Atmospheric Pressure Non-Thermal Plasma: Comparing Silane and Methane

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Abstract: Previously, we demonstrated the requirement of a constriction to form crystalline silicon nanoparticles in a millimeter-scale atmospheric pressure radiofrequency plasma. In an effort to further understand the influence of the plasma constriction on nanoparticle formation in similar reactors, we compare our previous findings with that of a methane/argon plasma under similar conditions.

1. Introduction

In previous work with a silane/argon atmospheric pressure non-thermal plasma, we were able to identify both a diffuse and constricted plasma formation based on the amount of silane precursor flown through the reactor.

Here we expand upon that work by varying the parameters of a methane/argon plasma in order to compare results in the formation of the plasma and the effect of the plasma on subsequent nanoparticles.

2. Methods

We used an atmospheric pressure nonthermal plasma reactor and a radiofrequency power supply to synthesize carbon nanoparticles. The reactor is operated in air, and has an outer diameter of 3mm. The power is coupled into the reactor via an impedance matching network and two ring electrodes which encircle the exterior of the reactor tube. In our prior experiments on silane/argon plasmas, we varied the silane concentration in the gas from 40 to 1073 ppm, and used a range of 200 to 10,714 ppm of methane in argon for the present study.

Visual analysis was performed using a Photron FASTCAM SA4 camera in order to identify changes in plasma formation. The species present in the plasma during various plasma modes were recorded through the use of OES via an Ocean Insight USB spectrometer.

The crystallinity and make-up of the nanoparticle samples were analyzed using a combination of FTIR, Raman, TEM, and SAED.

3. Results and Discussion

High speed imaging shows a notable difference between the silane and methane plasmas. While the silane plasma had two modes (diffuse and constricted), the methane plasma appears to have four unique modes that appear with increasing methane content which we have labelled 1, 2a, 2b, and 3. These modes are represented by a dim blue diffuse plasma (200 ppm), bright cyan diffuse plasma (1,186 ppm), bright cyan constricted plasma (3,846 ppm), and dim blue diffuse plasma (10,714 ppm). These modes alongside a constricted silane plasma are shown in Fig. 1.

The silane plasma required a constricted filament in order to achieve crystalline particles, whereas the methane plasma generated crystalline particles in each mode, including those which appear diffuse. Although crystallinity is present in each of these modes, spectroscopy and microscopy methods show an evolution

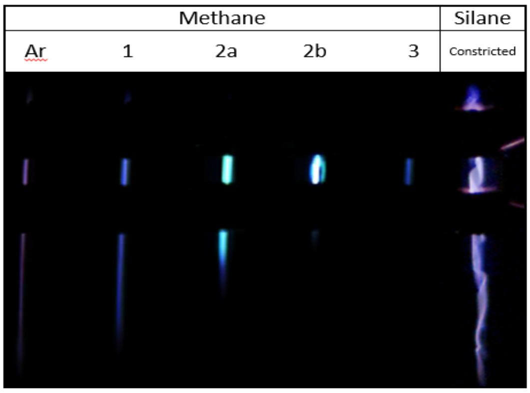

Fig. 1. Images of argon, methane modes 1-3, and constricted silane plasmas

of carbon content and crystal morphology through the progression from mode 1 to 3. The samples collected in modes 1 and 2a reveal nanoparticles of two types: a spherical morphology with lattice fringes visible, as well as onion-like nanoparticles commonly seen in the reaction of methane. However, in mode 2b (characterized by its bright cyan color and constricted shape), the nanocrystals are best described as graphitic flakes. Mode 3, which has even more methane content in the overall gas flow, yields samples with large increases in graphitic content.

4. Conclusion

Unlike with silicon nanoparticles, which require a plasma constriction for crystalline particle growth, carbon nanoparticles don't have the same requirement. This is likely due to the lower crystallization energy required for carbon nanoparticles, as compared to silicon nanocrystals. However, we did find that the color, emission spectra, and confinement of the plasma did shift with increasing methane composition. Analysis of the nanoparticles synthesized in the different plasma modes shows an evolution of crystal content from mode 1 to 3, from various single crystals to more flake-like graphitic content. These results point to the need for further diagnostics on plasma conditions during nanoparticle growth to fully understand how crystalline materials are formed.

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References

[1] C. Papson et al., APL, 125.5 (2024).