Femtosecond-laser hyperdoping and texturing of silicon for advanced nonequilibrium materials

2014 AFOSR Ultrashort Pulse Laser-Matter Interactions Program Review
Arlington, VA 30 May 2014
Femtosecond-laser hyperdoping and texturing of silicon for advanced nonequilibrium materials

2014 AFOSR Ultrashort Pulse Laser-Matter Interactions Program Review
Arlington, VA 30 May 2014
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 \((1 - R_{int} - T_{int})\)
absorptance \( (1 - R_{int} - T_{int}) \)
absorptance \((1 - R_{int} - T_{int})\)
absorptance \((1 - R_{\text{int}} - T_{\text{int}})\)
absorptance \( (1 - R_{int} - T_{int}) \)

![Graph showing absorptance vs. wavelength (µm) with annotations for multiple reflections, impurities and/or defects, and black silicon]
laser treatment causes:

- surface structuring
- inclusion of dopants
cross-sectional Transmission Electron Microscopy
disordered surface layer

1 µm
crystalline Si core

1 µm

properties
electron diffraction
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

carrier excitation
relevant time scales

- Carrier excitation
- Thermalization

- Cold
- Hot
relevant time scales

carrier excitation

cold

hot

thermalization

ablation

fs

ps

ns

μs

0.1

1

10

0.1

1

10

0.1

1

10

0.1

1

10

1

properties
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

1 properties
relevant time scales

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

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

relevant time scales

room temperature lattice
molten surface layer
cooling material
cold
hot

carrier excitation
thermalization
ablation
thermal diffusion
resolidification

0.1 1 10 0.1 1 10 0.1 1 fs ps ns µs

relevant time scales

different thresholds:

melting: $1.5 \text{ kJ/m}^2$

ablation: $3.1 \text{ kJ/m}^2$
decouple ablation from melting
decouple ablation from melting

doped
decouple ablation from melting

doped
decouple ablation from melting

doped
decouple ablation from melting
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
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

$E_g$ (eV)

$E_g$ (eV)

CB

CB

CB

VB

VB

VB

0 2 4

Cu Ge Si ZnO

1 properties

2 intermediate band
gap determines optical and electronic properties
shallow-level dopants control electronic properties

![Diagram showing the electronic properties of different materials with CB (conduction band) and VB (valence band) levels.

1. Properties
2. Intermediate band

Materials: Cu, Ge, Si, ZnO

Energy gap ($E_g$) in eV: 0, 2, 4]
deep-level dopants typically avoided

![Diagram showing the relationship between band structures and $E_g$ (eV)]

- Conductor
- Semiconductor
- Insulator

Band structures: CB (Conduction Band), VB (Valence Band)

Properties:
1. intermediate band

Elements: Cu, Ge, Si, ZnO
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

- properties
- intermediate band
laser-doped S:Si

![Graph showing absorptance vs. wavelength and energy for laser-doped Si and crystalline Si. Features include sulfur impurity states and Si band edge.]

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

- Properties
- Intermediate band

Diagram showing absorptance vs. wavelength and energy.

- Laser-doped Si
- Multiple reflections
- Sulfur impurity states
- Crystalline Si
- Si band edge
laser-doped S:Si

energy (eV)
wavelength (µm)

absorptance

1 properties
2 intermediate band
isolate surface layer for Hall measurements

- device layer
- buried oxide
- silicon substrate

1 properties 2 intermediate band
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
isolate surface layer for Hall measurements

1 properties
2 intermediate band

- buried oxide
- silicon substrate
1 properties
2 intermediate band
Hall measurements

![Graph showing Hall measurements for n-doped 5000 Ω-cm material at various temperatures. The graph plots temperature (K) against the ratio of the number of electrons N/N\text{room} on a logarithmic scale, and the inverse temperature (mK^{-1}) on a linear scale. The graph shows a steep decrease in N/N\text{room} as temperature increases, indicating intermediate band properties.](image-url)
Hall measurements

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

$n$-doped 5000 Ω-cm

$E_g = 1.217$ eV

$N^2 = C T^3 e^{-E_g/k_b T}$

$n$-doped 5000 Ω-cm

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

$E_g = 1.217$ eV

properties

intermediate band
Hall measurements

The graph shows the ratio of the density of states $N/N_{\text{room}}$ as a function of the inverse temperature $1/T$ (mK$^{-1}$) for two materials:

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

The graph is labeled with the temperature in Kelvin (K) on the x-axis and the ratio $N/N_{\text{room}}$ on the y-axis.

**1. properties**

**2. intermediate band**
Hall measurements

$E_d = 43 \text{ meV}$

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

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

1 properties
2 intermediate band
Hall measurements

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

Graph showing the ratio of carrier density to room temperature (N/N_{room}) as a function of the inverse temperature (1/T) for different doping types. The graph indicates properties of the intermediate band.
Hall measurements

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

$N = 10^{17}$ cm$^3$

$E_d = 310$ meV

1/ properties

2/ intermediate band
Hall measurements

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

Properties

Intermediate band
Hall measurements

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

Graph showing the ratio $N/N_{room}$ vs. $1/T$ (mK$^{-1}$) for different dopings and concentrations.

