Laser-assisted microstructuring of silicon surfaces for novel detector, sensing, and display technologies

Jim Carey
Tsing-Hua Her
Mike Sheehy
Claudia Wu
Rebecca Younkin
Catherine Crouch
Meng Yan Shen
Li Zhao

Lawrence Livermore National Laboratory
Livermore, 16 October 2001
Irradiate with 100-fs 10 kJ/m² pulses
Introduction

“black silicon”
Introduction

20 µm
Introduction
Introduction
Introduction
Introduction
Introduction

- maskless etching process
- self-organized, tall, sharp structures
- nanoscale structure on spikes
Outline

- Properties
- Structural and chemical analysis
- Outlook
Properties

reflectance (integrating sphere)

![Graph showing reflectance as a function of wavelength (in micrometers)]

- Wavelength (µm)
- Reflectance
- Crystalline silicon
**Properties**

reflectance (integrating sphere)
Properties

transmittance (integrating sphere)

![Graph showing transmittance vs wavelength for crystalline silicon.](image-url)
Properties

transmittance (integrating sphere)

![Graph showing transmittance vs. wavelength for crystalline silicon and microstructured silicon.](image-url)
Properties

absorptance \((1 - R - T)\)

![Graph showing absorptance as a function of wavelength.]
Properties

absorptance \((1 - R - T)\)

*Appl. Phys. Lett. 78, 1850 (2001)*
Properties

absorptance \((1 - R - T)\)

![Graph showing absorptance versus wavelength](image)

Properties

field emission setup
Properties

field emission setup

gold coating
Properties

field emission setup

20 µm mica spacers

gold coating
Properties

field emission setup

anode

gold coating
Properties

field emission setup

- Anode
- Gold coating
- 1 MΩ
- Current (A)
- Voltage (V)
Properties
Properties

turn-on field (1 \(\mu\text{A/cm}^2\)): 1.2 V/\(\mu\text{m}\)
Properties

threshold field (10 $\mu$A/cm$^2$): 2.1 V/$\mu$m
Properties

![Graph showing potential difference (V) vs. current (mA)](image-url)
Properties
Properties

maximum current: 20 mA (4 mm$^2$ sample)
Properties

\[ \ln \frac{I}{\Delta V^2} = \ln a - b \frac{1}{\Delta V} \]

Properties
Properties
Points to keep in mind:

- near unity absorption
- sub-band gap absorption
- IR photoelectron generation
- high field emission at low fields
Outline

- Properties
- Structural and chemical analysis
- Outlook
What causes these properties?

Other gases?
Structural and chemical analysis

Ion channeling and electron backscattering:

- spikes retain crystalline order
- high density of defects
Secondary ion mass spectrometry:

- $10^{20} \text{ cm}^{-3}$ sulfur
- $10^{17} \text{ cm}^{-3}$ fluorine
Structural and chemical analysis

cross-sectional TEM (F. Génin, M. Wall, LLNL)
cross-sectional TEM (F. Génin, M. Wall, LLNL)
Structural and chemical analysis

1 µm
	nanocrystallites

cross-sectional TEM (F. Génin, M. Wall, LLNL)
cross-sectional TEM (F. Génin, M. Wall, LLNL)

crystalline Si
Structural and chemical analysis

electron diffraction (F. Génin, M. Wall, LLNL)
Structural and chemical analysis

electron diffraction (F. Génin, M. Wall, LLNL)
cross-sectional TEM:

- core of spikes: undisturbed Si
- surface layer: disordered Si, impurities, nanocrystallites and pores
Structural and chemical analysis

anneal 4 hours at 1200 K

![Absorptance vs. Wavelength Graph]

For more detailed information, refer to:

Structural and chemical analysis

anneal 4 hours at 1200 K

Structural and chemical analysis

anneal 4 hours at 1200 K
Structural and chemical analysis

anneal 4 hours at 1200 K

Effects of annealing:

- IR absorption: reduced twofold
- SEM: fewer surface nanostructures
- SIMS: sulfur content reduced twofold
Structural and chemical analysis

sulfur introduces states in the gap

CB

VB
Structural and chemical analysis

sulfur introduces states in the gap

Structural and chemical analysis

states broaden into a band
Structural and chemical analysis
Structural and chemical analysis

- $E_F$
- $\phi$
- Metal
- Vacuum
Structural and chemical analysis

\[ E_F \]

metal \hspace{1cm} vacuum

\[ \phi \]
Structural and chemical analysis

$E_F$ 

$\phi$ 

$e^-$ 

metal

vacuum
Structural and chemical analysis
Structural and chemical analysis

\[ E_F \]
\[ \phi \]
\[ E_g \]

CB

VB

semiconductor

vacuum
Structural and chemical analysis
Structural and chemical analysis

Diagram: Semiconductor band structure with conduction band (CB) and valence band (VB). The Fermi level ($E_F$) is indicated, and electrons ($e^-$) are shown moving from the semiconductor into the vacuum.
Structural and chemical analysis

sulfur band provides additional electrons
Structural and chemical analysis

effect of ambient gas on absorptance

![Graph showing absorptance vs. wavelength for crystalline silicon and SF₆ gas.](image)

