Surface and Depth-Dependent Studies of Electron and Phonon Ultrafast Dynamics in Femtosecond Laser Induced Transient States of Matter

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Part I

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Sheldon Glashow, a Nobel Laureate in physics, describes our overriding physics challenge when he tells the story of a visitor named Arthur from another planet meeting earthlings for the first time: “Arthur [is] an intelligent alien from a distant planet who arrives at Washington Square [in New York City] and observes two old codgers playing chess. Curious, Arthur gives himself two tasks: to learn the rules of the game, and to become a grand master.”
By carefully watching the moves, Arthur is gradually able to reconstruct the rules of the game: how pawns advance, how queens capture knights, and how vulnerable kings are. However, just knowing the rules does not mean that Arthur has become a grand master! As Glashow adds: “Both kinds of endeavors are important—one more ‘relevant,’ the other more ‘fundamental.’” Both represent immense challenges to the human intellect.”
In some sense, science has finally decoded many of the fundamental “rules of Nature,” but this does not mean that we have become “grand masters”. Likewise, the dance of elementary particles deep inside stars and the rhythms of DNA molecules coiling and uncoiling within our bodies have been largely deciphered, but this does not mean that we have become master choreographers of life.
In fact, the end of the twentieth century, which ended the first great phase in the history of science, has only opened the door to the exciting developments of the next. **We are now making the transition from amateur chess players to grand masters, from observers to choreographers of Nature.**
Ultrafast studies at Vanderbilt
Center for Molecular and Atomic Studies at Surfaces

- Ti:Sapphire femtosecond lasers for pump-probe spectroscopy
- mJ/pulse OPA system
- Independently tunable nonlinear OPA systems from UV-NIR (200nm-20μm)
- 9T Oxford superconducting cryogenic magnet
- Low temperature and external B-field studies on spin systems
- Using ultra-fast laser pulses to characterize and choreograph matter in novel ways.
Thus, our Scientific Goals:

- Find new and better ways to critically observe nature and characterize materials.
  - New technologies---better fast tunable lasers.
  - Develop new techniques and approaches.
- Find new and better ways to choreograph matter---smart manipulation and patterning.
  - Growth and patterning on a nanoscopic-scale
  - Far from equilibrium
Part I---Ultrafast Dynamics Before and After Equilibrations on Surfaces Using Pump-Probe Techniques

- Probing the early stages of laser-induced non-equilibrium electron and lattice dynamics at crystal surfaces using Second Harmonic Generation (SHG) (ongoing research at an early stage).
- Measure carrier and phonon dynamics in graphene/diamond and nanoparticle layer systems.
- Low temperature diamond growth.

Part II---Combining Carrier and Phonon Dynamics as a Function of Depth.

- Doing surface physics on a Coherent Acoustic Phonons (CAP) wave moving surface to measure material properties for example defect/impurity concentrations and strain as a function of depth.
- Materials Modification using CAP, far from Equilibrium---Coherent Control (ongoing research).
What Happens when Energetic Photons are Incident on Semiconducting Surfaces

1. Electron-hole pair creation
2. Photo-Dember effect
3. Band Bending
4. Phonon generation (optical & acoustic)
5. Electrons removed from bonds -> e’s and ions experience an altered potential
Following Photo-Excitation

(a) Initially after photo-excitation: carriers will have delta function distribution in momentum and energy space

~10 fs

(b) Momentum randomization

~100 fs

(c) Thermalization of carriers into a Fermi-Dirac distribution

~1 ps

(d) Carriers lose energy by Optical Phonon Emission

~10 ps

(e) Optical Phonons decay into Acoustic Phonons
Electron and lattice temperatures far from equilibrium following an incident ultrafast laser pulse

Two Temperature Model

![Graph showing temperature change over delay time]
Probing the early stages of laser-induced non-equilibrium electron and lattice dynamics at crystal surfaces using Second Harmonic Generation (SHG)

This work is fundamental but impacts a variety of important condensed matter physics related fields including radiation damage, fast switching and device fabrication processes.

Certain materials, in particular GaAs, have been observed (using electron and X-ray diffraction) to undergo a non-thermal lattice disordering following ultrafast laser excitation. This non-thermal process is shown to lead at high fluences to a totally disordered molten state while the lattice remains cool.

