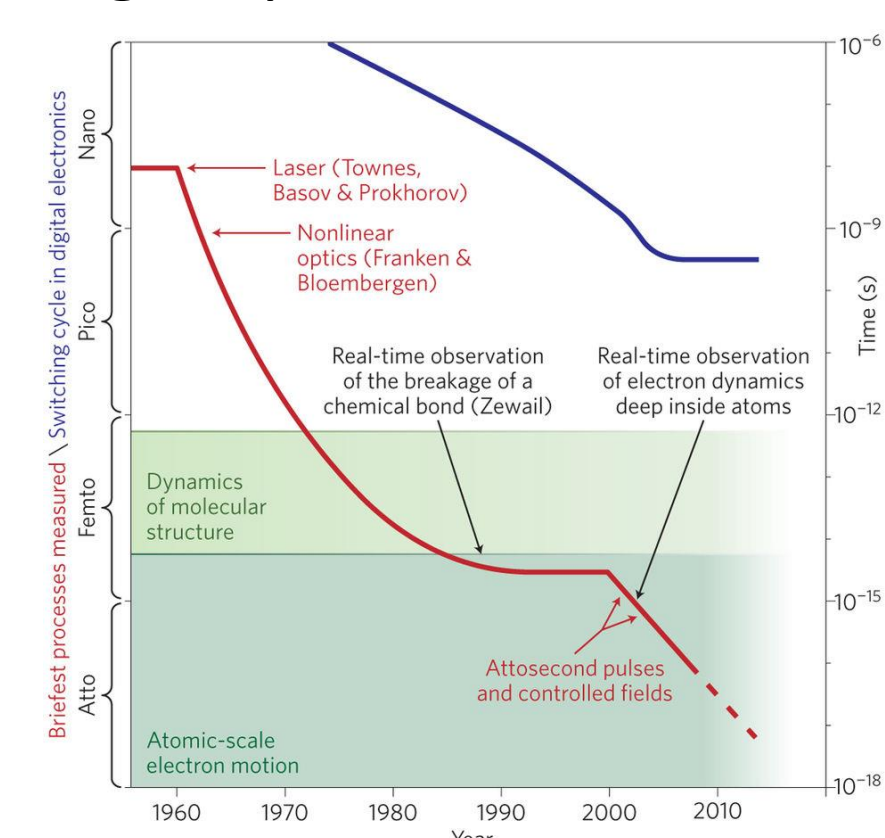


# Ultrafast Laser Processing of Silicon

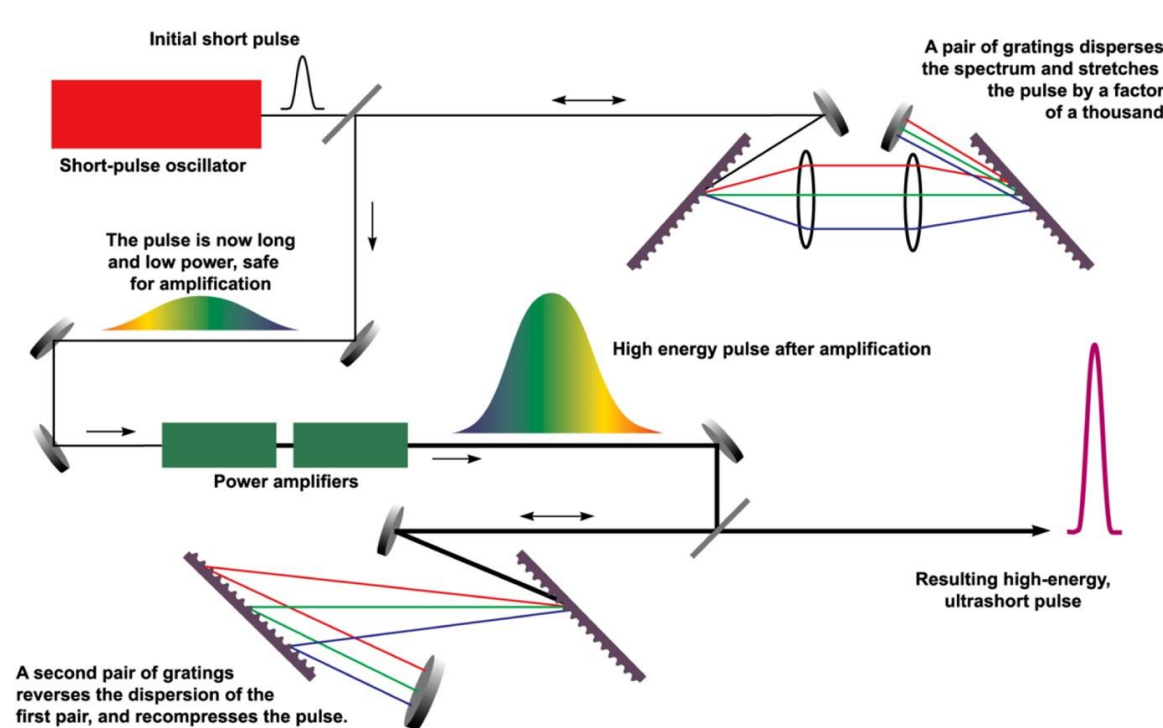
## Introduction

### Evolution of Ultrafast Science<sup>1</sup>

- **Red line** - Briefest measured time intervals
- **Blue line** - Shortest switching cycle (inverse of the clock rate) of digital processors

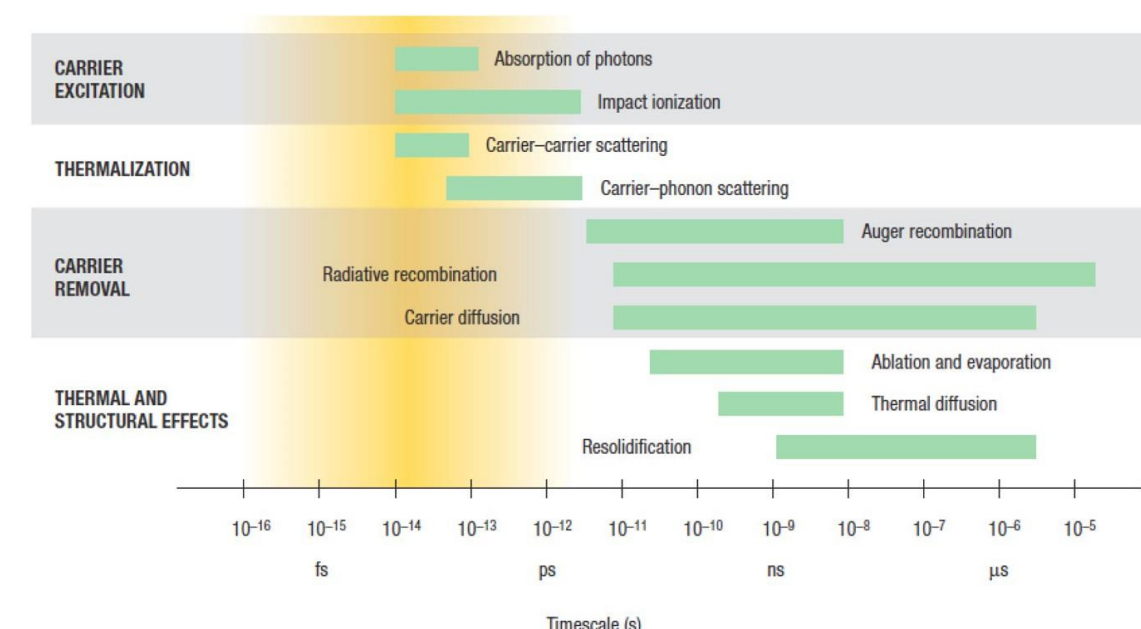


### Ultrashort Laser Pulses<sup>2</sup>



- Beam stretching, amplifying, and compressing system used in chirped pulse amplification

### Timescales of Electron-Lattice Excitation<sup>3</sup>



- Ultrafast laser- semiconductor interaction - the green bars represent a range of time durations for carrier densities varying from  $10^{17}$  to  $10^{22} \text{ cm}^{-3}$

