band
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 critical concentration, demonstrate that correlation is important to describing the transition accurately, and suggest that it is a classic impurity-driven Mott transition.

Of all the experimentally measurable physical properties of materials, electronic conductivity exhibits the largest variation, spanning a factor of $10^3$ from the best metals to the strongest insulators [1]. Over the last century, the puzzle of why some materials are conductors and others insulators, and the mechanisms underlying the transformation from one to the other, have been carefully scrutinized; yet even after such a vast body of research over such a long period, the subject remains the object of controversy. In 1956, Mott introduced a model for the insulator-to-metal transition (IMT) in doped semiconductors, in which long-range electron correlations are the driving force [2]. Hyperdoping (doping beyond the solubility limit) creates a new materials playground to explore defect-mediated IMTs in semiconductors. In this Letter, we identify a defect-induced IMT in silicon hyperdoped with selenium, which breaks the long-held belief that IMTs in doped silicon were driven by free carrier absorption. We show that sub-band-gap absorption arises from direct defect-to-conduction-band transitions, rather than free carrier absorption, and suggest that it is a classic impurity-driven Mott transition.

We prepared Se-doped silicon (Se:Si) samples using ion implantation followed by nanosecond pulsed-laser melting (PLM) and rapid resolidification. The PLM process enables chalcogen doping with concentrations exceeding 1% of the equilibrium solubility limit [3], while isolated S and Se dopants are well-established deep double donors in silicon [3,4]. The enhanced optical properties of hyperdoped silicon (in which these chalcogenic impurities are not yet well understood) are not yet well present at much higher concentrations. Further, unlike the prototypical system of phosphorus-doped silicon for which the IMT has been extensively studied and characterized [5,6], there are very few studies of an IMT resulting from deep defects such as chalcogens [7].

We prepared Se-doped silicon (Se:Si) samples using ion implantation followed by nanosecond pulsed-laser melting (PLM) and rapid resolidification. The PLM process enables chalcogen doping with concentrations exceeding 1% of the equilibrium solubility limit [3]. This fluence regimen was followed by nanosecond pulsed-laser melting (PLM) and rapid resolidification. The PLM process enables chalcogen doping with concentrations exceeding 1% of the equilibrium solubility limit [3,4]. 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 critical concentration, demonstrate that correlation is important to describing the transition accurately, and suggest that it is a classic impurity-driven Mott transition.
DFT calculations

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

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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. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4804935]

I. INTRODUCTION

Silicon hyperdoped with chalcogens can be synthesized by pulsed laser irradiation in a sulfur-bearing atmosphere, or ion implantation followed by pulsed laser melting. 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 titanium have aroused similar interest in this material. However, hyperdoping has been proposed to form an intermediate band in the silicon band gap. 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 titanium have aroused similar interest in this material. Hyperdoping has been proposed to form an intermediate band in the silicon band gap. The laser fluence was calibrated by comparing the melt duration with numerical solutions to the one-dimensional heat diffusion equation.

II. EXPERIMENT

Double side polished p type (001) Si wafers, resistivity of 5–25 Ω cm, were ion implanted at room temperature with 95 keV 32S+, 176 keV 35Se+, or 245 keV 129Te+. The dose of 32S+ was varied from 3 × 10^{16} ions/cm^2 to 3 × 10^{15} ions/cm^2 and pre-amorphized by 85 keV Si+ to doses of 3 × 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. Time-resolved reflectivity of a laser shot at 1.8 J/cm^2. Time-resolved reflectivity of a laser shot at 1.8 J/cm^2. Time-resolved reflectivity of a laser shot at 1.8 J/cm^2. Time-resolved reflectivity of a laser shot at 1.8 J/cm^2. Time-resolved reflectivity of a laser shot at 1.8 J/cm^2. Time-resolved reflectivity of a laser shot at 1.8 J/cm^2. The details of the sample preparation method are reported elsewhere. Chalcogen atoms observed by secondary ion mass spectrometry reported elsewhere. For samples, the same preparation procedure is the same as reported elsewhere.
Emergence of very broad infrared absorption band by hyperdoping of silicon with chalcogens

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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 pulsed laser irradiation in a sulfur-bearing atmosphere, ion implantation followed by pulsed laser mixing.

