

# Nanomanufacturing with Low Temperature Plasmas

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**Abstract:** Low-temperature plasmas are widely employed for producing nanomaterials with tunable composition and morphology. Here, the state of advanced nanomanufacturing with low-temperature plasmas is addressed. We report on synthesis and property control of silicon and carbon nanoparticles using both low-pressure and atmospheric pressure reactors, towards the goal of on-demand nanoparticle printing and direct deposition using plasmas.

## 1. Introduction

Flow-through low-temperature plasma (LTP) reactors are commonly used to synthesize nanomaterials from vapor- or gas-phase precursors. The vast range of experimental knobs in LTP reactors, such as pressure, gas composition, gas flowrate, supplied power, and source frequency, mean that a wide variety of nanostructures with tuneable elemental makeup, crystallinity, size, and morphology can be accessed. In this contribution, we share our work on nanomaterial synthesis towards advanced manufacturing with plasmas, including using techniques which are compatible with roll-to-roll or additive printing methods. We also present our recent work on combining power sources for controlling nanomaterial growth.

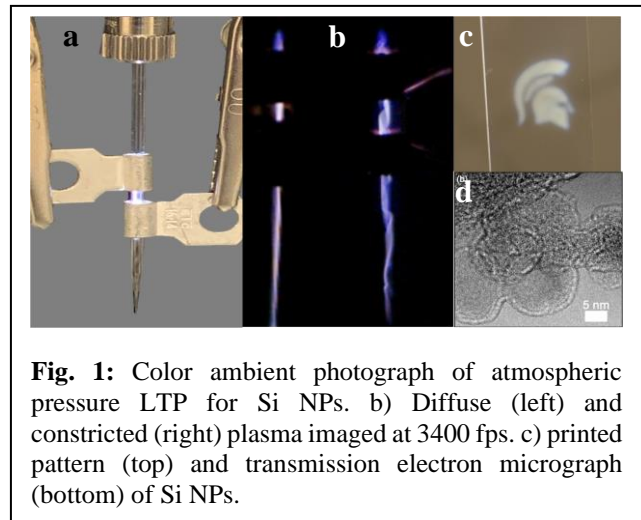
## 2. Methods

Here we focus on RF-driven LTPs for synthesis of nanoparticles (NPs), comparing results between low-pressure and atmospheric pressure reactors. The reactor diameter varied from 1 mm to 5 cm, and power was delivered via impedance matching networks via external ring electrodes. Silane (SiH<sub>4</sub>) and Methane (CH<sub>4</sub>) were the reactants for silicon NPs and carbon NPs, respectively, with Argon as background gas. We characterized the NPs using X-Ray Diffraction (XRD), Raman spectroscopy, and electron microscopy. We additionally performed optical emission spectroscopy (OES) and high-speed imaging to characterize the gas discharge during NP generation.

## 3. Results and Discussion

Modeling and calculations predict that higher-than-anticipated plasma density is required to reach the crystallization temperatures required for silicon NPs to become crystalline in atmospheric pressure LTPs.<sup>[1]</sup> Yet, numerous works show formation of crystalline silicon NPs at these pressures. We synthesized silicon nanocrystals at both 1-5 Torr and at atmospheric pressure. High-speed photography revealed that the atmospheric pressure plasma contains a high-density filament which is a requirement for crystallization of silicon NPs. This filament appeared only above a certain SiH<sub>4</sub> concentration.<sup>[2]</sup> In contrast, at low pressure, there was no filament or discharge constriction.

Aside from the presence of the filament, sufficient power was required to synthesize crystalline NPs. These parameters led to the demonstration of on-demand printing of silicon NPs with tunable crystallinity via this atmospheric pressure LTP. We are currently translating



**Fig. 1:** Color ambient photograph of atmospheric pressure LTP for Si NPs. b) Diffuse (left) and constricted (right) plasma imaged at 3400 fps. c) printed pattern (top) and transmission electron micrograph (bottom) of Si NPs.

this reactor to new materials such as carbon NPs, and will present preliminary data related to those findings.

Additionally, as carbon can crystallize as either graphite (sp<sup>2</sup> hybridization) or diamond (sp<sup>3</sup> hybridization), carbon NP synthesis in LTP reactors offers immense opportunities to explore the plasma parameters required for selective hybridization. Here we present a preliminary map of reactor parameters, plasma characteristics as evaluated using OES, and carbon NP properties.<sup>[3]</sup>

## 4. Conclusions

Continuing to reveal the direct correlations between plasma parameters (such as plasma density and atomic species) and resulting materials properties is an important step towards realizing advanced manufacturing with LTPs. This work takes steps towards those revelations by building out the known links between reactor settings and NP crystallinity, and points to the future of advanced manufacturing based on plasmas.

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## References:

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