Integrated Modeling of Carbon and Boron Nitride Nanotubes Synthesis in Plasma of High-Pressure Arc

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GEC meeting, October 9, 2020
• Motivation: Develop understanding how nanomaterial grow and identify plasma conditions in the synthesis area

• Modeling of arc structure

• Modeling of nanoparticle nucleation and growth

• Atomistic simulations of key processes of nanotube growth
  • Carbon nanomaterials
  • Boron-Nitride nanomaterials

• Summary
Plasma Science Studies of Nanomaterial Synthesis

- **Goal:** Uncover long standing puzzle how carbon and boron nitride nanotubes grow in plasma synthesis.

- **Devices:** Plasma arc and DC or RF plasma torches, laser-ablation.

- **Approach:** Perform detailed characterization of plasma and nanoparticles parameters using laser diagnostics; develop integrated and validated models comprised of numerical tools capable of simulating nucleation of nano-material growth and particle transport and plasma properties.

Images of boron-nitride nanotubes and boron catalyst particles.
Arc as a versatile method of nanomaterial synthesis

- Many nanostructures were synthesized at different arc conditions: C60, MWCNT, SWNT, graphene flakes, nanofibers
- A graphite anode provides carbon feedstock to produce plasma and nanomaterials.

1-2 kW input power, Helium buffer gas, atmospheric pressure.

See M. Keidar and I. Beilis, Plasma Engineering
Fundamental Studies of Synthesis of Nanomaterials: A joint challenge for plasma and materials sciences

A central objective of the research is to understand the synergistic roles of plasma and materials processes in arc synthesis of Carbon and Boron Nitride (BN) nanotubes (CNTs, BNNTs)

- Characterization of the plasma
- In-situ laser diagnostics of nanoparticles
- Ex-situ diagnostics of nanoparticles
- Development, validation, and integration of codes for multi-scale modeling of plasma nanomaterial synthesis.
Computational tools used for simulations of arc plasma and nucleation and growth of nanostructures
• Modeling of arc structure
What are conditions for carbon arc nanomaterial synthesis?

![Diagram of carbon arc synthesis](image)

- **T = 4000 K**
  - Evaporation, Dissociation
  - $C \approx 10^{17} - 10^{18}$ cm$^{-3}$
  - He $\approx 3 \cdot 10^{17}$ cm$^{-3}$
  - $C^+ \approx 10^{14} - 3 \cdot 10^{16}$ cm$^{-3}$

- **T = 3000 K**
  - Clusters, nucleation
  - $C \approx 10^{15} - 10^{16}$ cm$^{-3}$
  - He $\approx 3 \cdot 10^{18}$ cm$^{-3}$
  - $C^+ \approx 10^{12}$ cm$^{-3}$

- **T = 2000 K**
  - Growth, bundling
  - $C \approx 10^{14} - 10^{15}$ cm$^{-3}$
  - He $> 3 \cdot 10^{18}$ cm$^{-3}$
  - $C^+ \approx 10^{10}$ cm$^{-3}$
Governing plasma equations

2D-3D model, C-He plasma

Momentum equation: \[ \nabla \cdot (\rho \, \vec{v} \, \vec{v}) = -\nabla p + \nabla \cdot (\mu \, \nabla \vec{v}) + \rho \, \vec{g} \]

Continuity equation: \[ \nabla \cdot (\rho \, \vec{v}) = 0 \]

Neutral transport equation: \[ \nabla \cdot (\rho c_c \, \vec{v}) = \nabla (D \nabla (\rho c_c)) - S_i \]

Ions transport equation: \[ \nabla \cdot (n_i \vec{v}) = \nabla \left( D_a \nabla n_i + D_{th \, diff} \nabla T + D_{th \, diff \, e} \nabla T_e + j_e \gamma_{e, i} \right) + S_i, \quad S_i = \alpha n_e n_c A - \beta n_e^3 \]

Transport of electrons: \[ \vec{E} = \nabla V = -\frac{k}{e} (1 + C_{e}^{(e)}) \nabla T_e - \frac{k}{e} T_e \nabla \ln n_e + \frac{j_e}{\sigma} \]

