Femtosecond laser texturing and doping of semiconductors and metals for solar harvesting

Kasey Phillips & Ben Franta
Yu-Ting Lin, Meng-Ju Sher & Eric Mazur
Harvard University
SPIE Optics + Photonics, San Diego, CA
solar harvesting

sunlight in → electricity out
solar harvesting

sunlight in → electricity out → sunlight in

O₂ → H₂ → hydrogen fuel out
Our goal:

Create new materials to capture light more effectively.
femtosecond laser processing causes:

• surface texturing

• inclusion of dopants
improving silicon photovoltaics

1 Si texturing
2 Si doping
Improving watersplitting

Sunlight in

O₂

H₂

Hydrogen fuel out
Si texturing

Si doping

TiO2
Ultrafast laser irradiation creates surface textures with anti-reflective and light-trapping properties.
Ultrafast laser irradiation creates surface textures with anti-reflective and light-trapping properties. These properties are easily tunable.
irradiation in $N_2$ environment

Dopants:

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Substrates:

Si
laser-textured silicon
additional pulses lead to larger textures

Silicon wafers, 3 kJ/m² in N₂

25 pulses

100 pulses

3 µm
effect of texture depends on size of texture

Sher et al. (in preparation)
effect of texture depends on size of texture

Sher et al. (in preparation)
effect of texture depends on size of texture

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Sher et al. (in preparation)
effect of texture depends on size of texture

25 pulses

texture size: 600 nm
anti-reflection: $\lambda < 1500$ nm
light-trapping: $\lambda < 1200$ nm up to near-IR
effect of texture depends on size of texture

25 pulses
- texture size: 600 nm
- anti-reflection: $\lambda < 1500$ nm
- light-trapping: $\lambda < 1200$ nm, up to near-IR

100 pulses
- texture size: 3 um
- anti-reflection: $\lambda < 7.5$ um
- light-trapping: $\lambda < 6$ um, up to mid-IR
surface texturing gives enhanced absorptance
Surface texturing gives enhanced absorptance.
surface texturing gives enhanced absorptance
Using ultrafast laser processing, texture sizes are easily tunable.
Using ultrafast laser processing, texture sizes are easily tunable.

Challenge:
Independent control of texture width and height.
Using ultrafast laser processing, texture sizes are easily tunable.

Challenge:
Independent control of texture width and height.

Bigger challenge:
Controlling laser-induced damage.
1. Si texturing
2. Si doping
Hyperdoping with deep-level states produces a dopant band and infrared absorption.
Hyperdoping with deep-level states produces a dopant band and infrared absorption.

Dopant band can be tuned with thermal treatments.
we dope silicon with heavy chalcogens
1. Si texturing
2. Si doping
1 Si texturing  
2 Si doping
equilibrium doping leads to isolated defects

hyperdoping leads to an extended band

\begin{align*}
\text{CB} & \quad \text{0.318 eV} \quad \text{0.371 eV} \\
& \quad \text{0.188 eV} \quad \text{0.11 eV} \quad \text{0.09 eV} \quad \text{0.08 eV} \\
& \quad \text{0.614 eV} \quad \text{0.248 eV} \\
\text{VB} &
\end{align*}
hyperdoping leads to an extended band
hyperdoping leads to an extended band

Ultrafast laser hyperdoping produces new materials
hyperdoping leads to an extended band

Ultrafast laser hyperdoping produces new materials with new properties.
chalcogen-hyperdoped silicon absorbs in the infrared

![Graph showing absorbance vs. energy and wavelength]
Chalcogen-hyperdoped silicon absorbs in the infrared.

Diagram showing the absorbance of different silicon materials as a function of energy and wavelength.
hyperdoped silicon absorbs in the infrared

- Si texturing
- Si doping

**Diagram:***

- Hyperdoped + textured Si
- (S, Se, Te) impurity band + light-trapping
- Crystalline Si

**Graph:***

- Absorptance vs. energy (eV)
- Wavelength (µm)

1. Si texturing
2. Si doping
hyperdoped silicon absorbs in the infrared

- Si texturing
- Si doping

- 1248 pulses
- 1684 energy (eV)
- 0.5 1.0 1.5 wavelength (µm)
- 0.5 1.0 absorptance

- crystalline Si
- Si band edge
- (S, Se, Te) impurity band
- + light-trapping
- end of light-trapping
- hyperdoped + textured Si

1 Si texturing
2 Si doping
silicon is doped beyond its solubility limit
dopant concentration controlled with gas pressure

- **Si texturing**
- **Si doping**

![Graph showing dopant concentration controlled with gas pressure](image)

- **Sulfur concentration (cm⁻³)**
- **Depth (nm)**
- **SF₆ pressure (Torr)**
  - 500
  - 100
  - 10
  - 1

**Solubility limit**
dopant concentration controlled with gas pressure

Tune dopant concentration with gas pressure.

SF\textsubscript{6} pressure (Torr)

500

100

10

1

solubility limit

sulfur conc. (cm\textsuperscript{-3})

$10^{19}$

$10^{18}$

$10^{17}$

$10^{16}$

depth (nm)

0

20

40

60

80
dopant concentration controlled with gas pressure

Tune dopant concentration with gas pressure.

