Femtosecond laser doping of silicon beyond the equilibrium limit

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Photonics West West 2009
Understanding non-equilibrium doping:
Understanding non-equilibrium doping:

- Laser doping – how we do it and what we know
Understanding non-equilibrium doping:

- Laser doping – how we do it and what we know
- Non-equilibrium dopant concentrations
Understanding non-equilibrium doping:

- Laser doping – how we do it and what we know
- Non-equilibrium dopant concentrations
- Hall measurements – determining dopant energetics
femtosecond laser doped silicon
laser process  non-eq. doping  electronic structure
\[ \overline{A} = \frac{1-R-T}{1-R} \]

[Graph showing normalized absorptance vs. wavelength and photon energy]
\[ \bar{A} = \frac{1-R-T}{1-R} \]

**Graph:**
- **Normalized absorptance** vs **Wavelength (nm)**
- **Photon energy (eV)** range: 0 to 0.5
- **Normalized absorptance** range: 0 to 1
- **Wavelength (nm)** range: 0 to 2500
- **Black Silicon** and **Silicon**

**Legend:**
- **Red line:** Black silicon
- **Black line:** Silicon
\[ \bar{A} = \frac{1-R-T}{1-R} \]

![Graph showing normalized absorptance vs. photon energy](image)

The graph displays the normalized absorptance for different materials:
- **Black Silicon**
- **Doped Silicon**
- **Silicon**

The x-axis represents the wavelength in nanometers, and the y-axis represents the normalized absorptance.
Laser-doping yields interesting optoelectronic devices

quantum efficiency = 1
Laser-doping yields interesting optoelectronic devices

commercial Si PIN

quantum efficiency = 1
Laser-doping yields interesting optoelectronic devices

quantum efficiency = 1
Laser-doping yields interesting optoelectronic devices

Why?
Hypothesis: non-equilibrium doping yields impurity band

laser process  non-eq. doping  electronic structure
epoxy (used for sample preparation)

laser affected region

substrate

100 nm
fs lasers dope beyond equilibrium limit

secondary ion mass spectroscopy (SIMS)
fs lasers dope beyond equilibrium limit

secondary ion mass spectroscopy (SIMS)

![Graph showing concentration of dopant versus depth with a sharp drop-off beyond equilibrium limit.](image-url)
fs lasers dope beyond equilibrium limit

secondary ion mass spectroscopy (SIMS)
fs lasers dope beyond equilibrium limit

secondary ion mass spectroscopy (SIMS)

\[ n_{eq} < 10^{17} \text{ cm}^{-3} \]
epoxy (used for sample preparation)

laser affected region

substrate

100 nm
Isolate surface properties

device layer
buried oxide
silicon substrate
Isolate surface properties

- femtosecond laser pulse
- device layer
  - buried oxide
  - silicon substrate
Isolate surface properties

- buried oxide
- silicon substrate
laser process  non-eq. doping  electronic structure
\[ n = \frac{IB}{qdV} \]
\[ n = \frac{IB}{qdV} \]

\[ n \equiv n(\varepsilon_d, T) \]
Dopant levels from Hall measurements

\[ n^2 = C_0 \ T^3 \ e^{-\frac{\epsilon_g}{k_b T}} \]

\[ \log \left( \frac{n}{T^{1.5}} \right) = C_1 - \frac{\epsilon_g}{2 \ k_b} \left( \frac{1}{T} \right) \]
Dopant levels from Hall measurements

\[ n^2 = C_0 \ T^3 \ e^{-\epsilon_g / k_b T} \]

\[ \log \left( \frac{n}{n_{\text{room}}} \right) = C_1 - \frac{\epsilon_g}{2 \ k_b} \left( \frac{1}{T} \right) \]
Dopant levels from Hall measurements

\[ n^2 = C_0 \, T^3 \, e^{-\frac{\varepsilon_g}{k_b T}} \]

\[ \log \left( \frac{n}{T^{1.5}} \right) = C_1 - \frac{\varepsilon_g}{2 \, k_b} \left( \frac{1}{T} \right) \]

\[ \varepsilon_g = 1.11 \text{eV} \]

Temperature (K)

\[ \text{N/P 5000 } \Omega\text{-cm} \]
Dopant levels from Hall measurements

Temperature (K)

$\frac{n}{n_{room}}$

PRELIMINARY RESULTS
Dopant levels from Hall measurements

Temperature (K)

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

PRELIMINARY RESULTS
Dopant levels from Hall measurements

Temperature (K)

- N/P 5000 Ω-cm
- P/B 10 Ω-cm
- Laser doped Si

PRELIMINARY RESULTS
**PRELIMINARY RESULTS**

Dopant levels from Hall measurements

![Graph showing temperature versus normalized doping concentration](image)

- **N/P 5000 Ω-cm**
- **P/B 10 Ω-cm**
- **Laser doped Si**

\[ \varepsilon_d = 310 \text{ meV} \]
Preliminary conclusion: S takes \textit{substitutional} site
Conclusions

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<th>non-eq. doping</th>
<th>electronic structure</th>
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Conclusions
Laser doping dramatically alters optical properties

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We can extend spectral range of silicon.
Laser doping dramatically alters optical properties

Dopants exceed equilibrium concentrations

We can extend spectral range of silicon

Conclusions
Laser doping dramatically alters optical properties

We can extend spectral range of silicon

Dopants exceed equilibrium concentrations

Better knowledge of electronic structure will enable incorporation into devices
Acknowledgements

Eric Diebold, Albert Zhang, Jim Carey, Brian Tull
Mike Aziz, Brion Bob

the Mazur Group

Funding: NSF, ARO

Thanks! Questions?