Since SHG is sensitive to surface structural symmetry, we intend employ it to characterize the early stages of ultrafast laser induced disorder as a function of laser fluence.
Previous Research-1 High Fluence
Ultrafast electron diffraction to measure surface atom translation

Previous Research-2 High Fluence

Femtosecond x-ray crystallography to measure surface atom translation

![Graphical representation of time and angle resolved diffraction curves for optically excited GaAs.](image)

Experimentally measured (a), theoretically calculated (b), and iteratively inverted (c) time- and angle-resolved diffraction curves for optically excited GaAs. The horizontal axis is angular deviation from the Ka1 Bragg angle calculated assuming unit refractive index. Vertical axis is pump±probe time delay, with the zero of delay being chosen to coincide with the initial deviation of the lines from their unpumped appearance. For c, the iterative genetic-algorithm inversion procedure varied the depth-dependent strain, defined by a 200-nm-spaced, cubic-spline-interpolated grid, and calculated the corresponding diffraction patterns until a good fit was achieved. Five inversions with different parameters of the genetic algorithm, such as random number seed, population size, crossover probability, and mutation rate, were performed and subsequently averaged.

Used Second Harmonic Generation (SHG) Techniques-Time Resolved but not Polarization resolved. Performed over a wide range of high pump fluences

probe time delay for various pump fluences. The curves are drawn to guide the eye. Ⓡ: 0.2 kJ/m²; Ⓣ: 0.4 kJ/m²; □: 0.6 kJ/m²; ■: 0.8 kJ/m²; ▲: 1.5 kJ/m².

probe time delay of 130 fs. In contrast, at pump fluences less than or equal to 0.6 kJ/m², \( \chi^{(2)} \) undergoes a partial decrease, but it does not reach zero. For pump fluences below 0.5 kJ/m², \( \chi^{(2)} \) recovers to its initial value on a time scale of a few picoseconds.

Since \( \chi^{(2)} \) must go to zero for \( S_{\text{norm}}(\phi, t) \) to reach zero, the behavior of \( S_{\text{norm}} \) at fluences for which it drops to zero is similar to that of \( \chi^{(2)} \). Thus, for high fluences the conclusions from previous second-harmonic-generation experiments, in which changes in the dielectric constant are not explicitly taken into account, agree at least qualitatively with our \( \chi^{(2)} \) data.\(^3\)\(^-\)\(^7\) In contrast, the behavior we observe at lower fluences has not been reported before. At fluences for which \( \chi^{(2)} \) does not reach zero, it is particularly important to account for the effects of changes in the dielectric constant on the measured
Observation of Ultrafast Time Evolution of Structural Symmetry in Short Pulsed Laser Induced Transient States of Matter, at very low fluences—> 0.05 J/m² in contrast to 0.20 kJ/m²

Probe angle wrt the normal—45 degrees
Vary the incoming probe polarization
Use an appropriate non-linear Pump-Probe approach for TR- PRSHG measurements

Changes in time and polarization sensitivity can be monitored with time-resolved, polarization-resolved SHG (TR- PRSHG). Fundamental wavelength: 800 nm; SHG wavelength: 400 nm
Search for the Very Early Time Evolution of Structural Symmetry in Short Pulsed Laser Induced Transient States of Matter-1

Experiment:
• Use Second Harmonic Generation (SHG) which monitors changes in the tensor elements of $X^2$
• Using a single probe beam experiment results in the pattern shown
• The nonlinear response of angular input polarization resolved second harmonic generation (PRSHG) reflects changes in structural symmetry
Understanding laser-pump induced enhancement of SHG

- Laser induced motion of electrons in an anharmonic bond potential is the cause of nonlinear optical responses like second harmonic generation.
- The removal of a bond electron generally increases anharmonicity which results in enhanced emitted SHG intensity.

![Simple bond model with differing incoming laser polarizations](image1)

![Anharmonic potential energy function for a noncentrosymmetric medium](image2)

![Energy-level diagram describing second harmonic generation](image3)
Experiment (continued):

- Measure the nonlinear response of angular input polarization resolved second harmonic generation (TR-PRSHG) in the pump-probe mode, where using lock-in techniques one can determine the influence of the pump on atomic motion.

