### **Electronic Supplementary Information (ESI)**

# Real-time optical diagnostics of graphene growth induced by pulsed chemical vapor deposition

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#### 1. Modeling of Gas Dynamics

We have used general purpose CFD (Computational Fluid Dynamics) software called MFIX (Multiphase Flow with Interphase eXchanges).<sup>1-3</sup> For this work, we have only employed the single-phase capabilities of this software and the following continuity, momentum, species, and energy equations are solved. The complex geometry of the reactor utilizes the recently implemented Cartesian cut-cell technique in MFIX.<sup>4</sup>

#### **Continuity Equation**

$$\frac{\partial}{\partial t}(\rho_g) + \frac{\partial}{\partial x_j}(\rho_g U_{gj}) = 0 \tag{1}$$

#### **Momentum Equation**

$$\frac{\partial}{\partial t} \left( \rho_g U_{gi} \right) + \frac{\partial}{\partial x_j} \left( \rho_g U_{gj} U_{gi} \right) = - \left( \frac{\partial p_g}{\partial x_i} \right) + \frac{\partial \tau_{gij}}{\partial x_j} + \rho_g G_i \tag{2}$$

where,

$$\tau_{gij} = \mu_g \left[ \left( \frac{\partial U_{gi}}{\partial x_j} + \frac{\partial U_{gj}}{\partial x_i} \right) - \frac{2}{3} \frac{\partial U_{gi}}{\partial x_i} \delta_{ij} \right]$$
(3)

**Species Equation** 

$$\frac{\partial}{\partial t} (\rho_g X_{gn}) + \frac{\partial}{\partial x_j} (\rho_g U_{gj} X_{gn}) = \frac{\partial}{\partial x_i} \left( D_{gn} \frac{\partial X_{gn}}{\partial x_i} \right)$$
(4)

#### **Energy Equation**

$$\rho_g C_{pg} \left[ \frac{\partial T_g}{\partial t} + U_{gi} \frac{\partial T_g}{\partial x_i} \right] = -\frac{\partial}{\partial x_i} \left( k_g \frac{\partial T_g}{\partial x_i} \right) - \left[ \frac{\partial p_g}{\partial t} + U_{gi} \frac{\partial p_g}{\partial x_i} \right]$$
(5)

The above equations are spatially discretized using a finite volume technique (first-order upwinding in this case) and an implicit backward Euler method is used for

time discretization. At each time step, MFIX uses Picard fixed point iteration to solve the set of coupled, highly nonlinear equations that arise from the discretization of transport and conservation laws. The formulation of fluid velocity system of sparse, non-symm



**Fig. S1.** Schematic of the computational setup (plane cuts through the center line of the inlet and outlet pipes of the reactor) along with the boundary conditions.

and conservation laws. The set of nonlinear equations is linearized using the SIMPLE<sup>5</sup> formulation of fluid velocity correction and pressure correction. For each variable, a system of sparse, non-symmetric linear equations corresponding to a regular seven-point stencil on a logically rectangular grid are solved.

The computational setup of the pulse reactor is shown in the schematic above (not to scale). The mass-flow rate along with species composition is prescribed at the inlet. The temperature profile on the wall is prescribed. This case is run with very small time-steps (100  $\mu$ s – 1 ms) to resolve the injected pulse width of 10 ms (the C<sub>2</sub>H<sub>2</sub> pulse is distributed over 10 ms to account for the diffusion into the t-junction), and the pulse is injected after 0.5 seconds. By 0.5 seconds the solution has reached stationary state starting with initial conditions (reference temperature and constant velocity set to zero). The properties of the gases are calculated using the BURCAT thermochemical database.

Figure S2 shows the  $C_2H_2$  mass fraction distribution, the spatial distribution of temperature, and the gas velocity at t=0.02s, which corresponds to the maximum of the  $C_2H_2$  gas pulse.



**Fig. S2.** (a)  $C_2H_2$  mass fraction distribution at 0.02 s. (b) Spatial distribution of temperature (K) at 0.02 s. (c) Gas velocity (m/s) magnitude contours along with the gas velocity vectors at 0.02 s.

### Nomenclature:

 $\rho_g = gas \ density; U_{gj} = j \ component \ of \ gas \ velocity; \ p_g = gas \ pressure; \ \tau_{gij} =$ 

shear stress tensor;  $\mu_g = gas$  viscosity;  $G_i = gravity$  vector in i direction –

in this case taken to be zero;  $\delta_{ij} = dirac - delta$  function;  $X_{gn} =$ 

nth gas species mass fraction;

 $D_{gn} = diffusion \ coefficient \ of \ the \ nth \ gas \ species;$ 

 $C_{pq}$  = heat capacity of the gas mixture;  $k_q$  =

thermal conductivity of gas mixture

#### References

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### 2. Time-resolved reflectivity upon exposure to a pure Ar pulse



**Figure S3.** Normalized reflected intensity from a Ni substrate within the microscope stage as a function of time after exposure to a pure Ar pulse at 800 °C at the total backing pressure of 400 Torr plotted (a) from 0 to 12s and (b) from 0 to 60 s. The vertical arrows show the onset of an Ar pulse at t=0. The rectangular pulse (from t=10 s to t=10.5 s) is a reference time mark, the time of which with respect to the valve opening time is precisely known.