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http://mazur-www.harvard.edu
END OF TALK
Process: laser + SF6 → Property: IR absorption
laser doping  structural clues  new directions

Structure

Process
laser + SF6

Property
IR absorption
laser doping  structural clues  new directions
diffusion length = $\sqrt{D_i t} = f(T,t)$
normalized absorptance vs. diffusion length (nm)

S, Se, Te

laser doping  structural clues  new directions
Could this diffusion-related drop in absorptance be governed by grain size?
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Could this diffusion-related drop in absorptance be governed by grain size?
Conclusion: diffusion is the dominant mechanism involved in deactivation of optical response
FSLASER
3ULFUR
COMPOUND

- **Photon Energy (eV)**
  - 0
  - 1
  - 2
  - 3
  - 0.5

- **Absorbance**
  - 1.0
  - 0.8
  - 0.6
  - 0.4
  - 0.2

- **Wavelength (μm)**
  - 0
  - 1
  - 2
  - 3

- **Silicon Substrate**

**Keywords:**
- Laser doping
- Structural clues
- New directions

**Additional Image:** Laser doping with structural clues and new directions.
laser doping  structural clues  new directions

![Graph showing absorbance vs. photon energy for different materials.](image)

- **Absorbance vs. Wavelength (μm)**:
  - **Photon Energy (eV)**: 0.5, 1.0, 2, 3
  - **Absorbance**:
    - 0.0, 0.2, 0.4, 0.6, 0.8, 1.0

- **Materials**:
  - **Substrate**: Silicon
  - **Sub-bandgap**: IR absorption
  - **Laser Doped Silicon**: FS Laser doped silicon

- **Key Points**:
  - **Structural Clues**: Laser doping
  - **New Directions**: Sulfur compound
laser doping  structural clues  new directions

 photon energy (eV)

3  2  1  0.5

wavelength (μm)

0  1  2  3

absorptance

0.0  0.2  0.4  0.6  0.8  1.0

fs laser doped silicon

sub-bandgap IR absorption

silicon substrate

chemical clues

BIAS 6

CURRENT 6

no anneal

30 min @ 1075 K

Back bias

V < 0

Forward bias

V > 0

bias (V)
laser doping  structural clues  new directions

- fs laser
- doped silicon
- photon energy (eV)
- wavelength (μm)
- absorptance
- IR absorption
- sub-bandgap
- silicon substrate
- no anneal
- Back bias $V < 0$
- Forward bias $V > 0$
- 30 min @ 1075 K
- Back bias $V < 0$
- Forward bias $V > 0$

Sulfur compound
laser doping  structural clues  new directions

- fs laser doped silicon
- sub-bandgap IR absorption
- silicon substrate
- photon energy (eV)
- wavelength (μm)
- absorptance

- current (mA)
- bias (V)
- no anneal
- 30 min @ 1075 K
- Back bias V < 0
- Forward bias V > 0

- fs laser doping
- structural clues
- new directions
laser doping

- Absorptance vs. photon energy (eV)
  - fs laser doped silicon
  - Sub-bandgap IR absorption

- Current vs. bias (V)
  - No anneal
  - 30 min @ 1075 K

- Structural clues
  - New directions

- Laser doping
  - Sulfur compound

- Images: Coin, SEM micrograph of silicon substrate, laser doping setup.
laser doping  structural clues  new directions

- Photon energy (eV)
- Wavelength (μm)
- Absorptance
- Sub-bandgap IR absorption
- Silicon substrate
- Substrate
- Current (mA)
- Bias (V)

- No anneal
- 30 min @ 1075 K
- Back bias
- Forward bias

Cross-sectional TEM (F. Génin, LLNL)
laser doping  structural clues  new directions

![Image](https://example.com/image1.png)

$\text{wavelength (μm)}$

$\text{absorptance}$

$\text{photon energy (eV)}$

$\text{fs laser doped silicon}$

$\text{sub-bandgap IR absorption}$

$\text{silicon substrate}$

$\text{current (mA)}$

$\text{bias (V)}$

$\text{no anneal}$

$\text{30 min @ 1075 K}$

$\text{Back bias V < 0}$

$\text{Forward bias V > 0}$

$\text{RBS 1% sulfur}$

$\text{cross-sectional TEM (F. Génin, LLNL)}$
laser doping

structual clues

new directions

Activates surface roughness

Alters the optical properties of Si

Creates a p-n junction in Si

Dopes Si to high levels (~$10^{21}$/cm$^3$)

RBS 1% sulfur

cross-sectional TEM (F. Génin, LLNL)
quantum efficiency = 1
The graph illustrates the responsivity (A/W) as a function of wavelength (μm) for different types of photodiodes. The green line represents a commercial Si PIN photodiode, while the dotted line indicates a quantum efficiency of 1. Laser doping and new directions in structural clues are also mentioned in the context of improving photodiode performance.
Laser-doping extends silicon’s reach

Laser-doping extends silicon’s reach through the use of sulfur and commercial Si PIN. The quantum efficiency is 1.

Responsivity (A/W)

Wavelength (μm)

Commercial Si PIN

Quantum efficiency = 1
Laser-doping extends silicon’s reach

Why?

- Laser-doping
- Structural clues
- New directions
FIG. 1. Sulfur-related centers in silicon. $S^+_c(X_1)$, $S^0_c(X_2)$, and $S^0_c(X_3)$ are sulfur-related complexes not observed previously (see also, however, Refs. 29 and 30). The binding energies of all centers are taken from this paper and are similar to those found in the literature (Refs. 8, 15, 22, 23, 25, 30, 31, and 37–44).