Equation of state: \[ p = (n_{neutrals} + n_i) kT + n_e kT_e \]

Energy balance of electrons: \[ \nabla \cdot \left( \left( 2.5 + A_e \right) kT_e \frac{j_e}{e} \right) = \nabla \cdot \left( \lambda_e \nabla T_e \right) - S_e E_i - Q_{electrons \, - \, heavy} - Q_{rad} + \vec{j} \cdot \vec{E} \]

Energy balance of heavy particles: \[ \nabla \cdot (\rho c \vec{v}) = \nabla \cdot (\lambda \nabla (T)) + Q_{electrons \, - \, heavy} + \vec{j}_i \cdot \vec{E} \]

Quasi neutrality: \[ n_e = n_i \]

\[ Q_{electrons \, - \, heavy}, \sigma, \lambda_e \ are \ functions \ of \ (T_e, T, n_e, n_a, Q_{e,i}, Q_{e,a}) \]

\[ Q_{rad} = f(T_e, p) \]
2D setup: boundary and interfacial conditions

Plasma-electrode interfaces:

Ablation-deposition:

\[ G_{abl} = \left( p_{satur,k}(T) - p_k \right) \sqrt{M_e / (2\pi RT)} \]
\[ p_k = n_k kT \]

Electric current and potential:

\[ V_{solid} = V_{plasma} + \Delta V_{sh} \]
\[ j_{n,plasma} = j_e^{\text{emission}} - j_e^{\text{plasma to electrode}} + j_i = f(\Delta V_{sh}, T, T_e, n_e) \]

Heat fluxes include processes: ablation and deposition, emission, radiation, sheath, work function, ionization.

Very nonlinear self-consisted model with many parameters coupled at electrodes:

The current density is non-uniform at the electrode surfaces.
Benchmarcking of the model, 1D simulations

Argon arc, near-cathode layer: nonequilibrium region, effects of boundary conditions

- ... our code, ... simulations by N. Almeida et al. 


\[ P = 1 \text{ atm} \]
\[ j = 5 \cdot 10^6 \text{ A/m}^2 \]
\[ T_{\text{cathode}} = 3500 \text{K} \]

Collisionless sheath model:

\[ j = j_{e,c}^p + j_{e,c}^{\text{emiss}} + j_{i,c} \]

\[ j_{i,c} = q_e n_i \frac{k(T_e + T)}{m_e} \]

\[ j_{e,c}^p = q_e n_e \frac{1}{4} \frac{kT_e}{m_e} e^{-rac{V_{sh,c}}{kT_e}} \]

\[ q_{e,c} = j_{e,c}^{\text{emiss}} \left(V_{sh,c} + 2.5T_e\right) - j_{e,c}^p \left(V_{sh,c} + 2.5T_e\right) \]
Experiments with a segmented cathode:

- Y.-W. Yeh et al., Carbon 2016

Simulations: 75% of current flows through 3.2mm segment

Electric current streamlines:


Arc channel

Electric potential profile:

- Non-uniform potential profile along the cathode.

Middle plane plasma density profile:

- 2 radial segments, central segment d=3.2mm, 95% of current
Towards predictive modeling of atmospheric plasma for synthesis of nanomaterials

- Plasma density obtained from $\text{H}_\alpha$ OES and 2-D CFD simulations

  Arc operation: Current 55 A, He pressure 500 torr

  Inhomogeneity of the arc plasma is due to narrow arc channel

- $\text{C}_2$ density obtained from LIF (a) and 2-D CFD (b)

*Figure 4. Comparison of (a) simulated and (b) measured $\text{C}_2$ density distribution in the arc at current 50 A. Change in the cathode surface topology due to the growth of deposit (b) was not accounted for in the simulation (a).*
Gas flow controls transport of carbon in the arc

Flow pattern in the arc region

Mass fraction of carbon in C-He mixture

Temperature, K

Axis of symmetry

Cathode

Anode

Gravity

Gas flow (convection)

Axis of symmetry

2mm

Credit: Shurik Yatom, PPPL

Mass fraction of carbon in C-He mixture

Gravity

Temperature, K

Credit: Shurik Yatom, PPPL
Analytical model of low and high ablation regimes in carbon arcs

- The ablation rate is a strong nonlinear function of the arc current.
- We developed an analytical model that explains this transition.