- *Electron-hole creation means an electron has been removed from the bond.*

- These observations reflect time-dependent pump related changes in local potentials that result in small though detectable shifts in subsurface atom equilibrium locations at very early times far from equilibrium-not phonons!
Chopping the pump beam and using lock-in techniques, we vary $\Delta t$, the time between the Pump and the Probe, and observe Apparent Angular and Intensity Changes in the TR-PDSHG Data.
Apparent change in angle may be explained by noting a contribution relating to pump induced changes in surface temperature.

\[ \Delta T_{pump} \]

\[ \Delta T_{300K+probe} \]

Thus, our data arises both from electronic processes as well as from a pump induced temperature increase.
As we vary $\Delta t$, the time between the Pump and the Probe, we observe Angular Changes in the major axis of the symmetry pattern in the TR-PDSHG Data.
Removing the pump related thermal contribution by subtracting out the TR-PRSHG pattern prior to $\Delta t = 0.0$ an example-
Removing the pump related thermal contribution by subtracting out the TR-PRSHG pattern prior to $\Delta t = 0.0$ for all our measurement for small fluences gave very simple result.
The maximum SHG intensity as a function of \( \Delta t \), the time between the Pump and the Probe, is shown

- Using TR-PRSHG, the amplitude increases are seen to peak at 200 fs and then to relax back on the order of 500 fs.
- This suggests that between 0 fs and 200 fs, the remaining bonding electrons are subject to increased nonlinearity along the bond directions in accord with the simple bond hyperpolarizability model.
- After 200 fs the observed fast decrease intensity is due to what we assume to be restabilization of the bond due to hole filling by near surface electrons, not recombination.
Data related to particular elements of the $X^{(2)}_{ijk}$ tensor.

- Clearly, the observed increase in SHG amplitude with time is correlated with greatly enhanced nonlinear polarizability at angles corresponding to bond directions.

- This behaviour can be related to particular elements of the $X^{(2)}_{ijk}$ tensor. Increased amplitudes of $X^{(2)}_{ijk}$ tensor elements correspond to increased potential nonlinearity along the bond directions.
Summary and future directions

- At $\Delta t \sim -100$ fs, the electronic influence of the pump has diminished to zero. However the pump temperature contribution remains.

- At $\Delta t > 0.0$ fs, the electronic influence of the pump is pronounced which reflects time-dependent pump related changes in local potentials due to removal of a bond electron. This results in enhanced SHG and we postulate that this also results in small shifts in subsurface atom equilibrium locations at very early times far from equilibrium which at higher fluences we will be able to detect using the TR-PRSHG approach.

- Our future research directions include carrying our TR-PRSHG measurements over a wide range of fluences and looking at a wide range of other materials of interest, including centrosymmetric crystals.
Ultrafast Relaxation Dynamics of Hot Carriers and Phonons in Graphene-Substrate Systems

Substrates include diamond, quartz and sapphire

- CVD graphene on single crystal (100) diamond
- CVD graphene on poly crystal diamond
Why Graphene on different substrates?

Diamond as an inert substrate of graphene

Graphene-on-Diamond FET
Increased Current-Carrying Capacity

Graphene on (100) diamond


Ultrafast Pump-probe Spectroscopy

Mimic the behavior of electrons in a Field Effect Transistor

- Pathway through which the excited electrons lose their energy:
- Through phonons, electron scattering, defects?
- How fast?
- The extreme time resolution
Single layer CVD graphene

Graphene growth on Cu
PMMA coating
Transfer and etching PMMA
Pick up PMMA/Graphene
Etching Cu
Graphene on other substrates

Graphene on (100) diamond

Graphene on single crystalline diamond
Graphene on poly crystalline diamond
Femtosecond transient transmission pump probe spectroscopy

Graphene on (100) diamond

\[
\tau_1 = 0.25\, \text{ps} \\
\tau_2 = 0.44\, \text{ps}
\]

Graphene on polycrystalline diamond

\[
\tau_1 = 0.42\, \text{ps} \\
\tau_2 = 6.2\, \text{ps}
\]
Graphene on Quartz as a function of Fluence
Differential Transient Transmission of Graphene on Quartz Excited at 1.55 eV