- Absorptance values range from 0.0 to 1.0.
- Wavelength values range from 0.0 to 3.0 µm.
- Crystalline silicon and SF₆ gas are indicated on the graph.
Structural and chemical analysis

effect of ambient gas on absorptance

![Graph showing the absorptance of crystalline silicon and SF\textsubscript{6} and Cl\textsubscript{2} as a function of wavelength (\mu m).]
Structural and chemical analysis

effect of ambient gas on absorptance

![Graph showing the effect of ambient gas on absorptance. The graph plots absorptance against wavelength (µm) for SF₆, Cl₂, N₂, and crystalline silicon. The graph indicates that SF₆ has the highest absorptance, followed by Cl₂, N₂, and crystalline silicon, with the latter showing the least absorptance.]
Structural and chemical analysis

effect of ambient gas on absorptance

![Graph showing the effect of ambient gas on absorptance, with curves for SF$_6$, Cl$_2$, N$_2$, and air, along with crystalline silicon.](image)
Structural and chemical analysis

effect of ambient gas on field emission

![Graph showing the relationship between potential difference (V) and current (mA) with SF₆ gas.]
Structural and chemical analysis

effect of ambient gas on field emission

![Graph showing the effect of potential difference on current for SF₆ and Cl₂ gases.](image)
Structural and chemical analysis

effect of ambient gas on field emission

diagram showing the relationship between potential difference (V) and current (mA) for SF$_6$, N$_2$, and Cl$_2$ gases.
Structural and chemical analysis

effect of ambient gas on field emission
### Structural and chemical analysis

<table>
<thead>
<tr>
<th></th>
<th>SF$_6$</th>
<th>Cl$_2$</th>
<th>N$_2$</th>
<th>air</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR absorption</td>
<td>high</td>
<td>medium</td>
<td>low</td>
<td>low</td>
</tr>
<tr>
<td>field emission</td>
<td>high</td>
<td>low</td>
<td>medium</td>
<td>low</td>
</tr>
<tr>
<td>SIMS</td>
<td>high S</td>
<td>?</td>
<td>?</td>
<td>high O</td>
</tr>
<tr>
<td>nanostructure</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
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</table>
Structural and chemical analysis

- significant incorporation of ambient species
- nanostructured surface layer
- sulfur content correlates with IR absorption
A forest of silicon spikes could revolutionise solar cells and give you painless injections. **Bruce Schechter** peers into the mysterious world of black silicon.
Outlook

- detector technology
Outlook

- detector technology
- solar cells
Outlook

- detector technology
- solar cells
- display technology
Outlook

- detector technology
- solar cells
- display technology
- sensors
Outlook

- development of spikes
- spike formation through grids
- cell adhesion
- functionalization
can ordering of spikes be improved by using a grid?
Si or Ti substrate
Outlook

place grid in front of substrate

10 µm thick Cu or Ni grid
Si or Ti substrate
Outlook

scan laser beam

10 µm thick Cu or Ni grid

Si or Ti substrate
Outlook

scan laser beam

10 µm thick Cu or Ni grid

Si or Ti substrate
Outlook

remove grid

Si or Ti substrate
Summary

Microstructured silicon

- fabricated by simple, maskless process
Microstructured silicon

- fabricated by simple, maskless process
- can be integrated with microelectronics
Microstructured silicon

- fabricated by simple, maskless process
- can be integrated with microelectronics
- generates IR photocurrent
Microstructured silicon

- fabricated by simple, maskless process
- can be integrated with microelectronics
- generates IR photocurrent
- provides stable, high field emission current
Microstructured silicon

- fabricated by simple, maskless process
- can be integrated with microelectronics
- generates IR photocurrent
- provides stable, high field emission current
- is durable
Funding: ARO, DoE, NDSEG

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Dr. John Chervinsky (Harvard University)
Prof. Cynthia Friend (Harvard University)
Prof. Mike Aziz (Harvard University)

For a copy of this talk and additional information, see:

http://mazur-www.harvard.edu
Materials

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<th>SF$_6$</th>
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Si

Ti reacts

Only in SF$_6$:

Ge

InP

No spikes in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Materials

SF₆  Cl₂  N₂  air  vacuum

Si  Ti  Ge

Only in SF₆:  Ge, InP

No spikes in SF₆:  Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
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Si

Ti

Ge

Only in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

No spikes in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
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Si

Ti

Ge

Only in SF₆:

No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Materials

SF$_6$ | Cl$_2$ | N$_2$ | air | vacuum

Si

Ti

Ge

Only in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

No spikes in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Materials

SF\textsubscript{6} | Cl\textsubscript{2} | N\textsubscript{2} | air | vacuum

Si

Ti

Ge

Only in SF\textsubscript{6}: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

No spikes in SF\textsubscript{6}: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
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<td>Si</td>
<td>Only in SF\textsubscript{6}: Si</td>
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<tr>
<td>Ge</td>
<td>\text{No spikes in SF\textsubscript{6}: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs}</td>
<td>\text{No spikes in SF\textsubscript{6}: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs}</td>
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Materials

Only in SF₆:

- Cl₂
- N₂
- air
- vacuum

No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
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Si

Ti

Ge

Only in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

No spikes in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Materials

- Si
- Ti
- Ge

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Only in SF₆: Si, Ge

No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs