femtosecond laser pulses are extremely short in duration

Introduction

femtosecond laser pulses are extremely short in duration
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femtosecond laser pulses are extremely short in duration

our laser pulse = 100 fs

- computer processing
- fastest cameras
- a neuron firing
- a blink
- a minute

since dinosaurs

- a universe
- a day
- a year
- a Brian
- an hour
- a minute
- a second

time (seconds)

- $10^0$
- $10^3$
- $10^6$
- $10^9$
- $10^{12}$
- $10^{15}$
- $10^{18}$

- $10^{-15}$
- $10^{-12}$
- $10^{-9}$
- $10^{-6}$
- $10^{-3}$
- $10^0$
- $10^3$
femtosecond laser pulses are extremely intense
Basic experiment

- silicon wafer
- near atmosphere background gas
- fs laser pulses
Outline

Ejected material
  previous work
  formation of nanoparticles

Irradiated substrate
  previous work
  effect of thermal annealing
    optical properties
    photovoltaic properties
Ejected material: motivation

why femtosecond pulses?

no interaction with ejected material

higher energy densities can be achieved than with longer pulses
Ejected material: previous work

Theory paper: 800-nm, 100-fs

lattice $T \sim 10^3 - 10^5$ K
vacuum expansion, $10^{12} - 10^{18}$ K/s
particles (1 – 10 nm) form by fragmentation
Ejected material: previous work

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Experiments

800-nm, 200-fs particles form < 50 ps

780-nm, 120-fs particles 5 – 50 nm
Ejected material: previous work

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vacuum expansion, $10^{12} - 10^{18}$ K/s
particles (1 – 10 nm) form by fragmentation

Experiments

800-nm, 200-fs particles form < 50 ps
780-nm, 120-fs particles 5 – 50 nm

No structure data; vacuum only
Collecting ejected material

- **H₂ or H₂S gas**
- **Cu wire with TEM grids**
- **fs laser pulses**
- **silicon wafer**
Ejected material

selected area diffraction
Ejected material

selected area diffraction

crystalline
Ejected material

selected area diffraction

crystalline
Ejected material

selected area diffraction

crystalline

amorphous
Ejected material: amorphous?

amorphous silicon can form from the liquid phase
Ejected material: amorphous?

amorphous silicon can form from the liquid phase
Ejected material: amorphous?

Amorphous silicon can form from the liquid phase.

- Short pulsed laser irradiated target
- Electrohydrodynamic atomization

Cooling rate (K/s):

- Crystalline
- Amorphous
Ejected material: amorphous?

Amorphous silicon can form from the liquid phase.
Ejected material: varying pressure
Ejected material: varying pressure
Ejected material: varying pressure

Number of particles vs. particle diameter (nm) with a peak at 500 Torr.
Ejected material: varying pressure

![Graph showing the number of particles versus particle diameter for different pressures (500 Torr and 100 Torr). The graph demonstrates a peak particle diameter at around 20 nm with a higher number of particles at 500 Torr compared to 100 Torr.]
Ejected material: varying pressure

![Graph showing particle diameter (nm) vs. number of particles/area for 500 Torr and 100 Torr pressures.](chart.png)
Ejected material: varying pressure

lower pressure = more amorphous material

500 Torr  mixture of crystalline and amorphous
100 Torr  ~ 3 times more amorphous/unit area
10 Torr   nearly all amorphous
Ejected material: varying pressure

background pressure reduces the effect of expansion cooling

crystalline

fs laser vacuum expansion

amorphous

cooling rate
Ejected material: varying pressure

background pressure reduces the effect of expansion cooling

- 10 Torr
- 100 Torr
- 500 Torr

fs laser vacuum expansion

crystalline to amorphous

cooling rate
the background gas reduces the effect of expansion cooling allowing more time for crystalline particles to form.

the background gas offers control over the structure and size of the particles that form.
Outline

Ejected material
  previous work
  formation of nanoparticles

Irradiated substrate
  previous work
  effect of thermal annealing
    optical properties
    photovoltaic properties
Background

SF$_6$ gas
100 fs
800 nm
Background

SF₆ gas
100 fs
800 nm

3 μm
Background
absorptance: \( A = 1 - (T + R) \)
absorptance: \[ A = 1 - (T + R) \]
Background

absorptance: \( A = 1 - (T + R) \)
Background

absorbs infrared light

![Graph showing absorptance vs wavelength (µm)]

- Crystalline silicon
- SF$_6$
Background

selenium and tellurium too
Background

1 μm single crystal substrate
Background

polycrystalline

RBS: ~1.0 at. %
S, Se or Te

single crystal substrate
Background

thermal annealing reduces IR absorptance

![Graph showing the effect of thermal annealing on crystalline silicon absorptance across different wavelengths.](Image)

- Sulfur
- 675 K
- 725 K
- 775 K
- 825 K

absorptance vs. wavelength (µm)
Background

no significant change in RBS or TEM measurements
Background

IR absorptance reduction depends on dopant

![Graph showing absorptance vs. wavelength for various dopants at 775 K. The graph includes lines for Te, Se, and S, with crystalline silicon also shown.]
Background

what is changing?

![Diagram showing the absorptance of different elements at 775 K as a function of wavelength (µm). The elements include crystalline silicon, Te, 775 K, Se, 775 K, and S, 775 K.](chart.png)
Background

what do we expect from thermal annealing?
what do we expect from thermal annealing?

healing of the lattice: point defect diffusion
grain growth
recrystallization
what do we expect from thermal annealing?

healing of the lattice: point defect diffusion
grain growth
recrystallization

redistribution of the dopant
Background

redistribution of the dopant
Background

redistribution of the dopant

1 at. % $\sim 5 \times 10^{20}$ cm$^{-3}$
Background

redistribution of the dopant

\[ 1 \text{ at. \%} \sim 5 \times 10^{20} \text{ cm}^{-3} \]

max solubility of S, Se, or Te \( \sim 10^{17} \text{ cm}^{-3} \)
redistribution of the dopant

1 at. % $\sim 5 \times 10^{20} \text{ cm}^{-3}$

max solubility of S, Se, or Te $\sim 10^{17} \text{ cm}^{-3}$

driving force for precipitation of the dopant
Background

redistribution of the dopant

1 at. % \sim 5 \times 10^{20} \text{ cm}^{-3}

max solubility of S, Se, or Te \sim 10^{17} \text{ cm}^{-3}

driving force for precipitation of the dopant

within the grains

and at grain boundaries
Background

redistribution of the dopant

1 at. % ~ 5 x 10^{20} \text{ cm}^{-3}

max solubility of S, Se, or Te ~ 10^{17} \text{ cm}^{-3}

driving force for precipitation of the dopant

within the grains

and at grain boundaries

diffusion
Background

does dopant diffusion affect IR absorptance?
Background

does dopant diffusion affect IR absorptance?

bulk diffusivity in Si

\[ D_S > D_{Se} > D_{Te} \]
does dopant diffusion affect IR absorptance?

bulk diffusivity in Si

\[ DS > D_{Se} > D_{Te} \]
Annealing experiment

goal: test if decrease in IR absorptance is consistent with diffusion theory

samples:

> 40 anneals:
Annealing experiment

goal: test if decrease in IR absorptance is consistent with diffusion theory

samples: Si irradiated in SF$_6$

> 40 anneals:
Annealing experiment

**goal:** test if decrease in IR absorptance is consistent with diffusion theory

**samples:**
- Si irradiated in SF$_6$
- Si coated with 150 nm Se irradiated in N$_2$

> 40 anneals:
Annealing experiment

goal: test if decrease in IR absorptance is consistent with diffusion theory

samples:  Si irradiated in SF$_6$
Si coated with 150 nm Se irradiated in N$_2$
Si coated with 150 nm Te irradiated in N$_2$

> 40 anneals:
Annealing experiment

good: test if decrease in IR absorptance is consistent with diffusion theory

samples: Si irradiated in SF$_6$
Si coated with 150 nm Se irradiated in N$_2$
Si coated with 150 nm Te irradiated in N$_2$
Si irradiated in N$_2$ gas

> 40 anneals:
Annealing experiment

goal: test if decrease in IR absorptance is consistent with diffusion theory

samples: Si irradiated in SF$_6$
Si coated with 150 nm Se irradiated in N$_2$
Si coated with 150 nm Te irradiated in N$_2$
Si irradiated in N$_2$ gas

> 40 anneals: 575 – 1175 K
10 min – 24 hrs
Annealing experiment

absorptance after irradiation

![Graph showing absorptance vs. wavelength for crystalline Si and different irradiation conditions.](image-url)
Annealing experiment

absorptance after annealing at 775 K for 10 min
Annealing experiment

absorptance after annealing at 775 K for 30 min

![Graph showing absorptance as a function of wavelength for Si:Te, Si:Se, and Si:S after annealing at 775 K for 30 min. The graph plots absorptance on the y-axis against wavelength (nm) on the x-axis. The absorptance values range from 0.0 to 1.0. The graph indicates lower absorptance for Si:S compared to Si:Te and Si:Se.]
Annealing experiment

absorptance after annealing at 775 K for 100 min

The graph shows the absorptance of Si:Te, Si:Se, and Si:S as a function of wavelength (nm).
Annealing experiment

absorptance after annealing at 775 K for 6 hours

[Graph showing absorptance as a function of wavelength for Si:Te, Si:Se, and Si:S]
Annealing experiment

absorptance after annealing at 775 K for 24 hours

![Graph showing absorptance vs. wavelength for Si:Te, Si:Se, and Si:S after annealing at 775 K for 24 hours.](image-url)
Annealing experiment

average absorptance after annealing (1250–2500 nm)
Annealing experiment

average absorptance after annealing (1250–2500 nm)
Annealing experiment

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Annealing experiment

average absorptance after annealing (1250–2500 nm)

Te
Se
S
N

absorptance

temperature (K)

10 min
30 min
100 min
6 hr
24 hr
Annealing experiment

average absorptance after annealing (1250–2500 nm)
Annealing experiment

assign a characteristic diffusion length, $d_i$,
for each anneal and for each dopant $i = S, Se, Te$

$$d_i = \sqrt{D_i t}$$
assign a characteristic diffusion length, $d_i$, for each anneal and for each dopant $i = S, Se, Te$

$$d_i = \sqrt{D_i t}$$

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C)$$
assign a characteristic diffusion length, \( d_i \), for each anneal and for each dopant \( i = S, Se, Te \)

\[
d_i = \sqrt{D_i t}
\]

\[
\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C)
\]

\[
D_i = D_i^0 \exp\left(-\frac{E_i}{kT}\right)
\]

\( D_i^0, E_i = \text{diffusion constants} \)
assign a characteristic diffusion length, $d_i$, for each anneal and for each dopant $i = \text{S, Se, Te}$

$$d_i = \sqrt{D_i t}$$

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C)$$

$$D_i = D_i^0 \exp\left(-\frac{E_i}{kT}\right)$$

$D_i^0, E_i =$ diffusion constants

so

$$d_i = f(T, t)$$
Annealing experiment

For each dopant:

plot average IR absorptance vs diffusion length

\[ A_{IR} \text{ vs. } d_i \]
Annealing experiment

For each dopant:

plot average IR absorptance vs diffusion length

\[ A_{IR} \text{ vs. } d_i \]

normalize \( A_{IR} \) so,

\[ 1 = A_{IR} \text{ before annealing} \]

\[ 0 = A_{IR} \text{ of initial silicon wafer} \]
Annealing experiment

temperature (K) vs. normalized absorptance
Annealing experiment

absorptance now forms a continuous curve

![Graph showing the relationship between normalized absorptance and diffusion length (nm)].
Annealing experiment

IR absorptance decreases at similar rate

![Graph showing normalized absorptance versus diffusion length (nm)]
Annealing experiment

IR absorptance decreases at similar rate

![Graph showing the relationship between normalized absorptance and diffusion length (nm)].
Annealing experiment

there is a characteristic diffusion length for deactivation of IR absorption
could the characteristic diffusion length be set by grain size?
Annealing experiment

could the characteristic diffusion length be set by grain size?

plan: determine $C(r, d)$
Annealing experiment

could the characteristic diffusion length be set by grain size?

plan: determine $C(r, d)$

$$N(d) = \int_{0}^{R_0} C(r, d) 4\pi r^2 \, dr$$
could the characteristic diffusion length be set by grain size?

plan: determine \( C(r, d) \)

\[
N(d) = \int_{0}^{R_0} C(r, d) \, 4\pi r^2 \, dr
\]

\[
\frac{N(d)}{N_0} = \frac{N(d)}{\frac{4}{3} \pi R_0^3 C_0}
\]
Annealing experiment

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\[
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\]

compare \( \frac{N(d)}{N_0} \) to \( A_{IR}(d) \) for various \( R_0 \)
Annealing experiment

assume grain boundaries are perfect sinks for dopants

\[ C(r,d) = -\frac{2R_0C_0}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin\left(\frac{n\pi r}{R_0}\right) \exp\left(-\left(\frac{n\pi d}{R_0}\right)^2\right) \]
Annealing experiment

assume grain boundaries are perfect sinks for dopants

\[ C(r,d) = - \frac{2R_0C_0}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \frac{\sin(n\pi r/R_0)}{R_0} \exp\left(-\left(\frac{n\pi d}{R_0}\right)^2\right) \]
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could the characteristic diffusion length be set by grain size?

