and also....

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)

Dr. Elizabeth Landis
Dr. John Chervinsky

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

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)

...and the people at SiOnyx
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 \( (1 - R_{int} - T_{int}) \)
absorptance \( (1 - R_{int} - T_{int}) \)

- **impurities and/or defects**
- **multiple reflections**
- **black silicon**
- **crystalline silicon**

![Graph showing absorptance versus wavelength (µm)]
laser treatment causes:

• surface structuring

• inclusion of dopants
gap determines optical and electronic properties
shallow-level dopants control electronic properties
deep-level dopants typically avoided

conductor  semiconductor  insulator

CB  CB  CB
VB  VB  VB

$E_g$ (eV)

0  2  4

Cu  Ge  Si  ZnO
femtosecond laser-doping gives rise to intermediate band

\[
\begin{array}{c|c|c}
\text{Conductor} & \text{Semiconductor} & \text{Insulator} \\
\hline
\text{CB} & \text{CB} & \text{CB} \\
\text{VB} & \text{VB} & \text{VB} \\
\end{array}
\]

\[E_g (\text{eV})\]

\[0 \quad 2 \quad 4\]

\begin{itemize}
\item Cu
\item Ge
\item Si
\item ZnO
\end{itemize}
substrate/dopant combinations

dopants:

substrates:

Si
substrate/dopant combinations

dopants:

substrates:

Si
substrate/dopant combinations

dopants:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
<td>Li</td>
<td>Be</td>
<td>Na</td>
<td>Mg</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>Te</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
<td>Xe</td>
<td></td>
</tr>
</tbody>
</table>

substrates:

Si   Ge   ZnO  InP  GaAs
Ti   Ag   Al   Cu   Pd   Rh   Ta   Pt   TiO$_2$
1 intermediate band
1 intermediate band
2 Si devices
1. intermediate band
2. Si devices
3. X:TiO$_2$
intermediate band formation in chalcogen-hyperdoped Si

dopants:

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>He</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
</tr>
<tr>
<td>Be</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
</tr>
<tr>
<td>Li</td>
<td>Ca</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
</tr>
<tr>
<td>Na</td>
<td>Sr</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
</tr>
<tr>
<td>K</td>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>Kr</td>
</tr>
<tr>
<td>Rb</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
</tr>
<tr>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
</tr>
<tr>
<td>Si</td>
<td>Te</td>
<td>I</td>
<td>Xe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

substrates:

Si
intermediate band

10 μm
intermediate band
1 intermediate band
intermediate band
cross-sectional Transmission Electron Microscopy
disordered surface layer

1 intermediate band
crystalline Si core

1 intermediate band
electron diffraction

1 µm

electron diffraction

intermediate band
1 intermediate band
• 300-nm disordered surface layer

• undisturbed crystalline core

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

intermediate band
relevant time scales

carrier excitation

intermediate band
relevant time scales

carrier excitation

cold

thermalization

hot

intermediate band
relevant time scales

- Carrier excitation
- Thermalization
- Ablation

Time scales:
- fs
- ps
- ns
- µs

Intermediate band
relevant time scales

- Carrier excitation
- Thermalization
- Ablation
- Thermal diffusion

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

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

Time scales: fs, ps, ns, µs
relevant time scales

relevant time scales

- room temperature lattice
- molten surface layer
- cooling material

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

fs | ps | ns | µs
0.1 | 1 | 10 | 0.1 | 1 | 10 | 0.1 | 1 | 10 | 0.1 | 1 | 10

relevant time scales

- 10^(-15) s (fs)
- 10^-10 s (ps)
- 10^-8 s (ns)
- 10^-6 s (μs)

- Carrier excitation
- Cold
- Thermalization
- Resolidification
- Inclusion of dopants
- Molten surface layer
- Ablation
- Surface morphology
- Thermal diffusion
- Cooling material

different thresholds:

melting: 1.5 kJ/m$^2$

ablation: 3.1 kJ/m$^2$
decouple ablation from melting
decouple ablation from melting

doped

intermediate band
decouple ablation from melting

doped

intermediate band
decouple ablation from melting

doped

intermediate band
decouple ablation from melting

undoped

doped

intermediate band
decouple ablation from melting
decouple ablation from melting
decouple ablation from melting

1 intermediate band
decouple ablation from melting
decouple ablation from melting

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

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

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

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

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

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

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

1 intermediate band
$10^{-6}$ sulfur doping

![Graph showing absorptance vs. energy and wavelength for crystalline Si, sulfur impurity states, and Si band edge.](image)
laser-doped S:Si