Fig. Ablation rate of anode as a function of arc current.

Analytical model of low and high ablation regimes in carbon arcs

- Ablation flux grows drastically with the surface temperature $T_a$
- We developed analytical model for ablation flux $g_{abl}$

Fig. Schematics of carbon ablation into He gas.

$$g_{abl} = \left( p_{sat,C}(T_a) - p_{C,a} \right)/v_{th}$$

$$g_{abl} = D_{C-He} \frac{dn_C}{dx}$$

$$g_{abl}v_{th}(T_a) = p_{sat,C}(T_a) - p_0 \left[ 1 - \exp \left( - \frac{g_{abl}}{g_0} \right) \right]$$
Analytical model of low and high ablation regimes in laser ablated graphite

Fig. Schematics of laser experiment.


Fig. Ablation flux as a function of $1/$(surface temperature).

Low ablation

Langmuir’s ablation to vacuum

Full solution

Solution for low ablation regime

Diffusion-limited ablation

Experimental data

$10000 / T_a$, K$^{-1}$

$10000 / T_{low}$
Ablation rate as a function of arc current can be determined from the energy balance

\[ (1) + (2) + (3) = (4) + (5) \]

\[ \pi r_a^2 g_{abl}(T_a)L + C_1 T_a^{2.5} r_a^{1.5} + C_2 r_a^2 T_a^4 = C_3 r_a^2 + V_{eff} I \]

\[ V_{eff} = V_w + 2.5 \frac{k}{e} T_{e,a} + \max(V_{sh}, 0) = 9.5V \]

\[ C_1 = \pi \sqrt{\frac{4}{5} \sigma \varepsilon_a \lambda_a} \]

\[ C_2 = \pi \sigma \varepsilon_a (1 - \alpha_r) \]

\[ C_3 = \pi \sigma \varepsilon_a \varepsilon_c F_{c-a} T_c^4 \]

The ablation rate as function of arc current is in a good agreement with experimental data.


The ablation rate as function of anode radius is in a good agreement with experimental data.


\[ I = 65 \text{ A} \quad d = 1.5 \quad p = 67 \text{ kPa (500 Torr)} \]

Variable anode radius \( r_a \)

** J. Ng and Y. Raitses, Carbon 77, 80 (2014)
The ablation rate as a function of inter-electrode-gap width is in a good agreement with experimental data.

The ablation rate curves as function of current shift towards higher arc currents with the background pressure increase proving diffusion limited regime.

Arc anode spot formation observed and explained

Current density profiles on anode front surface

Surface temperature profiles on anode front surface

Characteristics observed in both simulations and experiments:
- Spot size increases with arc current
- Temperature inside the spot is relatively uniform and is about the carbon evaporation temperature.

Problem can be reduced to a cylindrical heat conduction problem in the anode:
The net heat flux from plasma are balanced by heat loss from its surface through heat conduction. Nonlinear processes in ablation and radiation give a unique nonuniform solution for the anode spot.

Outline

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• Summary

nano.pppl.gov
Measurements and simulations of nanoparticles

Experimental set up for laser-induced incandesce (LII), spectral imaging, and the laser beam intersection with the region of nanoparticle growth.

Areas from which a LII signal was collected are highlighted and the mean particle diameter for each area is shown from LII (yellow) and simulations (white). S. Yatom, et al, MRS (Material Research Society) Communications (2018).
Modeling of nucleation burst is very complicated because it involves solving for very complex nonlinear nucleation rate. Using an approximation for nucleation rate and Friedlander’s momentum model for cluster distributions we derived formulas for cluster mean diameter and dispersion.

