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Atmospheric Pressure rf Glow Discharge for Nanocrystal Synthesis

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Fundamental studies of dust-plasma interactions at atmospheric pressure are critical for the development of low-cost atmospheric pressure plasma (APP) sources for material processing and nanocrystal synthesis. Most radio-frequency (rf) APPs today are microplasmas due to the *pd* scaling in Paschen's law [1]. The small dimensions lead to small rates of production. Here we present a large-volume (non-microplasma) rf uniform glow plasma for nanocrystal synthesis and the investigation of high-pressure dust-plasma interact ions. In this reactor, plasma stability in a large volume is achieved through the electron-trapping produced by the rf field and the dielectric barrier, as well as a multi-stage ignition mechanism. The discharge is first initiated in a local region where the gap spacing is a minimum. The discharge then uniformly expands to fill the entire volume as the electrode voltage is increased. This expansion could be due to helium metastables being created by the initial discharge facilitating the formation of a uniform plasma, discouraging the formation of streamers and therefore suppressing the glow-to-arc transition [2].

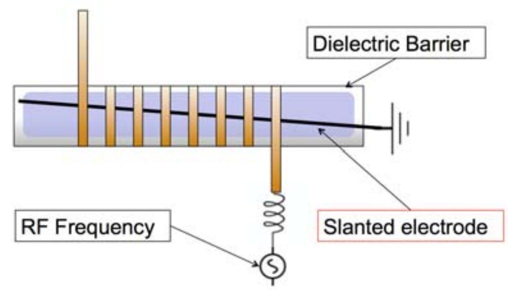


Figure 1 - Schematic of the atmospheric pressure rf uniform glow discharge reactor.

A schematic of the reactor is shown in Fig. 1. The outer copper electrode is coil-shaped and is wrapped around a quartz tube functioning as the dielectric barrier. The inner electrode is a slanted and grounded tungsten wire. A capacitive abnormal glow discharge is generated between the electrodes using a 13.56 MHz source and a flow of 3 slm (standard liters per minute) of helium or argon. The average reactor gap spacing is 2.4 mm. The electron density and temperatures, calculated using a global power balance model, are 10^{11} cm^{-3} and 1.1 eV. We injected oxygen and diethylzinc (DEZ) precursors into this plasma source and produced zinc oxide nanocrystals with a crystallite size of about 12 nm. At high flow rate (23 slm), the nanocrystals can elongate into large platelets more than 40 nm in size. This interesting phenomenon could suggest the presence of the competing effects of plasma heating and neutral gas heating on the nanocrystal growth, with plasma heating facilitating the growth and neutral gas heating inhibiting the growth. At higher gas flow rates, a larger plasma density can be achieved at lower gas temperature, leading to larger nanocrystal growth compared to low gas flow rate.

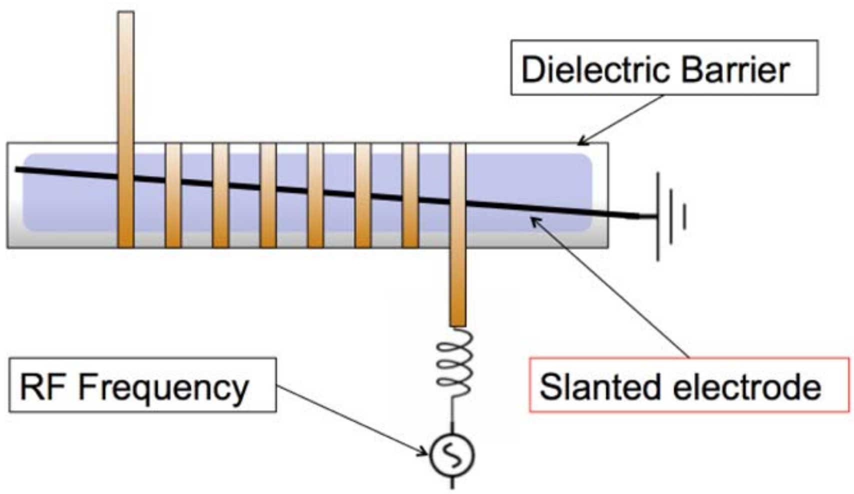
The next steps are to continue investigating the physics of plasma and neutral gas heating of the nanocrystals. We will also compare the experimental results to the atmospheric pressure nanocyrstal heating and charging model developed by Kramer [3] in order to achieve a detailed understanding of plasma-nanocrystal interactions at atmospheric pressures.

References

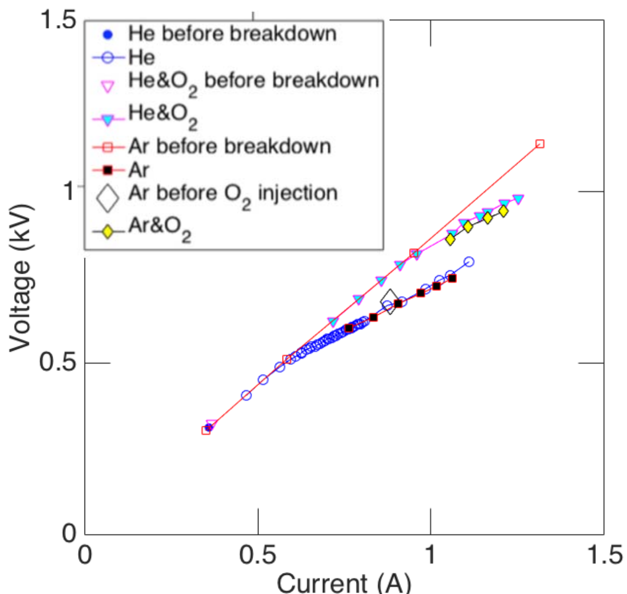
[1] D. Mariotti and R. Sankaran, J. Phys. D: Appl. Phys. **44**, 174024 (2011).
[2] A. Palmer, Appl. Phys. Letters. **25**, 138-140 (1974).
[3] N. Kramer, E. Aydil and U. Kortshagen, J. Phys. D: Appl. Phys. **48**, 035205 (2015).