The diagram shows the absorbance of laser-doped Si and crystalline Si as a function of energy (eV) and wavelength (µm). Key features include:

- **Sulfur impurity states**
- **Si band edge**
- **Intermediate band**

The absorbance peaks at different energy levels, indicating absorption properties in the laser-doped Si and crystalline Si materials.
laser-doped S:Si

- Properties
- Intermediate band
laser-doped S:Si

![Graph showing absorption vs. energy and wavelength for laser-doped Si, sulfur impurity band, crystalline Si, and Si band edge.](image)

- **Energy (eV)**: 0.5, 1.0
- **Wavelength (µm)**: 1, 1.5
- **Absorptance**: 0, 0.5, 1.0

1. **Intermediate band**
Things to keep in mind

- IR absorption rolls off around 8 µm
- evidence of intermediate band formation
- intermediate band due to substitutional S donors
- intermediate band 0–300 meV below CB
1 intermediate band
2 Si devices
should have shallow junction below surface

sulfur-doped layer

p-doped substrate

1 intermediate band

2 Si devices
excellent rectification (after annealing)

![Graph showing current density (A/m²) vs. bias (V)].

1 intermediate band
2 Si devices
responsivity

![Graph showing responsivity vs. wavelength (nm) for Si PIN devices. The graph indicates an intermediate band of responsivity (A/W) across different wavelengths.]
 responsivity

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

1 intermediate band  2 Si devices
The graph shows the responsivity as a function of wavelength (nm) for different materials:

- **S:Si**
- **Si PIN**
- **InGaAs, Ge**

The responsivity is measured in A/W (amperes per watt).

**Key Points**

1. **Intermediate band**
2. **Si devices**
responsivity

![Graph showing responsivity versus wavelength for different materials such as Si PIN, S:Si, and InGaAs, Ge, with a peak at 100% QE.](image)

1. intermediate band
2. Si devices
responsivity

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

- Intermediate band
- Si devices
What causes gain?

• impact excitation (avalanching)

• carrier lifetime >> transit time (photoconductive gain)

• some other mechanism
1 intermediate band  2 Si devices

http://www.sionyx.com
US Patents: US 8,058,615; US 7,928,355; US 7,968,834

1. intermediate band
2. Si devices
Potential benefits for photovoltaics

- surface structure
- absorption in submicrometer layer
- extended IR absorption
- intermediate band
Things to keep in mind

• can turn absorption into carrier generation
• very high responsivity in VIS and IR
• intermediate band photovoltaic devices?
water splitting

1. intermediate band
2. Si devices
3. X:TiO$_2$
water splitting

1. intermediate band
2. Si devices
3. X:TiO₂
water splitting

1. intermediate band
2. Si devices
3. X:TiO$_2$
water splitting

1 intermediate band  2 Si devices  3 X:TiO₂
water splitting

1 intermediate band
2 Si devices
3 X:TiO₂
water splitting

1. intermediate band
2. Si devices
3. X:TiO₂
water splitting

1. intermediate band
2. Si devices
3. X:TiO₂
water splitting

1 intermediate band
2 Si devices
3 X:TiO₂
water splitting

1 intermediate band  2 Si devices  3 X:TiO₂
water splitting

1. intermediate band
2. Si devices
3. X:TiO₂
water splitting

1. intermediate band
2. Si devices
3. X:TiO$_2$
solar radiation spectrum

![Graph of solar radiation spectrum with wavelength (nm) on the x-axis and spectral irradiance (W/m²/nm) on the y-axis. The spectrum is divided into UV, visible, and infrared regions.]

- **1** intermediate band
- **2** Si devices
- **3** X:TiO₂
solar radiation spectrum

![Graph of solar radiation spectrum showing the UV, visible, and infrared regions. The graph also includes the absorptance of TiO<sub>2</sub> and indicates intermediate band, Si devices, and X:TiO<sub>2</sub>.]
solar radiation spectrum

![Graph showing the solar radiation spectrum with various regions labeled UV, visible, and infrared. The graph also shows the spectral irradiance (W/m²/nm) and TiO₂ absorptance.]

