FORMATION OF ORGANOSILICON NANOPARTICLES IN A GAS AGGREGATION SOURCE AS WITNESSED BY IN SITU LIGHT SCATTERING

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Abstract

In this work, we applied a method of light scattering for in situ detection of organosilicon nanoparticles (NPs). Plasma polymerization of hexamethyldisiloxane (HMDSO) in its 10 % mixture with Ar was used to synthesize the NPs by means of a gas aggregation cluster source (GAS). The total pressure of 45 Pa and the RF discharge power in a range of 20 - 80 W were used. The GAS was constructed to allow passing of a laser beam (446 nm) across the beam of the NPs at the distance of 2 cm behind the exit orifice and acquiring the scattered light either by an optical emission spectrometer or by a CCD camera. Although for 20 W power constant intensity of the scattered light was obtained, cycling instabilities were detected for higher power. Both amplitude and period of such fluctuations increased with the discharge power increasing from 40 to 80 W. Cycling repelling of NPs and formation of plasma voids are suggested as possible mechanisms for the observed phenomena.

Keywords: Organosilicon nanoparticles, gas aggregation cluster source, light scattering, hexamethyldisiloxane

1. INTRODUCTION

Gas aggregation source is a well-known tool for the production of various metallic NPs (Cu, Ag, Au, Ti etc.) [1]. Recently, this technique was adapted for the deposition of plasma polymer nanoparticles (ppNPs). It was shown that plasma polymerization can be performed either utilizing volatile precursors (HMDSO, *n*-hexane etc.) or by RF sputtering of polymeric targets (nylon, PTFE etc.) [2]. Such nanoparticles have high potential in the fabrication of nanocomposite materials, for example, as fillers with unique chemical, physical or mechanical properties [3]-[5]. It is highly important to maintain a stable production rate of the NPs to allow good control over the amount of NPs embedded in the composites and to ensure better performance of the resulted coatings [6],[7]. However, plasma-based production of NPs often appears to be prone to the development of plasma instabilities which lead to the oscillations in the NP generation. Therefore, non-intrusive diagnostics methods are in high demand to control and analyze these processes. The aim of this work was to study the applicability of laser light scattering (LLS) technique for in-situ monitoring of the production of plasma polymer NPs by GAS.

2. EXPERIMENTAL

A gas aggregation cluster source of a Haberland's type was used for the production of ppHMDSO NPs [8] (**Figure 1**). The GAS was equipped with a capacitively-coupled radiofrequency graphite electrode (8 cm in diameter) powered with an RF supply (Dressler Cesar 133, 13.56 MHz). The generator was used in a continuous wave mode with the power applied in a range of 20-80 W. Plasma polymerization was performed in a working mixture of Ar (purity 99.99%) and HMDSO (purity 98.5%, Sigma-Aldrich) at the total pressure of

45 Pa (Ar flow 2sccm/HMDSO flow 0.2 sccm). The GAS was ended with an orifice that connected the aggregation chamber with another vacuum chamber where the depositions were performed.