Tune dopant band with annealing.

1 Si texturing
2 Si doping
annealing causes deactivation of infrared absorption

annealing causes deactivation of infrared absorption

annealing causes deactivation of infrared absorption

annealing causes deactivation of infrared absorption

![Graph showing the relationship between temperature (K) and average sub-bandgap absorptance for Si:Se](image)

annealing causes deactivation of infrared absorption

high-temp. annealing causes reactivation of infrared absorption

high-temp. annealing causes reactivation of infrared absorption

Annealing tunes dopant band.

high-temp. annealing causes reactivation of infrared absorption

Annealing tunes dopant band.
High-temperature annealing preserves dopant band.

We can:

create a dopant band in silicon with fs-laser hyperdoping.

tune the dopant band in silicon with thermal treatments.
Challenge:
Creating an ideal dopant band for photovoltaics.
Challenge:
Creating an ideal dopant band for photovoltaics.

Bigger challenge:
Controlling carrier recombination induced by the dopant band.
1. Si texturing
2. Si doping
3. TiO₂
water splitting

1. Si texturing
2. Si doping
3. TiO₂
water splitting

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2 \]
water splitting

water splitting

Graetzel, Nature (2001)
water splitting

Graetzel, Nature (2001)
water splitting

Graetzel, Nature (2001)
water splitting

Graetzel, Nature (2001)

1 Si texturing
2 Si doping
3 TiO$_2$
solar spectrum

spectral irradiance (W/m²/nm)

wavelength (nm)

0 500 1000 1500 2000 2500

UV visible infrared
solar spectrum

![Solar Spectrum Diagram](image-url)

1. Si texturing
2. Si doping
3. TiO₂
solar spectrum

UV
visible
infrared

spectral irradiance (W/m²/nm)

TiO₂ absorptance

TiO₂
solar spectrum

![Solar Spectrum Diagram](image)

- **Si texturing**
- **Si doping**
- **TiO₂**
Substrate/dopant combinations

Dopants:

Substrates:

Ti
1 Si texturing  
2 Si doping  
3 TiO$_2$
Si texturing                              Si doping                         TiO₂

50 pulses @ 2.5 kJ/m²
50 pulses @ 2.5 kJ/m²

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy

we form TiO$_2$ in the presence of oxygen

we form TiO$_2$ in the presence of oxygen
nitrogen peak means TiN formed

non-stoicimetric TiN formed

with both nitrogen and oxygen

1% oxygen prevents nitrogen incorporation

nitrogen and oxygen together form $\text{TiO}_2$

can incorporate $N_2$ or $O_2$ but not both
### substrate/dopant combinations

#### Dopants:

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#### Substrates:

- Ti
Si texturing  Si doping  TiO$_2$
increasing laser power
similar surface structures

1. Si texturing
2. Si doping
3. TiO$_2$
both manganese and oxygen incorporated
both manganese and oxygen incorporated
we form rutile TiO$_2$ when annealed

![Raman shift graph](image)
can incorporate a variety of transition metals in TiO₂
then measure photoelectrochemical response
then measure photoelectrochemical response
then measure photoelectrochemical response
water oxidation

![Graph showing current (mA) vs. voltage (V vs Ag/AgCl at pH 13) for light and dark current with laser structured TiO₂.](image)

**Key Points:**
1. Si texturing
2. Si doping
3. TiO₂
water oxidation

- light current
- dark current

voltage (V vs NHE)

overpotential

photocurrent

voltage (V vs Ag/AgCl at pH 13)

current (mA)

0 0.5 1 H₂O/O₂

0 0.2 0.4 0.6 0.8

-0.2 0 0.5 1
water oxidation

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**Diagram Description:**
- The graph shows the relationship between voltage (V vs NHE) and current (mA) for different conditions.
- The voltage range is from 0 to 1.5 V H2O/O2.
- The current is measured in milliamperes (mA).
- Two lines represent different conditions:
  - **Light current** (solid line)
  - **Dark current** (dashed line)
- The graph includes markers for:
  - Laser structured TiO2
  - Annealed TiO2

**Key Points:**
- **Si texturing**
- **Si doping**
- **TiO2**
water oxidation

![Graph showing water oxidation with various TiO₂ treatments.](image)

- **Si texturing**
- **Si doping**
- **TiO₂**
water oxidation

![Graph showing water oxidation with voltage vs NHE and current (mA) on the y-axis. The graph includes different lines for light current, dark current, laser structured TiO₂, annealed TiO₂, TiO₂:Mn, and TiO₂:Cr.](image)
water oxidation

![Graph showing the relationship between voltage and current for different materials]
Produce nanostructured and doped TiO$_2$

Oxidize water with laser-structured samples
Produce nanostructured and doped TiO$_2$

Oxidize water with laser-structured samples

Future work: Extend to other oxides and optimize dopants
Thank you!

Army Research Office
DARPA
Department of Energy
NDSEG
National Science Foundation

for more information and a copy of this presentation:
http://mazur.harvard.edu