Figure 1. (a) Differential transient transmission of graphene on quartz excited at 1.55 eV. The inset shows the normalized transmission at 10 incremental fluences. (All curves are shifted on both axes for clarity) (b) Simulated change in the transient transmission of graphene as a function of electronic temperature for a pumping energy of 1.55 eV and intrinsic carrier density of 1 x 10^{12} /cm^2. The blue and red curves show the calculated contributions from intraband and interband respectively and the black curve shows the total interband-intraband contribution. (c) Excitation energy dependence of the ultrafast transmission of graphene on quartz at a pumping fluence of 5.1 μJ/cm^2. (All curves have been shifted on x axis for clarity)
Figure 2. (a) Differential transient transmission of graphene transferred on diamond, quartz and sapphire. (The excitation and probing energies are 1.6 eV and the pumping fluence is 9.6 μJ/cm²). Inset: Normalized transmission response of graphene on different substrates. The slow recovery tail of the spectrum is fit to a mono exponential decay with the best fitting for relaxation times of ~ 0.24 ps for diamond, 1.47 for sapphire and 1.7 ps for quartz. (b) Illustration of the thermalization process after the activation of the substrate surface phonon energy relaxation channel for graphene on diamond, quartz and sapphire with respective highest energy surface phonon modes of 0.34 eV, 0.14 eV and 0.11 eV. In this time window, the distribution is hottest for diamond and coolest for sapphire.
Figure 3. (a) Raman mapping of the relative shift in the position of the G peak of graphene on quartz. The inset displays single point Raman spectra at a few different locations of the sample. (b) Simulation results for the dependence of the differential transmission response of graphene on the static Fermi level. (Pumped and probed at 790 nm.)
Ongoing projects and future work

• Understanding the relaxation dynamics of electrons and phonons in Graphene on different faces of diamond, (111), (100), (110).

• Contrasting H-terminated diamond surfaces with D-terminated surfaces.

• Create a conceptual model using rate equations.

Graphene on diamond Field Effect Transistor

Tuning the Fermi level of graphene while probing the ultrafast relaxation of excited electrons
Collaborating Team:

Zeynab (Zina) Jarrahi – Vanderbilt University
Dr. Jim Davidson – Vanderbilt University
Dr. James Butler – St. Petersburg Electrotechnical University (LETI)
Dr. Bridget Rogers - Vanderbilt University School of Engineering
Norman Tolk – Vanderbilt University
Low-Temperature H-related Diamond Growth Processes Mediated by Ultrafast Laser Excited Hot Electrons

Norman Tolk,1 Jim Davidson,1 Weng Poo Kang,1 Richard Mu1,2

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Our Goals


2. Evaluate the roles of laser wavelength, intensity, repetition rate, and pulse length on low-temperature nucleation and growth of Diamond.
Our Approach
What happens when a laser pulse hits a surface?

Answer depends on

- Wavelength
- Intensity
- Incident angle
- Polarization
- Pulse structure
- Pulse duration
- Surface structure

Possibilities

- Ablation
- Surface atom desorption
- Second Harmonic Generation
- Sum Frequency Generation
- Electron-hole pair generation
- Others
Diamond Growth--Reaction Energy Sources

**High-temperature Conventional Growth Process**

- Reaction energy is supplied thermally from lattice and from reactant species.

**Low-temperature Laser-assisted Growth Process**

- Reaction energy is supplied by ultrafast laser pulse with minimal lattice heating.

- Works at high pressure or in vacuum!
Two Critical Reactions

Goal: Generation of open reaction sites for carbon radical adsorption

Laser-excited carriers near surface

A Photon Pulse Simulation (sigma = 1.60x10^{-16} \text{ cm}^2, \beta = 6.50\times10^0 \text{ cm})
Low duty cycle of pulsed lasers ➔ little ‘thermal’ effects

- fs laser pulse
- electron cloud
- localized phonons

Time duration:
- t=0
- 1ps
- 2ps
- 3ps
- 4ps
- 5ps

Thermal equilibrium (conductive samples):
- t x 10^3

Average temperature is unchanged:
- t=0
- 1ms
- 2ms

1ms and 2ms indicate thermal equilibrium time.
Reaction Energy Sources

High-temperature
Conventional Growth Process

- High-temperature kinetic species
- High-temperature lattice phonons

Reaction energy is supplied thermally from lattice and from reactant species

Low-temperature
Laser-assisted Growth Process

- Ultrafast laser
- Low-temperature Kinetic species
- Nonequilibrium
- Energetic electrons

- Works at high pressure or in vacuum
- Electrons break bonds and vibrationally excite the C-H stretch mode

Reaction energy is supplied by ultrafast laser pulse with minimal lattice heating

P. Saalfrank, Surface Science 390, 1 (1997)
Transient electron occupation of the **antibonding** state transfers vibrational energy (i.e., a “nudge”) to the adsorbed species.

