

Supporting Information

Laser-Synthesized Epitaxial Graphene

Sangwon Lee¹, Michael F. Toney², Wonhee Ko^{3,4}, Jason C. Randel^{3,4}, Hee Joon Jung¹,
Ko Munakata³, Jesse Lu⁵, Theodore H. Geballe³, Malcolm R. Beasley³, Robert Sinclair¹,
Hari C. Manoharan^{4,6}, and Alberto Salleo^{1*}

¹*Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA*

²*Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA*

³*Department of Applied Physics, Stanford University, Stanford, CA 94305, USA*

⁴*Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA*

⁵*Department of Electrical Engineering, Stanford University, Stanford, CA 94305, USA*

⁶*Department of Physics, Stanford University, Stanford, CA 94305, USA*

**To whom correspondence should be addressed. Email: asalleo@stanford.edu*

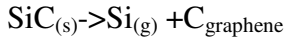
Calculation of the Si thermal effusion rate

The maximum effusion rate from a solid surface having an area A kept at a temperature T is given by the Hertz-Knudsen-Langmuir equation:

$$\frac{dn}{A dt} = \frac{P}{\sqrt{2\pi MRT}}$$

where P is the partial pressure of the effusing species having molar mass M. The effusion rate is in moles.s⁻¹.m⁻².

Here we assume that the following reaction takes place:



The equilibrium pressure of Si above SiC at temperature T is given by:

$$P_{\text{Si}}(T) = \exp\left(-\frac{\Delta G_T^0}{RT}\right) \text{ with the usual definition of standard states, } P_{\text{Si}} \text{ is in atmospheres.}$$

The standard Gibbs free-energy of decomposition of SiC ΔG_T^0 is expressed as:

$-\Delta G_T^0 = \Delta G_f^0(\text{SiC}) - [\Delta G_f^0(\text{Si}) + \Delta G_f^0(\text{C}_{\text{graphite}})]$ where ΔG_f^0 is the standard Gibbs free-energy of formation of a compound or an element, which is obtained from tabulated data (JANAF tables).

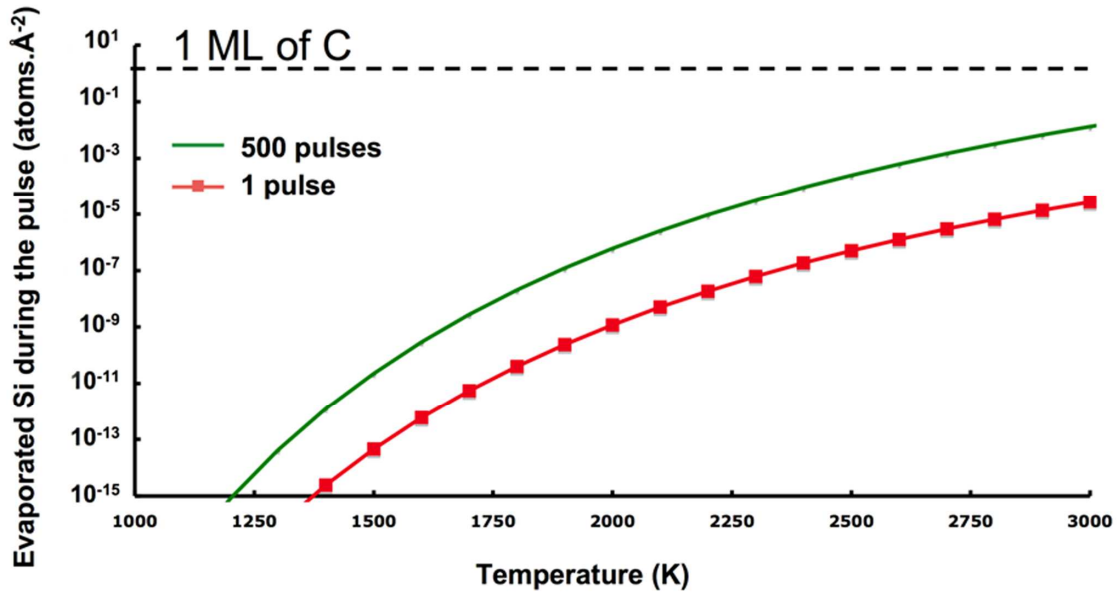
The total amount of evaporated Si per unit area during a laser pulse is approximated by multiplying the Hertz-Knudsen-Langmuir equation by the pulse duration (~25 ns).

In the thermal diffusion regime (*i.e.* when the thermal diffusion length during the pulse is much larger than the optical absorption depth), the surface temperature is given by:

$$T(x,t) = \frac{I_0(1-R)}{K} \left[\sqrt{\frac{4D_T t}{\pi}} e^{-\frac{x^2}{4D_T t}} - x \operatorname{erfc}\left(\frac{x}{\sqrt{4D_T t}}\right) \right] + T_0$$

where x is the distance from the irradiated surface, R is the reflectivity of the surface, I_0 is the laser irradiance (in W/m^2), K is the thermal conductivity of SiC, D_T is the thermal diffusivity of SiC, t is the irradiation time and T_0 is the initial surface temperature. Assuming for simplicity that the thermal properties of SiC are approximately temperature independent and using the room-temperature values ($R=0.27$, $K=3.7 \text{ W}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$ and $D_T=1.7 \text{ cm}^2\cdot\text{s}^{-1}$), after $t=25 \text{ ns}$, we obtain for a $1 \text{ J}/\text{cm}^2$ pulse a temperature increase $\Delta T=(T-T_0)\sim 1800 \text{ K}$. Thus, in our irradiation conditions, the surface temperature is $\sim 2100 \text{ K}$.