Fig. Mean diameter after nucleation as a function of the cooling rate normalized on \( \dot{T}_0^* = 1000K/s \), analytic formula (crosses) Friedlander's model (lines) for two ambient gas pressures. \( \Delta T \) is the temperature change after nucleation burst.

• Atomistic simulations of key processes of nanotube growth
  • Carbon nanomaterials
Charging of nanotubes affects adatom absorption and diffusion

- Charging of nanoparticles and nanostructures is a plasma effect on nucleation and growth processes
- DFT and Kinetic Monte-Carlo simulations of charging effect
- Armchair (5,5) SWCNT (Fig. a)
- Charging of the CNT causes the higher adsorption energy $E_a$, increasing the migration distance

DFT results (Fig. b)- additional charges distribute in the covalent bond space between adatom and CNT, increasing its covalent coupling.

L. Han, P. Krstic, I. Kaganovich, and R. Car, Carbon 116, 174 (2017)
Condensation of carbon gas

- Simulations by Quantum-Classical Molecular Dynamics with Density Functional Tight Binding Theory

- Cooling carbon forms chains and fullerenes.
- No available carbon vapor for carbon nanotube growth. => Need catalyst for nanotube growth

L. Han, P. Krstic et al.,
Outline

• Atomistic simulations of key processes of nanotube growth

  • Boron-Nitride nanomaterials
Synthesis of Boron Nitride Nano Tubes (BNNT) in arc

Boron-rich anode and tungsten cathode 40V-40A arc at 400 torr of N₂ (Zettl 2000)

Hypothesis of BNNT synthesis

How $\text{N}_2$ molecules are converted into BNNTs?

$\text{N}_2$ is dissolved in boron droplets

Root growth mechanism

Boron Nitride Nanotubes (BNNTs) Growth
Understanding root growth of BNNT

1. Accumulation of N on the surface of liquid boron
2. Formation of a BN island on the liquid surface
3. Fluctuation and nucleation of a protruding BN cap
4. Growth of the nanotube with root feeding

Where BN radicals can come from?

Simulations show that $N_2$ is not easily dissolved in boron droplets. What else?

There a large barrier to form stable NBN from $B+N_2$ 

$$B + N_2 \rightarrow BNN \rightarrow NBN$$

References


$1\text{eV} = 23.061 \text{ kcal/mol}$
DFT can only simulate the species with the lowest energy for multiple species with the same geometry. This prevents DFT from predicting mechanisms involving other species with the same geometry but higher energy level.

**Restrictions of DFT**

1. DFT can localize the \( \text{BN}_2(\text{^2A}_1) \) state because this state has the lowest energy at the current geometry.

2. DFT cannot localize the \( \text{BN}_2(\text{^2B}_2) \) state because the energy of this state is higher than energy of \( \text{BN}_2(\text{^2A}_1) \) state at the same geometry. Thus, DFT can predict cycle BN2 dissociation through TS3 only and cannot predict dissociation through TS2!

3. NBN(2Π) needs to overcome significant barrier to achieve the valley of cyclic BN2 molecule, therefore this state was observed experimentally.
Simulations show that $N_2$ is not easily dissolved in boron droplets. What else?

We proposed Mechanism for BNBN formation through a Boron dimer and a Nitrogen Dimer. O. Dwivedi et al. (2019)

$$B_2 + N_2 \rightarrow BBN_2 \rightarrow B_2N_2 \rightarrow BNBN$$

$B_2 + N_2 \rightarrow$ BNBN Quantum chemistry modeling by Y. Barsukov et al. (2020)

BNBN Formation


BNBN formation is observed through DFTB+.
BNBN form more complex molecules

Movies: Reaction of two B$_3$N$_3$ rings to form B$_6$N$_6$ ring, and Reaction of four rings to form B$_{12}$N$_{12}$ ring at 2500K; O. Dwivedi, S. Jubin, S. Ethier, et al. (2019)

Four rings react to form B$_{12}$N$_{12}$ nanocage.
BN clusters bond energies

Y. Barsukov, et al. (2020)
New hypothesis of BNNT synthesis

Production of B-N compounds can proceed thorough BNBN molecule formation.