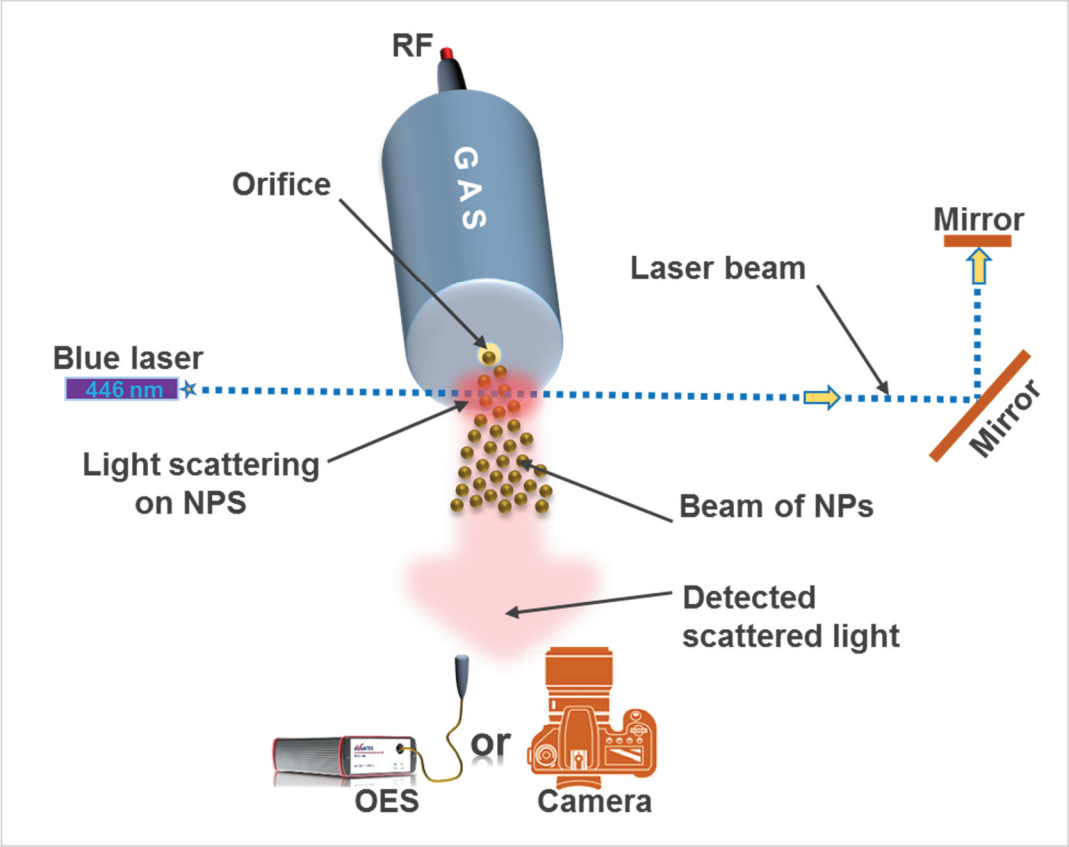

Figure 1 Graphical visualization of the experimental setup

A laser beam (446 nm, vertical polarization) was allowed to pass across the beam of the NPs behind the GAS at the distance of 2 cm from the orifice. The position of the laser beam was shifted at 5 mm below the axis of the orifice. The laser was powered by a DC power supply (U=5.4 V, I=780 mA). The scattered light was measured either by an optical emission spectrometer (AvaSpec 3648, Avantes) or by a CCD camera (Nikon D700). Both were situated 50 cm from the exit orifice so that the scattered light was acquired at an angle of 90 degrees from the direction of the laser beam. OES spectra were obtained through a quartz window in the range of 350 - 850 nm with a constant integration time of 2000 ms. All scans were saved automatically every 15 s. A Nikon D700 camera with a 12.1-megapixel FX-format (23.9 x 36mm) CMOS sensor and 14-bit color resolution was used as an imaging device. The camera body was equipped with a kit 24-120mm, f/3.5-5.6G ED IF VR Nikkor zoom lens to provide high-quality images of scattered laser light. Scanning electron microscopy (SEM, Tescan Mira 3) with a secondary electron detector and the acceleration voltage of 15kV was used to study the morphology of the NPs.

3. RESULTS AND DISCUSSION

The formation efficiency (number) and growth process (size) of ppHMDSO NPs were found to be highly dependent on the working conditions (pressure, flow, power etc.) in the aggregation chamber. In this study, we changed the discharge power from 20 to 80 W to obtain the NPs with various size and fluxes. The SEM images reveal that the mean size of the NPs decreases from 240±61 nm to 78±8 nm with the increasing power. It is interesting to note that the size distribution becomes more narrow as the power increases. At the same time, the number density of the NPs increases from 1 NPs $\mu m^{-2} min^{-1}$ to 27 NPs $\mu m^{-2} min^{-1}$ (**Figure 2**).