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)
impurity (donor) band centered at 310 meV

<table>
<thead>
<tr>
<th>CB</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>0.318 eV</td>
<td>0.188 eV</td>
<td>0.09 eV</td>
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<tr>
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<td>0.371 eV</td>
<td>0.11 eV</td>
<td>0.08 eV</td>
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<td>0.614 eV</td>
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<table>
<thead>
<tr>
<th>VB</th>
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<tbody>
<tr>
<td></td>
<td>0.248 eV</td>
</tr>
</tbody>
</table>
Insulator-to-Metal Transition in Selenium-Hyperdoped Silicon: Observation and Origin

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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.

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PACS numbers: 71.30.+h, 61.72.sd, 73.61.Cw, 78.20.Bh

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-ranged 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 and we demonstrate that correlation is important to describing the transition accurately.

Silicon appears to justify such interest. While isolated S and Se dopants are well-established deep donors in silicon [3,14], the enhanced optical properties of hyperdoped silicon (in which these chalcogenic impurities are not yet well present at much higher concentrations) have not been understood. Further, unlike the prototypical system of phosphorus-doped silicon for which the IMT has been extensively studied and characterized [15,16], there are very few studies of an IMT resulting from deep defects such as chalcogens [17].

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] of about $10^6$ cm$^{-3}$ and we show that the high density of Se present at the IMT yields excellent agreement with experimental evidence up to photon energies as low as 0.5 eV [3].

Hyperdoping is currently being used to engineer new materials with unique and exotic properties. Silicon hyperdoped with chalcogens exhibits strong subband gap absorption down to photon energies as low as 0.5 eV [3]. Such samples exhibit unexplained optical properties that spark substantial recent interest in applications such as infrared detection and intermediate band photovoltaics [18].

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] of about $10^6$ cm$^{-3}$ and we show that the high density of Se present at the IMT yields excellent agreement with experimental evidence up to photon energies as low as 0.5 eV [3]. Such samples exhibit unexplained optical properties that spark substantial recent interest in applications such as infrared detection and intermediate band photovoltaics [18].
Insulator-to-Metal Transition in Selenium-Hyperdoped Silicon: Observation and Origin


DFT calculations

![Graph showing E-E\text{VBM} (eV) vs. Se Content (% Atomic)](image)

1. properties
2. intermediate band
Emergence of very broad infrared absorption band by hyperdoping of silicon with chalcogens

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 ion 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 titanium have aroused similar interest in this material. Hyperdoping has been proposed to form an intermediate bandgap. However, the nature of hyperdoping has been reported elsewhere. The details of the sample preparation and characterization procedure is the same as that in the previous work for sulfur doped samples, whereas the previous work employed a somewhat higher fluence for the laser melts.

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 32S+, 176 keV 60Sr+, or 245 keV 197Te+ ions. The dose of 32S+ varied from 3 × 1014 to 1 × 1016 ions/cm2 and was pre-amorphized by doses of 3 × 1015 ions/cm2 when the 32S+ dose is not greater than 1 × 1015 ions/cm2. 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/cm2 followed by a fourth laser shot at 1.8 J/cm2. Time-resolved reflectivity of a laser shot was measured at 1.8 J/cm2. The laser fluence was calibrated by comparing the melt duration to doses of 32S+.

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1  properties
2  intermediate band
Emergence of very broad infrared absorption band by hyperdoping of silicon with chalcogens

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7Harvard School of Engineering and Applied Sciences, Cambridge, Massachusetts 02138, 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 in the silicon con band gap. We also report the effects of impurity dose and time recovery for sufficiently high concentrations of titanium as a candidate for infrared (IR) photodetectors because of its sub band gap absorption and has been studied in 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.

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.

Second, 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 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.

The optical properties of S-doped Si are also investigated at low temperatures. 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 framework for the appropriate selection of impurity-band candidate materials is provided.
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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 properties.


properties

intermediate band
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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, we can assess the viability of using S-doped Si as an absorber layer for an impurity-band photovoltaic device.
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

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

![Graph showing current density vs. bias voltage]

- Current density (A/m²)
- Bias (V)

1. properties
2. intermediate band
3. devices
responsivity

![Graph showing responsivity versus wavelength (nm). The y-axis represents responsivity (A/W) and the x-axis represents wavelength (nm). The graph displays a dashed line labeled Si PIN.]