Y. Barsukov, et al. (2020)
Summary: Carbon Arc

• Developed self-consistent model of carbon arc including effects of ablation, electron emission, radiation, sheath.
• Model was benchmarked and validated with PPPL experimental data.
• Developed an analytical model which explained transition from low to high ablation regimes.
• Numerical simulations and analytical theory explained anodic spot formation.
• Showed that charging of nanotube surface affects adatom desorption and surface diffusion.
• DFTB modeling revealed how condensing carbon vapor forms linear chains and fullerenes during cooling implying root growth mechanism and need for metal catalyst to dissolve carbon to form carbon nanotubes.
• Formation of boron nanotube on the boron droplet has two obstacles: large energy barrier for BN cap to lift and low probability of molecular nitrogen to dissolve in boron.

• Fixation of $N_2$ molecule can proceeds through BNBN molecule formation in the $B_2 + N_2 \rightarrow BNBN$ reaction. The highest barrier of the reaction towards BNBN formation is 1.9 eV (significantly less than $N_2$ bond energy, 9.7 eV).

• The formation of BNBN molecule is energetically favourable process, because from one $N_2$ molecule three B-N bonds are formed in BNBN molecule. It is expected that BNBN molecule is only intermediate and complex $(BN)_n$ molecules followed by rings and then fullborenes and nanotubes will be preferably accumulated in the gas phase in equilibrium conditions as plasma cools.

• This gives a stronger argument that BNNTs growth can be achieved directly through BNBN molecule formation without boron droplets formation as it is accepted in the “root growth” mechanisms.

• Developed analytical theory for nucleation burst droplet formation.
Acknowledgment

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- The simulations have been performed using Eddy cluster of PPPL and Princeton University.

- Experimental colleagues: Yevgeny Raitses, Shurik Yatom, Vladislav Vekselman, Brent Stratton, Tianyuan Huang
For those interested to use PPPL and PU diagnostics, numerical tools and facilities, please attend talk at 1pm. The upcoming solicitation for Princeton Collaborative Research Facility (PCRF) will be announced.

73rd Annual Gaseous Electronics Virtual Conference
Monday–Friday, October 5–9, 2020; Time Zone: Central Daylight Time, USA.

Session YF1: Federal Agency Perspectives in Plasma Research
1:00 PM–3:15 PM, Friday, October 9, 2020

Chair: Scott Walton, Naval Research Laboratory

Abstract: YF1.00004 : Princeton Collaborative Low Temperature Plasma Research Facility
2:15 PM–2:30 PM  Live

Preview Abstract

Author:
Yevgeny Raitses
(Princeton Plasma Physics Laboratory)
Observed two ablation modes affecting synthesis of carbon nanotubes

- Correlation between synthesis selectivity, yield, and arc current:
  - Enhanced ablation → Higher C₂ density → Deposition with higher yield
  - Smaller ablation → Reduced carbon flux → Deposition with better selectivity
• Nonstationary processes in arcs

37 Publications, 14 presentations are available at nano.pppl.gov
Arc oscillations affect synthesis of nanotubes

- Synthesis of SWCNT by carbon arc with metal catalysts
- Metal – Carbon mixed powder filled in the hollow graphite anode rod
- Multi-mode oscillations: LF ($10^2$ Hz) and HF ($10^3$ Hz) modes, inside and outside the hollow anode
- Oscillations cause of low purity and poor selectivity of the arc synthesis

- C$_2$ Filtered Fast Imaging, 10,000 fps

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Cathode

Graphite Anode with Ni+Y catalysts

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SWCNT Synthesis OFF

SWCNT Synthesis ON
- 5% of time

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Cathode

Graphite Anode with Ni+Y catalysts

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SWCNT Synthesis OFF

SWCNT Synthesis ON
- 5% of time

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Cathode

Graphite Anode with Ni+Y catalysts

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SWCNT Synthesis OFF

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- 5% of time

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Cathode

Graphite Anode with Ni+Y catalysts