The amount of evaporated Si atoms at the end of the 25 ns pulse can be plotted as a function of temperature, from room temperature to the melting point of SiC ($\sim 3000 \text{ K}$):



Amount of evaporated Si per unit area during a 25 ns pulse as a function of temperature. The amount of Si equivalent to one monolayer is indicated in the plot.

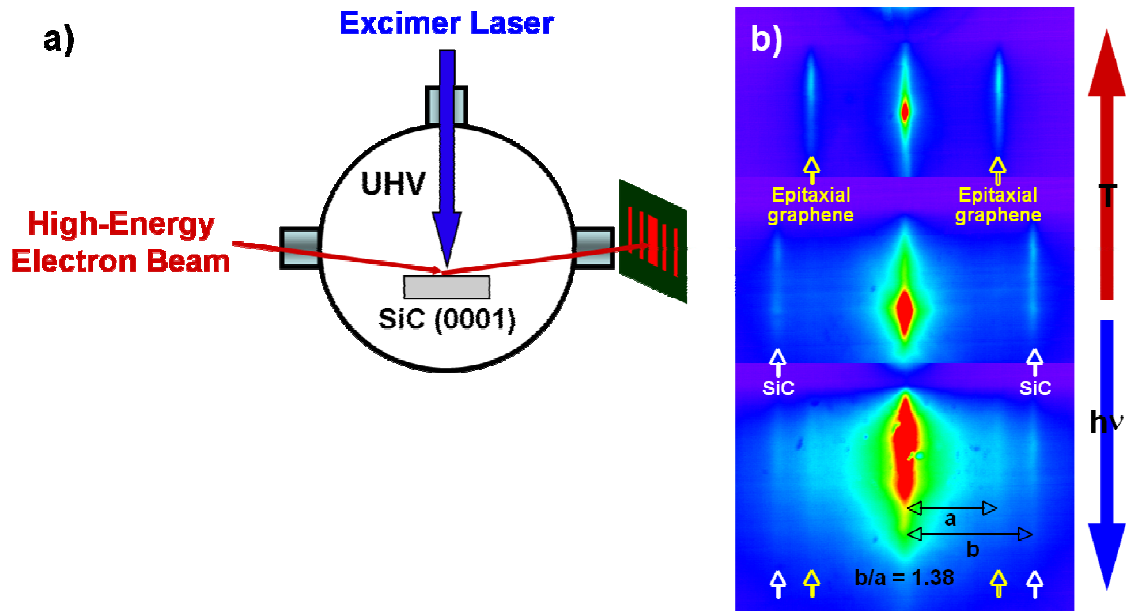


Figure S1. (a) Schematic of *in-situ* RHEED experiment during laser process. The SiC substrate was loaded perpendicular to the direction of excimer laser. (b) RHEED pattern of thermally grown epitaxial graphene (EG) (4-5 layers) (top), bare-SiC in a $[10\bar{1}0]$ azimuth (middle), and laser-processed SiC in the same angle with thermally grown EG (bottom). The SiC streaks are observed with the graphite streaks in the bottom pattern due to the large RHEED beam compared to the laser-processed region. The relative distance between graphite and SiC streaks ($= 1.38$) is in agreement with the spacing and orientation of a graphene layer grown epitaxially on SiC.

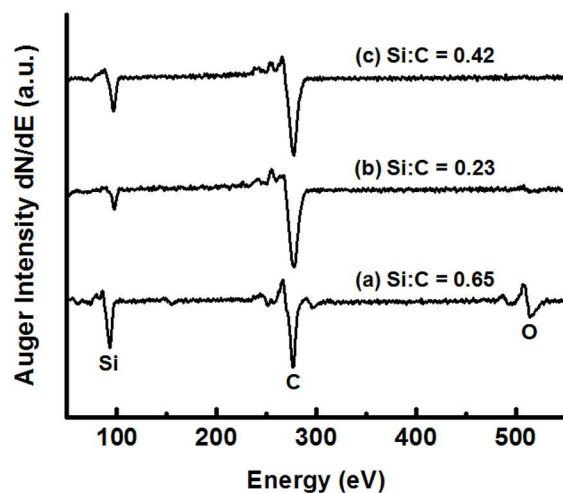


Figure S2. Auger spectra (acceleration voltage = 3 keV) corresponding to different areas after laser process in Figure 1B. (a) bare-SiC region (blue), (b) bi-layer graphene region (yellow), (c) mono-layer graphene region (red). The oxygen is not detected in (b) and (c). The electron escape length at 92 eV (Si LVV) is ~0.5 nm.¹

1. Seah, M. P.; Dench, W. A. Quantitative Electron Spectroscopy of Surfaces: A Standard Data Base for Electron Inelastic Mean Free Paths in Solids. *Surf. Interface Anal.* **1979**, *1*, 2-11.