ATMOSPHERIC PRESSURE RF GLOW DISCHARGE FOR NANOCRYSTAL SYNTHESIS

- A large-volume rf glow plasma was built for the study of high-pressure dust-plasma interactions. Plasma stability in a large volume is facilitated by a multi-stage ignition mechanism enabled by a slanted center electrode.
- The size of synthesized nanocrystals varies depending on the gas flow rate, indicating possible competing effects of heating mechanisms: plasma heating facilitates crystal growth while neutral gas heating inhibits growth.



- Reactor schematic with slanted center electrode



- Plasma operates as an abnormal glow with a variety of carrier gas mixtures

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Advanced Diagnostics of Atmospheric Pressure Plasma Jets Contacting Surfaces

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Interest in low-temperature, atmospheric-pressure plasmas continues to increase due to realized or potential applications in plasma medicine and nanomaterials synthesis. For selected area exposure, as required for many biomedical applications, use of the plasma jet is most common. The high operating pressure, however, presents severe challenges to plasma diagnostics. A novel diagnostic, **Evanescent Wave Optical Emission Spectroscopy** (EWOES), is under development based on evanescent wave coupling (a near-field effect), under conditions of total internal reflection. EWOES is estimated to have a spatial resolution of ≈10 nm. It is useful for monitoring species over the last 100 nm above the substrate, which corresponds to the species mean free path (mfp) at 1 atm.

In EWOES, a plasma jet is directed at the flat surface of a semicircular prism made of a transparent material (e.g., quartz). Light emanating from the prism at various angles θ above and below the critical angle θ_c is collected by an optical fiber. When $\theta > \theta_c$, light can only be detected from a region within a distance d from the surface, given by the penetration depth of the evanescent wave. For quartz ($\theta_c = 43^o$) and with $\lambda = 200$ nm, d = 15 nm at $\theta = 75^o$. Thus, the spatial resolution can be made much smaller than the mfp (≈100 nm) at a pressure of 1 atm. The signal as a function of θ can be de-convoluted to produce the emission and the concentration, via actinometry as a function of distance from the surface.

Preliminary measurements are shown in Fig. 1 for a He plasma jet in open air. Emission from both He and O-atoms first falls with increasing θ from normal incidence, and then increases as θ is increased to just below θ_c. Emission peaks within ≈1 mm of the surface. When θ passes through θ_c, intensities drop by more than 100-fold, and then continue to decrease with increasing θ to the largest angle accessible (75^o). In addition, the relative intensities of O and He are opposite on opposite sides of θ_c. Though seemingly very encouraging, other sources of signal at $\theta > \theta_c$ must be considered. In particular, light entering the prism at $\theta < \theta_c$ could scatter off surface defects or internal voids or inclusions and achieve an angle greater than θ_c. Experiments suggest that much of the signal recorded at $\theta > \theta_c$ is in fact due to this background. Higher quality prisms with fewer inclusions and voids and a better surface polish are needed. Also, the emission will be time-resolved, using an ICCD system to isolate emission very near the surface that will only occur in the short times when the ionization front reaches the surface. Light scattered from defects will arise from the entire discharge over a much longer time.

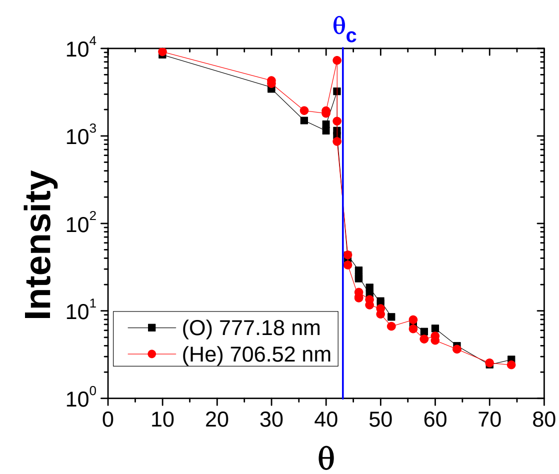

Figure1 - Optical emission intensities from He and O-atoms in a He plasma jet as a function of the angle of observation.

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ADVANCED DIAGNOSTICS OF ATMOSPHERIC PRESSURE PLASMA JETS CONTACTING SURFACES

- Novel diagnostic, ***Evanescent Wave Optical Emission Spectroscopy*** **(EWOES), based on evanescent wave coupling (a near-field effect), under total internal reflection (TIR) conditions.**
- **Estimated spatial resolution of ≈10 nm << species mean free path at 1 atm (≈ 100 nm).**
- **Can measure concentration gradients over the last 100 nm over the surface.**
- **Able to be used for optical absorption as well.**
- **Requires measurement of optical emission intensity at the desired wavelength as a function of angle.**
- **Extreme spatial resolution may be obtained for angles greater than the critical angle, θ_c, corresponding to TIR.**
- **Need to suppress scattering background for the technique to provide valid results at $\theta < \theta_c$.**