## Processing Details

### Three Regimes<sup>3</sup>

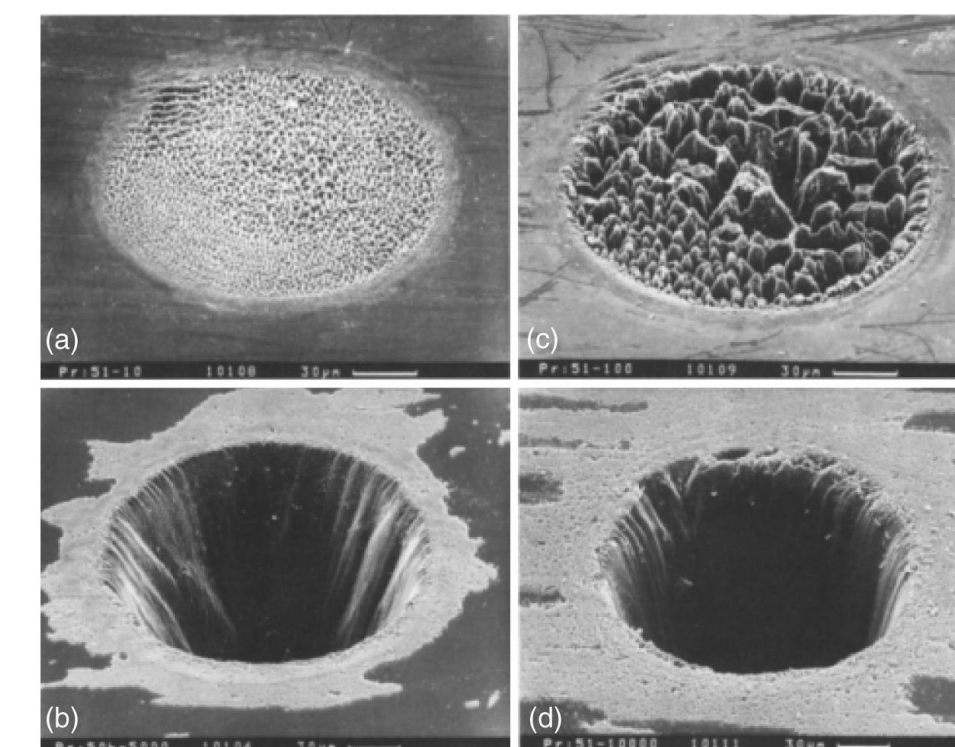
- **Nonthermal melting** - A pulse energy large enough to rip 10%–15% bonded valence electrons and achieve a critical density of conduction band electrons ( $10^{22} \text{ cm}^{-3}$ ) will induce a nonthermal ultrafast phase transition.
- **Thermal phase melting** – If the pulse energy does not cause such sudden disordering of the lattice, the plasma energy will spread via electron–phonon coupling to the lattice over several picoseconds. This heat from the excited surface diffuses inward, raising the local lattice temperature. If the solid temperature exceeds its melting temperature, a thin layer near the surface transitions to a liquid state, called the melt. The melt depth increases with laser energy.
- **Ablation** - Large pulse energies cause boiling at the melt surface. The resulting superheating of the liquid phase and high nucleation rates of the gas phase eject material from the surface in a process known as ablation. When the laser fluence exceeds that of the ablation threshold, one can achieve laser-induced periodic surface structures (LIPSS).

### Unique Features and Phenomena<sup>3-5</sup>

- LIPSS
- Hole drilling
- Surface texturing
- Hyperdoping
- **Glass strengthening**
- **Microstructural modification**
- **Decomposition**
- **Nonthermal – Thermal Continuum!**