plan: determine \( C(r, d) \)

\[
N(d) = \int_{0}^{R_0} C(r, d) \ 4\pi r^2 \ dr
\]

\[
\frac{N(d)}{N_0} = \frac{N(d)}{\frac{4}{3} \pi R_0^3 C_0}
\]

compare \( \frac{N(d)}{N_0} \) to \( A_{IR}(d) \) for various \( R_0 \)
Annealing experiment

\[
\frac{N(d)}{N_0} = \frac{6}{\pi^2} \sum_{n=1}^{100} \frac{1}{n^2} \exp\left(-\left(n\pi d/R_0\right)^2\right)
\]
Annealing experiment

compare $\frac{N(d)}{N_0}$ to $A_{IR}(d)$.
Annealing experiment

Compare \( \frac{N(d)}{N_0} \) to \( A_{IR}(d) \).
Annealing experiment

modify theory for a distribution of grain sizes
Annealing experiment

modify theory for a distribution of grain sizes
Annealing experiment

modify theory for a distribution of grain sizes
modify theory for a distribution of grain sizes
Annealing experiment

modify theory for a distribution of grain sizes

![Graph of normalized absorptance vs diffusion length](image1)

![Graph of number of grains vs radius](image2)
if we assume bulk diffusion coefficients, there is a characteristic diffusion length for deactivation of IR absorption
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it is plausible this length could be set by the grain size, especially for a lognormal size distribution
if we assume bulk diffusion coefficients, there is a characteristic diffusion length for deactivation of IR absorption

it is plausible this length could be set by the grain size, especially for a lognormal size distribution

although dopant clustering within the grains could also contribute to deactivation of IR absorption
Ejected material
  previous work
  formation of nanoparticles

Irradiated substrate
  previous work
  effect of thermal annealing
  optical properties
  photovoltaic properties
Motivation

solar spectrum

![solar spectrum graph](image)

The graph illustrates the solar spectrum, showing the spectral irradiance (kW/m²·µm) as a function of wavelength (µm). The maximum spectral irradiance is 1353 W/m², occurring around 0.5 µm.
Motivation

solar spectrum

crystalline silicon: transparent to 23\% of sun’s energy
Hall measurements show:

surface layer is $n$-doped upon irradiation

$n$-doping increases with thermal annealing
Photovoltaic properties: $I-V$ curves

commercial polycrystalline silicon solar cell
Photovoltaic properties: $I-V$ curves

commercial polycrystalline silicon solar cell
Photovoltaic properties: $I-V$ curves

characteristic solar cell properties

![Graph showing $I-V$ curves for dark and illuminated conditions with key points labeled $V_{oc}$ and $I_{sc}$]
Photovoltaic properties: $I$-$V$ curves

characteristic solar cell properties

\begin{figure}
\centering
\includegraphics[width=\textwidth]{solar_cell_characteristics.png}
\caption{Characteristic solar cell properties: dark and illuminated $I$-$V$ curves.}
\end{figure}
characteristic solar cell properties

$$\eta = \frac{V_{\text{max}} I_{\text{max}}}{P_l}$$
Photovoltaic properties: \( I-V \) curves

characteristic solar cell properties

\[
\eta = \frac{V_{\text{max}} I_{\text{max}}}{P_l}
\]

\[
FF = \frac{V_{\text{max}} I_{\text{max}}}{V_{\text{oc}} I_{\text{sc}}}
\]
 Photovoltaic properties: $I$-$V$ curves

characteristic solar cell properties

$$\eta = \frac{V_{\text{max}} I_{\text{max}}}{P_l}$$

$$\eta = \frac{FF V_{\text{oc}} I_{\text{sc}}}{P_l}$$

$FF = \frac{V_{\text{max}} I_{\text{max}}}{V_{\text{oc}} I_{\text{sc}}}$
Photovoltaic properties: $I$-$V$ curves

characteristic solar cell properties

\[ V_{oc} \quad I_{sc} \quad FF \]

\[
\eta = \frac{V_{\text{max}} I_{\text{max}}}{P_l}
\]

\[
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FF = \frac{V_{\text{max}} I_{\text{max}}}{V_{\text{oc}} I_{\text{sc}}}
\]
Photovoltaic properties: results

dark curves with increasing anneal $T$

![Graph showing dark curves with increasing anneal.](image)
Photovoltaic properties: results

dark curves with increasing anneal $T$

575 K
Photovoltaic properties: results

dark curves with increasing anneal $T$

![Graph showing dark current-voltage characteristic](image)
dark curves with increasing anneal $T$