I. INTRODUCTION

Silicon-based infrared (IR) photodetectors have found widespread use in many applications, due to their sub band gap absorption and due to the efficient carrier multi-phonon relaxation at room temperature.

II. EXPERIMENTAL

A. Sample Preparation

Silicon hyperdoping has been shown to cause an insulator-to-metal transition and has been proposed to form an impurity band from isolated deep donor levels as the concentration of chalcogen atoms in metastable local configurations increases. Silicon hyperdoped with chalcogens can be synthesized by pulsed laser irradiation in a sulfur-bearing atmosphere, ion implantation followed by pulsed laser melting, or pre-amorphized by ion implantation followed by 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. However, the origin of the broad absorption band gap has remained unclear. One reason for this is that most measurements of optical absorption have been limited to the near IR (NIR) region, or to photon energies above the con 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.

B. Optical Absorption Spectroscopy

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

C. Results and Discussion

The absorption coefficient over a broad range of photon energies spanning near- to mid-IR (MIR) wavelengths. The results are consistent with the formation of an impurity band in the silicon conduction band gap.

D. Conclusion

In addition, observations of carrier life-time recovery for sufficiently high concentrations of titanium ions have been reported elsewhere. For the present work, the hyperdoping-induced changes causing the sub-bandgap absorption are consistent with the formation of a new impurity band with a lower conduction band gap.
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. The optical properties are studied using Fourier transform infrared spectroscopy. Extraction of the complex index of refraction is performed using numerical simulation and both the transmission and reflection measurements. Analysis of the position of the sulfur-induced states within the band structure at different sulfur concentrations and the metal-insulator transition, the mobility-lifetime product is measured from low-temperature photoconductivity experiments. Combining all the measured properties provides a framework for the appropriate selection of impurity-band candidate materials.
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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 provide a comprehensive understanding of the material properties necessary for the development of impurity-band photovoltaic devices.

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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 electronic band structure, and the optical properties of the impurity-band material are understood.

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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 potential.

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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 properties of sulfur-doped silicon.

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
properties

intermediate band

devices
should have shallow junction below surface

sulfur-doped layer

p-doped substrate

1 properties  2 intermediate band  3 devices
excellent rectification (after annealing)
responsivity

Responsivity vs. wavelength (nm)

- Properties
- Intermediate band
- Devices
responsivity

![Graph showing responsivity vs wavelength (nm)]

- **Si PIN**
- **InGaAs, Ge**

1. properties
2. intermediate band
3. devices
responsivity

![Responsivity graph showing the responsivity (A/W) of different materials as a function of wavelength (nm).](image)

1. **properties**
2. **intermediate band**
3. **devices**
Responsivity

Responsivity (A/W)

Wavelength (nm)

200  600  1000  1400  1800

1000

100

10

1

0.1

0.01

Si PIN, InGaAs, Ge

100% QE

S:Si

1 properties  2 intermediate band  3 devices
responsivity

![Responsivity graph](image)

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

1. **properties**
2. **intermediate band**
3. **devices**
• enhanced sensitivity

• extended IR response
near-IR is next wave in imaging!
gesture recognition
night vision
biometrics

image: kusic.ca

1 properties  2 intermediate band  3 devices
robotics

1 properties
2 intermediate band
3 devices

image: AP images
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
US Patents: US 8,058,615; US 7,928,355; US 7,968,834

properties

intermediate band

devices
<table>
<thead>
<tr>
<th>Resolution</th>
<th>Pixel (µm)</th>
<th>Noise (e/pix)</th>
<th>$I_{dark}$ (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
- properties
- intermediate band
- devices
properties

intermediate band
devices

visible

Si CCD

G3 image intensifier

SiOnyx XQE

quantum efficiency

wavelength (µm)

0 0.4 0.6 1.0 1.2 1.4
no compromises in visible

Sony color CCD
no compromises in visible

Sony color CCD

SiOnyx XQE sensor
90+ dB dynamic range

Sony color CCD
90+ dB dynamic range

Sony color CCD

SiOnyx X1 sensor
0.9 mlux irradiance from 2850 K source

SiOnyx (50 mm, F1.4, 30 fps)
SiOnyx XQE

Si CCD

G3 image intensifier

quantum efficiency

wavelength (µm)
NIR gesture detection

quantum efficiency

wavelength (µm)