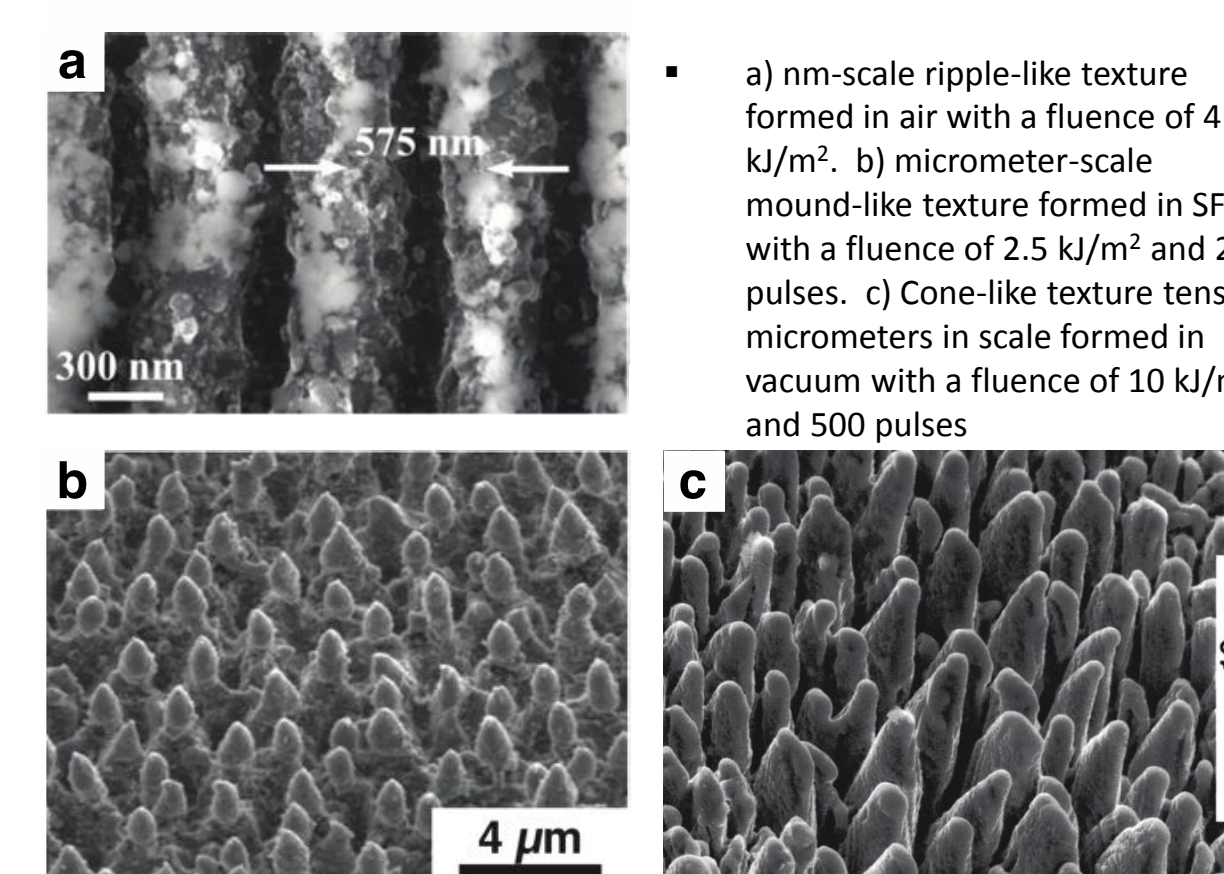
## Results and Data

### Hole Drilling<sup>4</sup>

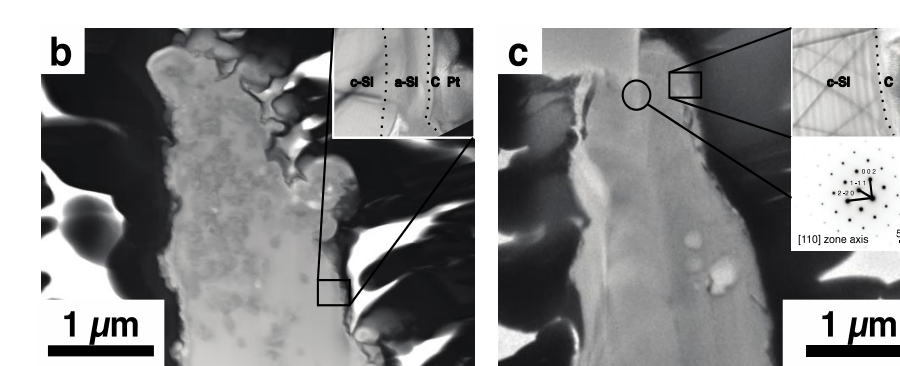
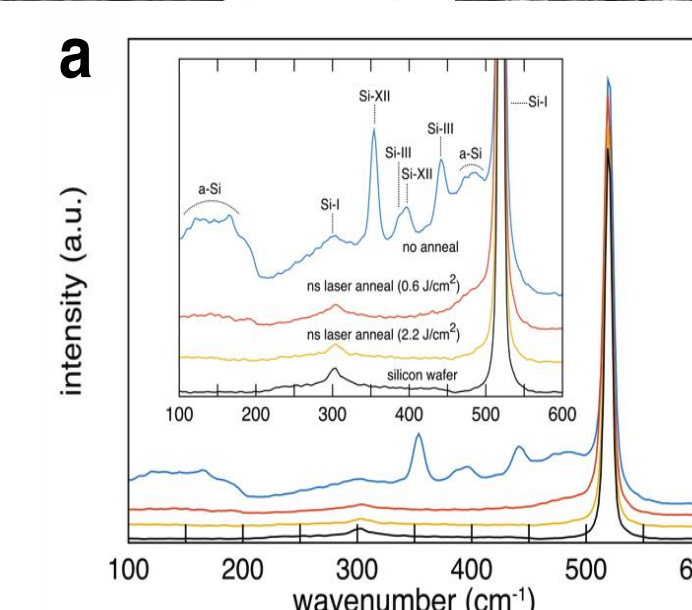


- Hole formation via laser ablation of a silicon target with (a) 10, (b) 100, (c) 5000, and (d) 10,000 pulses