3. Raman map of graphene transferred to a SiO<sub>2</sub>/Si substrate.

**Figure S4.** (a) Optical image of graphene grown on a 0.5- $\mu$ m thick Ni film on SiO<sub>2</sub>/Si at 840 °C using a 5% mix (see text) of C<sub>2</sub>H<sub>2</sub> and transferred to a SiO<sub>2</sub>(0.3 $\mu$ m)/Si substrate using a standard procedure, which involves spin-coating with PMMA followed by etching of the Ni film with HCl (10 volume % aqueous solution) and removing the PMMA layer in acetone. The square in the center marks the area used for Raman mapping. (b) Raman map (62 $\mu$ m x 62 $\mu$ m) of the I(2D)/I(G) ratios measured for graphene transferred to a SiO<sub>2</sub>(0.3 $\mu$ m)/Si substrate. The 12 dots on the map indicate the positions for the corresponding Raman spectra shown in Fig. S5 (a) points 9-12 and (b) points 1-8. The map was acquired using a 532nm excitation wavelength (laser spot size at the sample ~ 2  $\mu$ m) with 1s acquisition time for each point and 2 $\mu$ m increments.

4. Selected Raman spectra of graphene transferred to a SiO<sub>2</sub>/Si substrate.



**Figure S5.** Selected set of the Raman spectra corresponding to the 12 dots marked on the Raman map (see Fig. S4b). (a) Points 9-12 and (b) points 1-8.

Raman spectrum number (Fig. S4)	Raman bands	Band positions, cm <sup>-1</sup> (±1cm <sup>-1</sup> )	Bandwidth (FWHM), cm <sup>-1</sup> (±0.5 cm <sup>-1</sup> )	I(2D)/I(G)
1	2D G	2670 1584	25.7 19.5	11.0
2	2D G	2699 1584	24.3 19.0	11.1
3	2D G	2700 1584	24.3 19.0	13.3
4	2D G	2700 1584	23.7 18.7	13.5
5	2D G	2699 1584	26.3 19.9	10.7
6	2D G	2699 1584	27.9 20.4	9.7
7	2D G	2701 1584	39.5 20.2	4.5
8	2D G	2700 1584	27.4 19.9	6.8
9	2D G	2726 1583	21.1	0.8
10	2D G	2703 1584	45.8 21.3	0.3
11	2D G	2703 1584	73.0 21.3	0.6
12	2D G	2699 1585	51.3 20.7	0.5

**Table S1.** Positions, bandwidths, and I(2D)/I(G) ratios estimated from the Raman spectra shown in Fig. S4.

5. Raman map of the I(2D)/I(G) ratios (graphene on Ni film).



**Figure S6.** (a) Raman map (62  $\mu$ m x 62  $\mu$ m) of the I(2D)/I(G) ratios measured for graphene grown on a 0.5- $\mu$ m thick Ni film on SiO<sub>2</sub>/Si at 840 °C using a 20% mix (see text) of C<sub>2</sub>H<sub>2</sub>. The average intensities of the 2D- and G-bands in the range of 2690-2701cm<sup>-1</sup> and 1574-1585cm<sup>-1</sup>, respectively were used to calculate the ratios. The corresponding SEM image is shown in Fig. 2f. The 9 dots on the map indicate the positions for the corresponding Raman spectra shown below in (b). The map was acquired using a 532nm excitation wavelength (beam spot size at the sample ~ 2  $\mu$ m) with 1s acquisition time for each point and 2 $\mu$ m increments.



6. Raman map of the I(2D)/I(G) ratios (transferred graphene on SiO<sub>2</sub>/Si substrate).

**Figure S7.** (a) Raman map (62  $\mu$ m x 62  $\mu$ m) of the I(2D)/I(G) ratios measured for graphene grown on a 0.5- $\mu$ m thick Ni film on SiO<sub>2</sub>/Si at 840 °C using a 20% mix (see text) of C<sub>2</sub>H<sub>2</sub> and transferred to a SiO<sub>2</sub> (0.5  $\mu$ m)/Si substrate. The map was acquired using a 532nm excitation wavelength (laser spot size at the sample ~ 2  $\mu$ m) with 2s acquisition time for each point and 2 $\mu$ m increments. The 9 dots on the map indicate the positions for the corresponding Raman spectra shown below in (b).

## 7. Comparison of Raman spectra of single layer suspended graphene at 532 nm and 404.5 nm



**Figure S8.** Raman spectrum of suspended single layer, single crystal graphene grown on Cu foil by low pressure, continuous CVD and transferred to a 2000 mesh microscope grid measured at 532 nm and 404.5 nm using the same spot. The spectra are normalized to the intensities of the G-bands. These spectra demonstrate that at 404.5 nm excitation the relative intensity of the 2D-band drops by factor of 3.7 when compared to operating at 532 nm.

# 8. Processing of the reflectivity curves for comparison with the growth kinetics based on Raman measurements



**Figure S9.** (1-R/R<sub>0</sub>) as a function of time (R<sub>0</sub> and R are the reflected intensities before and after opening the pulsed valve. The rectangular 0.5s-pulse with the onset at 3.4s is a time mark generated using a pulsed generator triggered from a microphone attached to the valve (see Experimental section). The vertical bands show the acquisition time intervals used for kinetics measurements by Raman scattering (Figs. 5 and 6). (Insert) Normalized reflected intensity as a function of time measured using the growth parameters identical to those used for the Raman measurements shown in Fig. 6 (800°C, 400 Torr Ar/H<sub>2</sub> (4:1) backing pressure).