SiOnyx XQE
Si CCD
G3 image intensifier
NIR gesture detection

SiOnyx XQE

quantum efficiency

wavelength (µm)

0.4 0.6 1.0 1.2 1.4

Si CCD
G3 image intensifier

2x

1 properties
2 intermediate band
3 devices
3D imaging for gesture user interface (850 nm)

SiOnyx XQE

standard CCD
SiOnyx XQE

Quantum Efficiency vs Wavelength (µm)

- Si CCD
- G3 image intensifier

Nightvision range:

- Wavelength (µm) 0.4 to 1.4
- Quantum Efficiency 0 to 100

10x improvement in quantum efficiency compared to Si CCD.
dark room 1050 illumination

SiOnyx (F1.4, 33 ms, 24x)
nightvision

quantum efficiency

wavelength (µm)

SiOnyx XQE

Si CCD

G3 image intensifier

properties

intermediate band

devices
solar spectrum

![Solar Spectrum Diagram]

Properties

1. Intermediate band
2. Devices
solar spectrum

- **solar spectrum**

- **properties**
- **intermediate band**
- **devices**

- **spectral irradiance (kW/m² μm)**

- **wavelength (μm)**

- **1353 W/m²**
crystalline silicon: transparent to 23% of solar radiation

![Graph showing spectral irradiance vs. wavelength]

- **c-Si band gap** = 1.12 μm
- **1042 W/m²**

**Legend:**
1. properties
2. intermediate band
3. devices
amorphous silicon: transparent to 53% of solar radiation

α-Si band gap = 0.71 μm

spectral irradiance (kW/m²) vs. wavelength (μm)

636 W/m²
black silicon: potential to recover transmitted energy

- Properties
- Intermediate band
- Devices
1 properties  2 intermediate band  3 devices

CB

VB
photon with gap energy

CB

VB
photon creates electron-hole pair...

1 properties
2 intermediate band
3 devices
...whose energy can be extracted

![Diagram showing electron (e) transitions between conduction band (CB) and valence band (VB).]

- properties
- intermediate band
- devices
photons with energy smaller than gap...
...do not get absorbed

1 properties  2 intermediate band  3 devices
photons with energy larger than the gap...
...create electron-hole pairs with excess energy...
…which is lost rapidly
black silicon has an intermediate band

1 properties  2 intermediate band  3 devices
absorbs same photons as ordinary silicon...
...but extends absorption to longer wavelengths
could theoretically get efficiencies over 50%
water splitting

properties

intermediate band

devices
water splitting

(anode)
semiconductor

(cathode)
meteral

1 properties
2 intermediate band
3 devices
water splitting

(anode)
semiconductor

(cathode)
metal

1 properties
2 intermediate band
3 devices
water splitting

1 properties
2 intermediate band
3 devices
water splitting

CB e

VB h

H₂O

(anode) semiconductor

(cathode) metal

1 properties

2 intermediate band

3 devices
water splitting

(anode) semiconductor

(cathode) metal

1. properties
2. intermediate band
3. devices
Water splitting

1. Properties
2. Intermediate band
3. Devices
water splitting

1 properties
2 intermediate band
3 devices
water splitting

- Anode: Semiconductor
- Cathode: Metal
- CB: Conduction Band
- VB: Valence Band
- $O_2$
- $H^+$
- $e^-$

1. properties
2. intermediate band
3. devices
water splitting

(anode) semiconductor

CB

VB

O₂

H⁺

e

(cathode) metal

1 properties

2 intermediate band

3 devices
water splitting

1. properties
2. intermediate band
3. devices
solar radiation spectrum

- UV
- visible
- infrared

spectral irradiance (W/m²/nm)

wavelength (nm)
solar radiation spectrum

The graph shows the spectral irradiance (W/m²/nm) as a function of wavelength (nm). The spectrum is divided into UV, visible, and infrared regions. The TiO₂ absorptance is also indicated, with markers for properties and intermediate band devices.
solar radiation spectrum

- UV
- visible
- infrared

spectral irradiance (W/m²/nm)

wavelength (nm)

TiO₂ absorptance

1 properties

2 intermediate band

3 devices
TiO$_2$, N$_2$, N$_2$ & O$_2$, O$_2$
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
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
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for more information and a copy of this presentation:

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