975 K
Photovoltaic properties: results

dark curves with increasing anneal $T$

![Graph showing dark curves with increasing anneal $T$.]
illuminated curves with increasing anneal $T$

![Graph showing illuminated curves with increasing anneal $T$]
illuminated curves with increasing anneal $T$
Photovoltaic properties: results

illuminated curves with increasing anneal $T$

![Graph showing illuminated curves with increasing anneal $T$.]
illuminated curves with increasing anneal $T$

975 K
Photovoltaic properties: results

illuminated curves with increasing anneal $T$

![Graph showing illuminated curves with increasing anneal $T$.](image)
Photovoltaic properties: results

Summary of annealing results

- $V_{oc} = 420$ mV
- $I_{sc} = 3.6$ mA
- $\eta = 2.2\%$
- $FF = 0.36$
- area = 0.25 cm$^2$

at 1075 K
Photovoltaic properties: results

Summary of annealing results

![Graph showing temperature vs. normalized Voc at 1075 K]

- $V_{oc} = 420$ mV
- $I_{sc} = 3.6$ mA
- $\eta = 2.2\%$
- $FF = 0.36$
- area = 0.25 cm$^2$
Photovoltaic properties: results

Summary of annealing results

- at 1075 K
- $V_{oc} = 420 \text{ mV}$
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Photovoltaic properties: results

Summary of annealing results

At 1075 K

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Photovoltaic properties: results

summary of annealing results

at 1075 K

\[ V_{oc} = 420 \text{ mV} \]
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\[ \eta = 2.2 \% \]
\[ FF = 0.36 \]

area = 0.25 cm\(^2\)
Photovoltaic properties: discussion

Commercial solar cell

- $p$-doped substrate
- $n$-doped surface layer
- Depletion region

Diffusion length of charge carriers: 10 – 100 µm
Photovoltaic properties: discussion

Commercial Solar Cell
- p-doped substrate
- n-doped surface layer
- depletion region
- Diffusion length of charge carriers: 10 – 100 µm

Fs-laser Irradiated Solar Cell
- p-doped substrate
- n-doped, laser modified region
- depletion region
- Diffusion length of charge carriers: << 100 nm
why is fill factor low?

diffusion length of charge carriers $<< 100$ nm
why is fill factor low?

diffusion length of charge carriers $<< 100$ nm
Photovoltaic properties: discussion

At $V < 0$, depletion region grows and photocurrent grows.

The diagram shows a graph of current (mA) vs. voltage (V) with a curve indicating the behavior of photovoltaic properties. The text mentions that the diffusion length of charge carriers is $<< 100$ nm.
Photovoltaic properties: discussion

At $V > 0$, depletion region shrinks and photocurrent decreases.

Diffusion length of charge carriers $\ll 100$ nm.
V_{oc} increases due to increase in n-doping

1. normalized to T = 1075 K

2. diffusion length of charge carriers << 100 nm
Photovoltaic properties: discussion

$I_{sc}$ increases due to healing of defects in depletion region

diffusion length of charge carriers $<< 100$ nm
Photovoltaic properties: discussion

FF unchanged as carrier diffusion outside depletion region is small

![Graph showing FF as a function of temperature normalized to T = 1075 K. The graph indicates that FF remains relatively constant across the temperature range shown.]

- $p$-doped substrate
- $n$-doped, laser modified region
- Depletion region

**Diffusion length of charge carriers** $\ll 100$ nm
changes with annealing:

\[ V_{oc} \text{ and } I_{sc} \text{ increase due to increased } n\text{-doping of surface and removal of defects} \]
changes with annealing:

\[ V_{oc} \text{ and } I_{sc} \text{ increase due to increased } n\text{-doping of surface and removal of defects} \]

\[ FF \text{ remains low due to small carrier diffusion length outside depletion region and absorption of light only at the surface} \]
try other dopants such as Se, and Te
try other dopants such as Se, and Te

explore the use of doping thin films with this process
try other dopants such as Se, and Te

explore the use of doping thin films with this process

use a $p-i-n$ design to improve $FF$, $I_{sc}$
Summary
Summary
Summary