Single or multiple such events induce desorption of species, **bypassing the thermal mechanism**!

Result: Laser-assisted growth

Ultrafast laser

H abstraction

CH\textsubscript{x} adsorption

sp\textsuperscript{3} formation
Efficacy of laser-induced electrons on CVD growth depends on substrate band gap!

- Silicon: CB at 810 nm, VB, 1.1 eV
- Diamond: CB at 405 nm, VB, 5.5 eV
Experimental Configurations

Efficacy of laser-induced electrons on CVD growth depends on substrate band gap

**Lasers on Si substrates**

$\text{hv} \sim 1.5 \text{ eV (810 nm)}, \text{ pulse } 150 \text{ fs, rep. rate } 1\text{kHz}$

**Lasers on diamond substrates**

$\text{hv} \sim 3 \text{ eV (405 nm)} \text{ or } 2 \times 3\text{eV}$, pulse 150 fs, rep. rate 1kHz
Two Directions

- Laser pre-treatment of surfaces influences nucleation and growth
- In-situ laser exposure enhanced nucleation and growth found to be dependent on photon energy
Schematic Diagram

Hydrogen

Methane

Mass Flow Controller

Sample Holder

XYZ Manipulator

Deposition Chamber

Sample

Heated Filament

Capacitance Monometer

Vacuum Pump

Downstream Pressure Control Valve

Hot Filament

XYZ Manipulator

top view
LoCo HFCVD Reactor in Operation
Determination of surface modification thresholds: Optimal power and substrate temperature

**Silicon Substrate**

Filament on; Ambient: H, no CH₄

<table>
<thead>
<tr>
<th>Laser Intensity</th>
<th>57 GW/cm²</th>
<th>94 GW/cm²</th>
<th>132 GW/cm²</th>
</tr>
</thead>
</table>

Substrate: Si  
Ambient: H₂ (201 sccm), no CH₄  
Filament temperature: ~1940 °C  
Filament distance to substrate: 10 mm  
Laser wavelength: 810 nm  
Laser pulse length: 150 fs  
Laser repetition rate: 1 kHz  
Laser spot size: 1-2 mm  
Experiment duration: 10 min. each
Laser Pre-treatment results in enhanced nucleation and growth

Silicon Substrate at 530 °C, $h\nu = 1.5$ eV
Suggests a direct writing process

Substrate: Si
Ambient: H$_2$ (201 sccm) and CH$_4$ (2.7 sccm)
Filament temperature: ~2050 °C
Filament distance to substrate: 10 mm
Laser wavelength: 810 nm
Laser pulse length: 150 fs
Laser repetition rate: 1 kHz
Pretreatment time: 5-10 minutes
Experiment duration: 5 hours
Substrate temperature: 530 °C

No laser

Laser at 100 GW/cm$^2$
(spot offscreen)

Laser at 140 GW/cm$^2$
Laser exposure during growth conditions enhances nucleation and growth.

Silicon Substrate

Laser intensity = 70 GW/cm²

Substrate: Si
Ambient: H₂ (201 sccm) and CH₄ (2.7 sccm)
Filament temperature: ~2050° C
Filament distance to substrate: 10 mm
Laser wavelength: 810 nm
Laser pulse length: 150 fs
Laser repetition rate: 1 kHz
Laser power: 180 mW
Experiment duration: 5 hours
Substrate temperature: 530 ° C
Laser exposure during growth conditions enhances nucleation and growth

Silicon Substrate
Laser intensity = 70 GW/cm²

Substrate: Si
Ambient: H₂ (201 sccm) and CH₄ (2.7 sccm)
Filament temperature: ~2050° C
Filament distance to substrate: 10 mm
Laser wavelength: 810 nm
Laser pulse length: 150 fs
Laser repetition rate: 1 kHz
Laser power: 180 mW
Experiment duration: 5 hours
Substrate temperature: 530 ° C
Raman Spectrum (325 nm)

Intensity (a.u.)