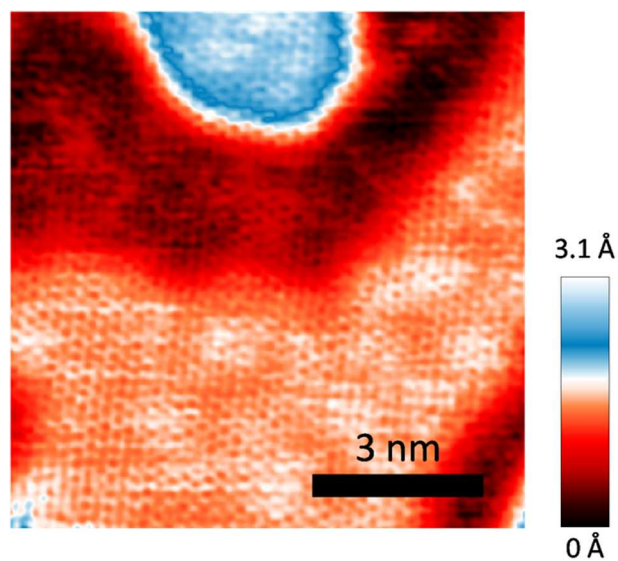


Figure S3. STM topograph of laser-synthesized graphene in the region of the sample characterized in Figure 1c. A graphene monolayer with signature honeycomb lattice is exhibited over large areas and varied topography. In addition, no periodic surface reconstruction of SiC (0001) is observed. (Bias voltage $V_B = 300$ mV, tunneling current $I_T = 100$ pA). A bilayer region is visible as well.

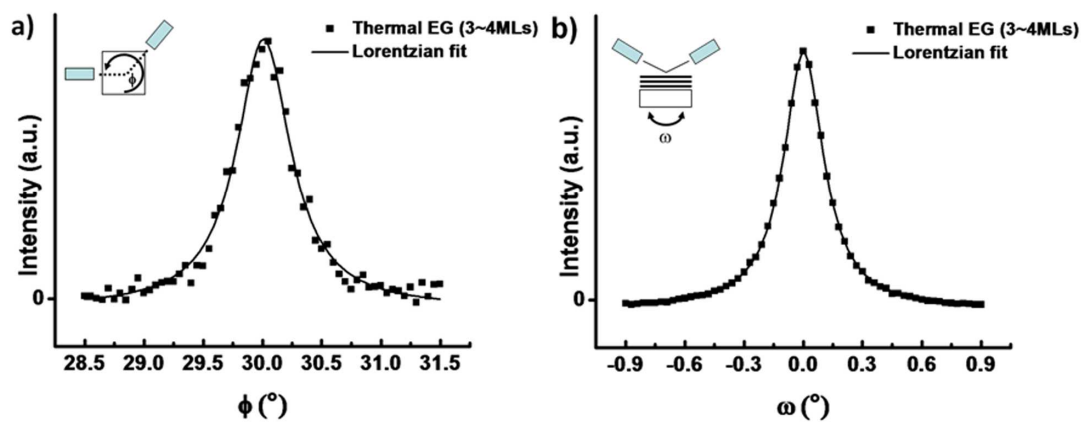


Figure S4. Synchrotron X-ray diffraction of thermally grown Epitaxial Graphene (EG).

(a) Azimuthal ϕ -scan of the (100) in-plane peak of thermally grown EG (FWHM = 0.56°). (b) Rocking scan about the (0002) peak of thermally grown EG (FWHM = 0.25°).

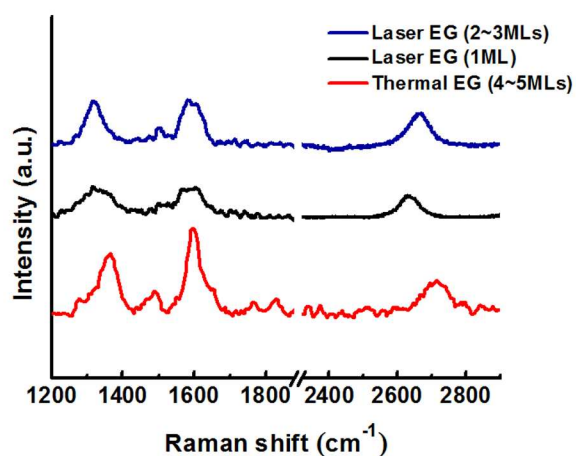


Figure S5. Raman spectra of laser-synthesized EG and thermally grown EG. The D, G and 2D peaks were visible in the differential spectra obtained by subtracting the Raman spectrum of the bare SiC sample from that of the graphitized samples. The D-to-G intensity ratio was similar in thermally-grown EG and laser-synthesized EG suggesting a similar degree of disorder in both materials.