1 properties  2 intermediate band  3 devices
Responsivity as a function of wavelength (nm) for different materials: Si PIN, InGaAs, Ge. The graph shows the responsivity (A/W) on a logarithmic scale.
responsivity

responsivity (A/W)

wavelength (nm)

S:Si
Si PIN
InGaAs, Ge

1 properties
2 intermediate band
3 devices
Responsivity vs. Wavelength (nm)

Responsivity (A/W)

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

Wavelength (nm): 200, 600, 1000, 1400, 1800

Properties: 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
robotics

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

1 properties  2 intermediate band  3 devices
<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
The graph shows the quantum efficiency of different devices as a function of wavelength (µm). The red line represents the Si CCD, and the green line represents the G3 image intensifier. The quantum efficiency values range from 0 to 100, and the wavelength values range from 0.4 to 1.4 µm.
The graph shows the quantum efficiency of different devices as a function of wavelength. The black line represents SiOnyx XQE, the red line represents Si CCD, and the green line represents G3 image intensifier. The graph indicates that SiOnyx XQE has the highest quantum efficiency across a wide range of wavelengths, while G3 image intensifier has a lower efficiency but is effective in certain wavelength ranges.
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)
0.9 mlux irradiance from 2850 K source

SiOnyx (50 mm, F1.4, 60 fps)
NIR gesture detection

quantum efficiency

wavelength (µm)

SiOnyx XQE

Si CCD

G3 image intensifier
NIR gesture detection

quantum efficiency

wavelength (µm)

SiOnyx XQE

Si CCD

G3 image intensifier

2x
3D imaging for gesture user interface (850 nm)

SiOnyx XQE

standard CCD
1 properties  2 intermediate band  3 devices
nightvision

quantum efficiency

Si Onyx XQE

Si CCD

G3 image intensifier

wavelength (µm)

properties

intermediate band

devices
dark room 1050 illumination

SiOnyx (F1.4, 33 ms, 24x)
dark room 1050 illumination

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

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

quantum efficiency

wavelength (µm)

SiOnyx XQE

Si CCD

G3 image intensifier

properties

intermediate band

devices
1. properties
2. intermediate band
3. devices

- nightvision
- Si CCD
- G3 image intensifier
- SiOnyx XQE
- starlight illumination

Quantum efficiency vs. wavelength (µm)

- Irradiance (10^-8 W/cm²/µm)

Graph showing the quantum efficiency and irradiance for different devices across various wavelengths.
starlight illumination

SiOnyx
25 mm
F1.4
30 fps

clear, moonless night (laser targeting spot: 30 µJ at 100 m)
solar spectrum

- Spectral irradiance (kW/m² μm)
- Wavelength (μm)

Properties
1. Intermediate band
2. Devices
solar spectrum

```
spectral irradiance (kW/m^2 \mu m)

spectral irradiance (W/m^2)

wavelength (\mu m)

1353 W/m^2

1 properties

2 intermediate band

3 devices
```
crystalline silicon: transparent to 23% of solar radiation

![Graph showing spectral irradiance vs. wavelength with c-Si band gap = 1.12 μm and 1042 W/m² at 1.0 μm.]
amorphous silicon: transparent to 53% of solar radiation

\[ \text{a-Si band gap} = 0.71 \mu m \]

![Graph showing spectral irradiance vs wavelength](image)

- **spectral irradiance (kW/m² • μm)**
- **wavelength (μm)**

- **636 W/m²**

1. **properties**
2. **intermediate band**
3. **devices**
black silicon: potential to recover transmitted energy

![Graph showing spectral irradiance (kW/m² m) as a function of wavelength (µm). The graph indicates a peak at 1.353 W/m² at around 0.5 µm.]

- properties
- intermediate band
- devices
1 properties
2 intermediate band
3 devices
photon with gap energy

1 properties
2 intermediate band
3 devices
photon creates electron-hole pair...

1 properties
2 intermediate band
3 devices
...whose energy can be extracted
photons with energy smaller than gap...
...do not get absorbed
photons with energy larger than the gap...

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

```
CB

VB
```

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

(anode)
semiconductor

(cathode)
metal

1 properties
2 intermediate band
3 devices
water splitting

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
VB
\(e\)
\(h\)
\(\text{H}_2\text{O}\)

(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
VB

O₂
H⁺

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

properties

intermediate band

devices
solar radiation spectrum

- UV
- visible
- infrared

spectral irradiance (W/m²/nm)

wavelength (nm)

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

The diagram shows the spectral irradiance of solar radiation, with peak irradiance in the visible region around 500 nm. The UV, visible, and infrared regions are clearly marked. The absorbance of TiO2 is highlighted, showing its efficiency in absorbing light across a range of wavelengths, with a peak absorbance in the visible spectrum.

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

![Graph of solar radiation spectrum with UV, visible, and infrared regions marked. The graph shows the spectral irradiance (W/m²/nm) plotted against wavelength (nm). The TiO₂ absorptance is also indicated on the right y-axis.]
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

1. properties
2. intermediate band
3. devices
Funding:

Army Research Office
DARPA
Department of Energy
NDSEG
National Science Foundation

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