500 1000 1500 2000 2500 3000

Wavenumber (cm$^{-1}$)

1332

O$_2$

$	ext{N}_2$

Raman Spectrum (325 nm)

Intensity (a.u.)

500 1000 1500 2000 2500 3000

Wavenumber (cm$^{-1}$)

1332

O$_2$

$	ext{N}_2$

(Specimen 10)
810 nm laser exposure during growth shows some enhanced nucleation

Silicon Substrate

Due to electrons generated on the silicon but not on the diamond

Substrate: Si
Ambient: H₂ (201 sccm) and CH₄ (2.7 sccm)
Filament temperature: ~2050° C
Filament distance to substrate: 10 mm
Laser wavelength: 810 nm
Laser pulse length: 150 fs
Laser repetition rate: 1 kHz
Laser power: 220 mW
Laser intensity: 80 GW/cm²
Experiment duration: 5 hours
Substrate temperature: 430 ° C
810 nm laser exposure during growth shows some enhanced nucleation

Silicon Substrate

Due to electrons generated on the silicon but not on the diamond
Efficacy of laser-induced electrons on CVD growth depends on substrate band gap.
Conclusions

• We have shown that laser pre-treatment of surfaces influences nucleation and growth

• We have shown that in-situ laser exposure enhances nucleation and growth, dependent on photon energy

• We have demonstrated growth on both silicon and diamond substrates consistent with the proposed model of laser-induced electrons
Future Directions

In support of experimental efforts

- CVD-laser growth experiments will be extended to lower temperatures
- Further examination of laser influence on CVD processed substrates
- Collaborate/correspond with project partners for integration details of experimental apparatus (e.g., flux)
- Development of sophisticated process modeling
- Direct vibrational mode excitation from laser pulse

Measurements in support of theoretical efforts

- H adsorbate vibrational lifetimes (C-H stretch): Pump-probe transient bleaching spectroscopy
- Laser-induced electron energy distribution: Time-of-flight detection
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Varga Theory Group

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• DOE
Normalized Raman Spectrum (325 nm)

With laser

1332 cm\(^{-1}\) peaks normalized to 1.0

Without laser

Magnification: 15X
Power: 6 mW
Aperture: 200 um
Resolution: 1.5 cm\(^{-1}\)
Exposure Time: 20 secs
Accumulations: 6
Thanks for your attention!

Left to Right: Norman Tolk, Mick Howell, Jim Davidson, Weng Poo Kang, Richard Mu, Hank Paxton, John Kozub, Justin Gregory

Not Shown: Halina Krzyzanowska, Mesut Yilmaz, Anthony Mayo, Zina Jarrahi
First measurements of CVD growth on polycrystalline diamond substrate with laser exposure at reduced temperatures

Substrate: polycrystalline diamond
Ambient: H₂ (201 sccm) and CH₄ (2.7 sccm)
Filament temperature: ~2090 °C
Filament distance to substrate: 10 mm
Laser wavelength: 810 nm
Laser pulse length: 150 fs
Laser repetition rate: 1 kHz
Laser power: 220 mW
Laser intensity: 330 GW/cm²
Experiment duration: 3 hours
Substrate temperature: 530 °C
Effect of Laser Exposure During Growth Conditions – Smaller grain size

Polycrystalline Diamond Substrate

Substrate: polycrystalline diamond
Ambient: H\textsubscript{2} (201 sccm) and CH\textsubscript{4} (2.7 sccm)
Filament temperature: ~2090° C
Filament distance to substrate: 10 mm
Laser wavelength: 810 nm
Laser pulse length: 150 fs
Laser repetition rate: 1 kHz
Laser power: 220 mW
Laser intensity: 330 GW/cm\textsuperscript{2}
Experiment duration: 3 hours
Substrate temperature: 530 ° C
- Button Heater
- Stainless steel "sandwich" sample holder
- Filament
- Single-crystal Diamond substrate
- Mounting clips
First measurements of CVD growth on single crystal diamond substrate with laser exposure at reduced temperatures

Substrate: single-crystal N-incorporated e6 CVD diamond (unpolished)
Ambient: H₂ (201 sccm) and CH₄ (2.7 sccm)
Filament temperature: ~2050° C
Filament distance to substrate: 10 mm
Laser wavelength: 405 nm
Laser pulse length: 150 fs
Laser repetition rate: 1 kHz
Laser power: 100 mW
Laser intensity: 40 GW/cm²
Experiment duration: 4 hours
Substrate temperature: 430 ° C
First measurements of CVD growth on single crystal diamond substrate with laser exposure at reduced temperatures

