Definitions

- **Plasma** - partially ionized gas containing an equal number of positive and negative charges, as well as some other number of non-ionized gas particles
- **Glow discharge** - globally neutral, but contains regions of net positive and negative charge
- **Most thin film processes utilize glow discharges, but “plasmas” and “glow discharges” are often used interchangeably**
Plasma Properties

- Plasma Density (n) – number of species/cm$^3$
  - $10^7 - 10^{20}$
  - Typical glow discharges and arcs have an electron and ion density $\sim 10^8 - 10^{14}$

DC Glow Discharge

- Before application of the potential, gas molecules are electrically neutral and the gas at room temperature will contain very few if any charged particles. Occasionally however, a free electron may be released from a molecule by the interaction of, for example, a cosmic ray or other natural radiation, a photon, or a random high energy collision with another particle.

\[
\text{hv} \rightarrow \text{0V} \rightarrow \text{A} \rightarrow \text{A}^+ + e^-
\]
When a large voltage is applied between the electrodes, say 100 V/cm, any free electrons which may be present are rapidly accelerated toward the anode. They quickly attain high velocity (kinetic energy) because they have such low mass. Since kinetic energy can be related to temperature, the electrons are “hot” - they achieve extremely high temperatures because of their low mass, in an environment of heavy, slow-moving “cold” gas molecules.

Electrons begin to collide with gas molecules, and the collisions can be either elastic or inelastic.
- Elastic collisions deplete very little of the electron’s energy and do not significantly influence the molecules because of the great mass difference between electrons and molecules: Mass of electron = 9.11 e-31 kg, Mass of Argon = 6.64e20 kg.
- Inelastic collisions excite the molecules of gas or ionize them by completely removing an electron. (The excitation - relaxation processes are responsible for the glow)
DC Glow Discharge

- Other electron/particle inelastic events

\[ e^-(100\text{eV}) + AB \xrightarrow{\text{inelastic}} e^-(<100\text{eV}) + A + B + e^- \quad \text{Dissociation/Fragmentation} \]

\[ e^-(100\text{eV}) + AB \xrightarrow{\text{inelastic}} e^-(<100\text{eV}) + A^+ + B + 2e^- \quad \text{Dissociative Ionization} \]

\[ e^-(100\text{eV}) + AB \xrightarrow{\text{inelastic}} e^-(<100\text{eV}) + A^+ + B^- + e^- \quad \text{Dissociative Ionization with Attachment} \]

Newly produced electrons are accelerated toward the anode and the process \textit{cascades} (Breakdown).
With sufficient voltage, the gas rapidly becomes filled with positive and negative particles throughout its volume, i.e. it becomes ionized.

Positive ions are accelerated toward the negative electrode (cathode). Collision with the cathode causes the emission of secondary electrons which are emitted from the cathode into the plasma.
Secondary Electron Coefficient

- Secondary Electron Coefficient ($\delta$) vs Incident Electron Energy
- Secondary Electron Coefficient ($\gamma_i$) vs Incident Ion Energy

---

DC Glow Discharge

- Free electrons from secondary emission and from ionization are accelerated in the field to continue the above processes, and a steady state self-sustaining discharge is obtained.
Sputtering

Angular Distribution

\[ I(\theta) = I \cos(\theta) \]

Substrate

Target

Positive Glow

Dark space

Ar\(^+\) Ar\(^+\)

Rf Magnetron Sputtering System

Load-lock chamber
Simultaneous 3 Source Sputtering

Source 1

Source 2

Source 3

Angular Distribution

Modified Cosine Distribution

\[ I(\theta) = I \cos^n(\theta) \]

\( n \approx 10 \)

Target

Film Thickness (nm)

Position (cm)
Process Modeling

**Input variables:**
- Source power, voltage, current
- Material sputter yield
- Source tilt angle
- Substrate position
- Source time

Determines substrate composition as a function of position

$$ p_{\text{total}} = \sum_{j=1}^{i=k} \left[ \sum_{i=1}^{\text{total}} n_i \right] = \sum_{j=1}^{\text{total}} \left[ \sum_{i=1}^{\text{total}} C_i \right] \left( \int_{0}^{360} \int_{0}^{32.7} \cos \theta \sin \phi d\theta d\phi \right) \left( \int_{0}^{360} \int_{0}^{32.7} \sin \theta \sin \phi d\theta d\phi \right) \left( \text{PrS} / V_q \right) \left( n+1 \right) \cos^\phi \cos \theta$$

MATLab Process Model

Binary Composition Profile

Ternary Composition Profile

Thickness Modeling
Recent Applications

- Ternary Phase Diagrams: Fe-Ni-Cr
  - With Pharr et al.
- Catalysts for Carbon Nanofiber Growth: Cu-Ni
  - With Simpson et al.
- Bulk Metallic Glass Alloy Development
  - With Liaw et al.
- Ultraviolet Emitting Materials: Y₃Al₅O₁₂:Gd

Fe-Ni-Cr Ternary Phase Diagrams

- Co-sputter Fe (160W), Cr (60W), Ni (60W) onto (1 –1 0 2) single crystal sapphire substrates
- Anneal 200, 400, 600, 800 °C for 2 hours
- Rapid synchrotron fluorescence and XRD measurements
- Future Work: Nano-indentation
Non-Equilibrium Ternary Phase Diagrams (Fe-Ni-Cr)

With Pharr et al.

Modeled versus Measured Composition

Measured Composition Space

Modeled Composition Space
Phase Diagram Temperature Evolution

As deposited
200°C
400°C
600°C
800°C
Equilibrium

Phase Analysis versus Temperature

Cr₆Fe₄Ni₄₀
Cr₆Fe₄Ni₇₀
Particle Size

![Graph showing XRD Particle Size (nm) vs. Annealing Temperature (°C)]

Carbon Nanofiber Catalyst

*Cu-Ni Alloy*

- Modeled Results
- Measured Results

Alloy Strip Deposited on Si

With Klien et al.
The morphology and shape of vertically-aligned carbon nanofibers are a strong function of the composition of the Cu–Ni catalyst particle that acts as the nucleation site for individual fiber growth. An optimum fiber geometry is realized at 80% Cu.

With Klien et al.
Al-Cu Phase Diagram

Atomic % On Substrate
Test Setup

- Base pressure = 6x10^-7 Torr
- Operating pressure = 5 mTorr
- Q (Ar) = 25 sccm
- Power Al = 200W
- Power Cu = 34W
- S (Al) = 1.2
- S (Cu) = 2.3
- Gun Tilt (Al,Cu) = 7.7 mm
- Bias = 0 VDC
- Substrate Height = 7.5 cm
- Temp = 30 ºC
- Time = 1.5 hr