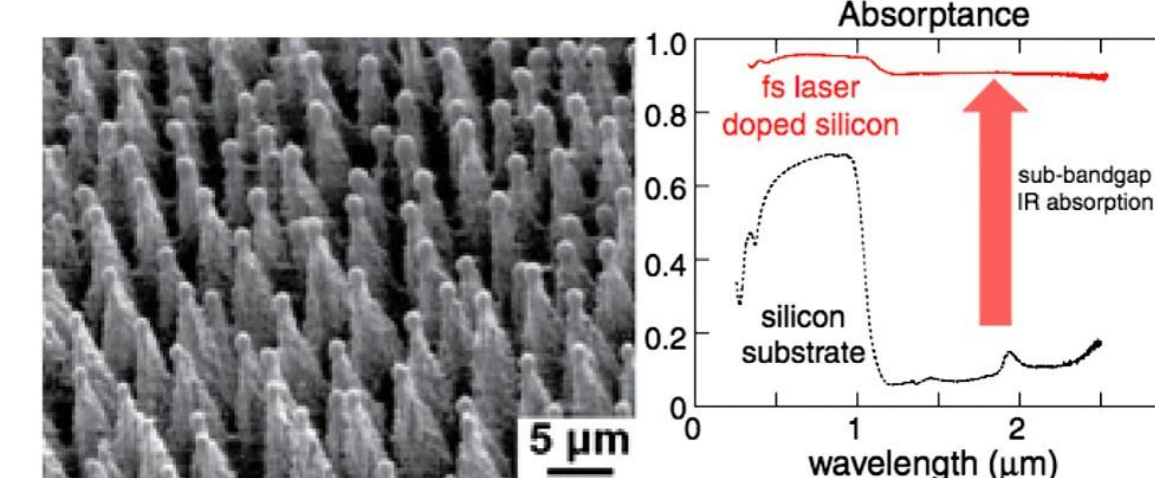
### Surface Texturing<sup>5</sup>



- a) nm-scale ripple-like texture formed in air with a fluence of  $4 \text{ kJ/m}^2$ . b) micrometer-scale mound-like texture formed in SF<sub>6</sub> with a fluence of  $2.5 \text{ kJ/m}^2$  and 200 pulses. c) Cone-like texture tens of micrometers in scale formed in vacuum with a fluence of  $10 \text{ kJ/m}^2$  and 500 pulses



- a) Raman spectra showing the presence of high pressure phases (Si-III, Si-XII, and amorphous Si) after fs irradiation, as well as removal of high pressure phases after ns laser annealing. Transmission electron microscope cross-sections of textures b) before and c) after laser annealing, showing removal of amorphous material and recovery of monocrystalline structure



- Left: Spiky, high-aspect-ratio, laser-induced periodic structures in silicon upon exposure to SF<sub>6</sub> and fs-laser irradiation.
- Right: Absorption enhancement due to **black silicon** light-trapping conical tips and hyperdoping. Hyperdoping leads to strong sub-bandgap absorption, and texturing leads to increased absorption across the spectrum.

## Summary

- Ultrafast laser processing produces a wide range of features and structures with unique properties. Ultrafast laser texturing in photovoltaics manufacturing is feasible.
- Use of hyperdoping for intermediate band silicon photovoltaics likely requires concurrent surface texturing or other absorption enhancement techniques to yield photoconversion efficiency improvements.
- Future plan is to study electronic processes in energy materials (oxides) in real time. Challenges include **larger  $E_g$ , and advanced laser equipment and control.**

## References

1. F. Krausz and M. I. Stockman, “Attosecond Metrology: From Electron Capture to Future Signal Processing,” *Nature Photonics* **8**, 205-213 (2014).
2. M. Perry, “Multilayer Dielectric Gratings: Increasing the Power of Light,” *Sci. Technol. Rev.*, 24–33 (1995).
3. S. K. Sundaram and E. Mazur, “Inducing and Probing Non-thermal Transitions in Semiconductors using Femtosecond Laser Pulses,” *Nature Materials*, **1**, 217-224 (2002).
4. B. N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, A. Tunnermann, F. Alvensleben, and A. Tünnermann, “Femtosecond, picosecond and nanosecond laser ablation of solids,” *Appl. Phys. A* **63**, 109-115 (1996).
5. B. Franta, E. Mazur, and S. K. Sundaram, “Ultrafast Laser Processing of Silicon for Photovoltaics,” *International Materials Reviews*, 2017.

## Acknowledgements

- Support from AU leadership
- Eric Mazur group at Harvard University for active collaboration over the years. Ben Franta led the review<sup>5</sup>.
- DOE support on various projects
- Kyocera Foundation for the endowment.