Substrate: single-crystal N-incorporated e6 CVD diamond (unpolished)
Ambient: $\text{H}_2$ (201 sccm) and $\text{CH}_4$ (2.7 sccm)
Filament temperature: ~2050° C
Filament distance to substrate: 10 mm
Laser wavelength: 405 nm
Laser pulse length: 150 fs
Laser repetition rate: 1 kHz
Laser power: 100 mW
Laser intensity: 40 GW/cm$^2$
Experiment duration: 4 hours
Substrate temperature: 430° C
First measurements of CVD growth on single crystal diamond substrate with laser exposure at reduced temperatures

SEM of surface as received
Laser at 405 nm shows enhanced growth at 430 °C

Single-crystal Diamond Substrate

- Substrate: single-crystal CVD diamond
- Ambient: H₂ (201 sccm) and CH₄ (2.7 sccm)
  - Filament temperature: ~2050 °C
  - Filament distance to substrate: 10 mm
- Laser wavelength: 405 nm
- Laser pulse length: 150 fs
- Laser repetition rate: 1 kHz
- Laser power: 100 mW
- Laser intensity: 40 GW/cm²
- Experiment duration: 4 hours

Substrate temperature: 430 °C
Laser at 405 nm shows enhanced growth at 430 °C

Single-crystal Diamond Substrate

Substrate: single-crystal CVD diamond
Ambient: H₂ (201 sccm) and CH₄ (2.7 sccm)
  Filament temperature: ~2050 °C
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  Laser pulse length: 150 fs
  Laser repetition rate: 1 kHz
  Laser power: 100 mW
  Laser intensity: 40 GW/cm²
Experiment duration: 4 hours

Substrate temperature: 430 °C
ΔSHG Intensity (a.u.) vs Time Delay (ps)
Vary $\Delta t$, the time between the Pump and the Probe: Observe structural symmetry changes.
Acknowledgements

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Transfer and Processing

Optimization of the CVD graphene transfer process

The Challenge of removing PMMA residue

We need very clean graphene for transient optical spectroscopy

Diamond surface H termination

Acid cleaning
sulfuric acid (H2SO4) - hydrogen peroxide (H2O2)

Hydrogen plasma treatment
substrate temp 700 C, H2 flow 50 sccm
chamber pressure 30 mbar for 10 min

XPS measurements in every step

10x

optimized graphene transfer
Diamond film growth rate vs. growth temperature

Growth Rate (µm/h) vs. Growth Temperature (°C)
sp\textsuperscript{3} fraction increases as growth temperature decreases

sp\textsuperscript{3}/sp\textsuperscript{2} intensity ratio vs. growth temperature

<table>
<thead>
<tr>
<th>Growth Temperature (°C)</th>
<th>sp\textsuperscript{3}/sp\textsuperscript{2} Intensity Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>4.73</td>
</tr>
<tr>
<td>300</td>
<td>2.83</td>
</tr>
<tr>
<td>400</td>
<td>1.88</td>
</tr>
<tr>
<td>500</td>
<td>1.91</td>
</tr>
</tbody>
</table>
Quantitative Laser-Induced Diamond Growth
Projected Rates

We have demonstrated that laser illumination at appropriate photon energies stimulates nucleation and growth of diamond.

Based on our measured growth rates at reduced temperatures (both with and without lasers) we project that growth rates of at least 10 $\mu$m/hr are presently feasible under laser illumination at temperatures 100-200 °C. By optimizing growth conditions including laser rep rate and flux, chamber pressure, gas species, we anticipate that rates in excess of 100 $\mu$m/hr are attainable.
Figure 4. (a-c) Fluence dependent ultrafast transmission of graphene transferred on quartz, sapphire and diamond. (The excitation energy: 1.6 eV) (d-g) Slow relaxation time $\tau_2$ is plotted against pump fluence for graphene on diamond, sapphire and two different quartz substrates with different surface roughness's. (The time constants were obtained by fitting the slow relaxation tail of the dynamics to a mono exponential decay.)
Vary $\Delta t$, the time between the Pump and the Probe
Observe structural symmetry changes