- **1** intermediate band
- **2** Si devices
- **3** X:TiO₂
increase efficiency by:

• increasing surface area

• shifting band edge
TiO$_2$ density of states


1. intermediate band
2. Si devices
3. X:TiO$_2$
need to create band(s) in gap

need to create band(s) in gap

need to create band(s) in gap

need to create band(s) in gap

structuring TiO$_2$ in N$_2$ doesn’t work
1 intermediate band
2 Si devices
3 X:TiO$_2$
1 intermediate band  
2 Si devices  
3 X:TiO$_2$
1 intermediate band
2 Si devices
3 X:TiO$_2$
50 pulses @ 2.5 kJ/m²

1. intermediate band
2. Si devices
3. X:TiO₂
50 pulses @ 2.5 kJ/m²

1 intermediate band
2 Si devices
3 X:TiO₂
X-ray photoelectron spectroscopy

![Graph showing binding energy (eV) vs. relative counts with a peak labeled "untreated".]

1. intermediate band
2. Si devices
3. X:TiO$_2$
X-ray photoelectron spectroscopy

- O (1s)
- Ti (2p)

Binding energy (eV)

Relative counts

Untreated

Intermediate band

Si devices

X:TiO₂

1 2 3
X-ray photoelectron spectroscopy

Graph showing binding energy (eV) vs. relative counts for untreated and O₂ samples. Peaks labeled O (1s) and Ti(2p) are visible.
X-ray photoelectron spectroscopy

![Graph showing binding energy (eV) and relative counts for untreated and O2 samples. Peaks for O(1s) and Ti(2p) are marked.]

1. intermediate band
2. Si devices
3. X:TiO₂
oxygen is incorporated!

![Graph showing binding energy (eV) vs. relative counts for Ti^0, Ti^4+, and O_2. The graph compares untreated and treated samples.](image)
oxygen is incorporated!

![Graph showing relative counts vs. binding energy (eV) for untreated and O₂ samples. Peaks at O (1s) and Ti(2p) are indicated.](image)

1 intermediate band  
2 Si devices  
3 X:TiO₂
nitrogen peak appears...
... but nitrogen not chemically incorporated
... but nitrogen not chemically incorporated
with both nitrogen and oxygen...
... just 1% of oxygen prevents nitrogen incorporation...
... although oxygen is incorporated
can get $N_2$ or $O_2$ incorporated, but not both
how about incorporating chromium with oxygen?
evaporate 10 – 70 nm chromium on titanium...
...place in oxygen atmosphere...
...irradiate with laser...

- objective
- oxygen
- 10 – 70 nm Cr
- Ti

1 intermediate band
2 Si devices
3 X:TiO₂
...and raster scan to structure

1. intermediate band
2. Si devices
3. X:TiO₂
titanium/chromium in oxygen

- titanium only
- titanium/chromium

1. intermediate band
2. Si devices
3. X:TiO₂
X-ray photoelectron spectroscopy

Graph showing relative counts vs. binding energy (eV) for untreated and treated samples. Peaks for O (1s) and Ti (2p) are indicated. Notations: 1. intermediate band, 2. Si devices, 3. X:TiO$_2$.
both chromium and oxygen incorporated!
Can produce:

- microstructured TiO$_2$

- can dope TiO$_2$ with Cr, but not N
Summary

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

1. intermediate band
2. Si devices
3. X:TiO₂
What is different about this process?

1. intermediate band
2. Si devices
3. X:TiO₂
Compare femtosecond laser doping to:

- inclusion during growth
- thermal diffusion
- ion implantation

1  intermediate band
2  Si devices
3  X:TiO$_2$
Funding:

Army Research Office
DARPA
Department of Energy
NDSEG
National Science Foundation

for more information and a copy of this presentation:

http://mazur.harvard.edu

Follow me! eric_mazur
Funding:

Army Research Office
DARPA
Department of Energy
NDSEG
National Science Foundation

for more information and a copy of this presentation:

http://mazur.harvard.edu

Follow me! eric_mazur
“pl junction”
formation of partially depleted region

1 intermediate band

2 Si devices
formation of partially depleted region

- *p-doped* substrate
- *laser-doped* layer

1. intermediate band
2. *Si* devices
apply backward bias...

1 intermediate band

2 Si devices
...incident photon generates electron-hole pair...

1 intermediate band

2 Si devices
incident photon generates electron-hole pair...
...carriers accelerate away from each other...

1 intermediate band

2 Si devices
...hole is trapped
meanwhile electron exits sample…

laser-doped layer

partially depleted region

E → E

1 intermediate band
2 Si devices

meanwhile electron exits sample…
...and source provides new electron

1 intermediate band  2 Si devices