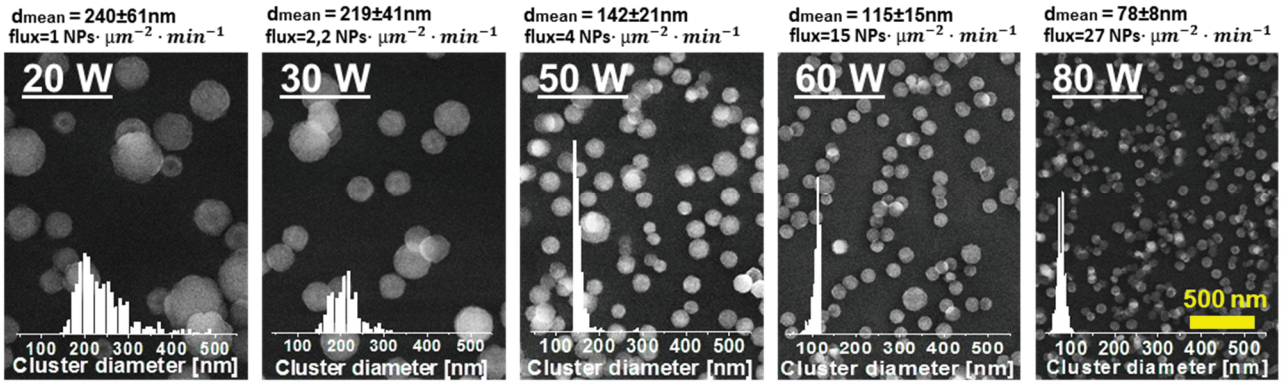

Figure 2 SEM images of ppHMDSO NPs prepared at different RF powers with corresponding histograms of their size distribution (insets)

It is known that Rayleigh-Mie scattering may occur when the laser beam passes through the beam of the NPs [9],[10]. In our experiments, the Nikon D700 camera detected the LLS as it is shown in **Figure 3** for the case of 40 W power. The inset figure shows the decomposition of the original image into three components: Red, Green, and Blue. The scattered light is present only in the blue channel that coincides with the laser light wavelength. The profile of the intensity distribution of scattered light for different powers shows that the intensity grows, reaches the maximal value for 40 W power and then decreases at higher power. The non-trivial dependence of the LLS intensity on power can be attributed to the competing effects of changing the NP size and their number in the beam.

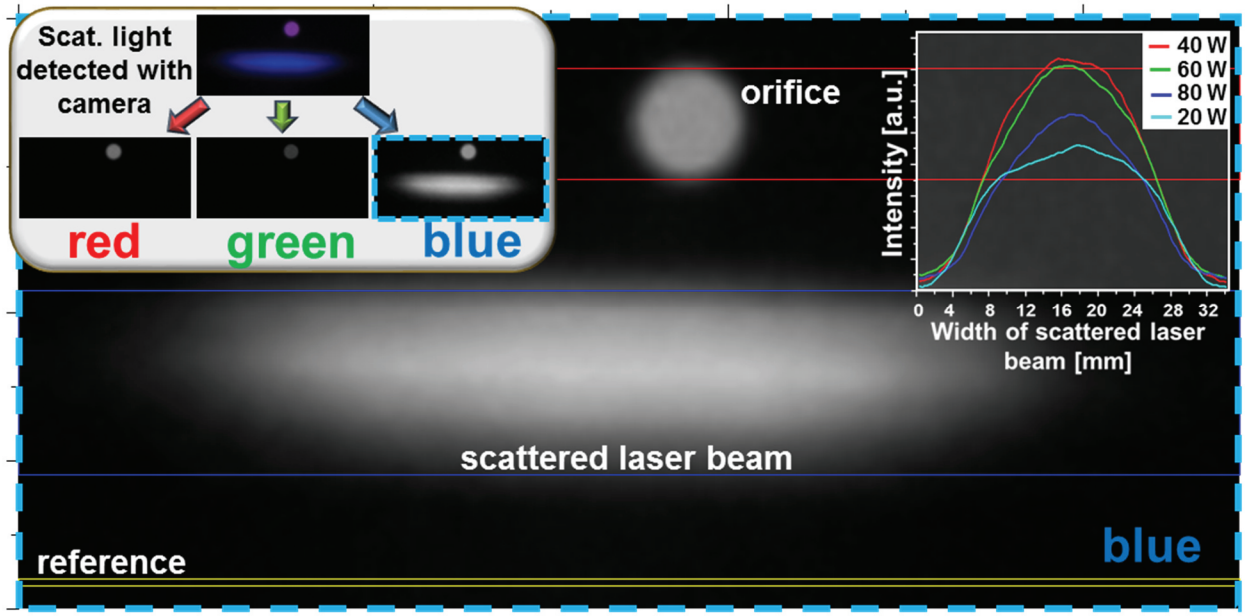

Figure 3 Image of the laser light scattering captured with the CCD camera. The left inset shows the decomposition of the original image into three RGB components. The right insert represents the intensity profile of LLS for different powers

In **Figure 4**, the time evolution of the intensity of the scattered light is represented for 20, 40, 60 and 80 W power as measured at λ = 446 nm by OES. In the case of 20 W power, almost constant intensity of the LLS was obtained. With the power increase, cycling instabilities become prominent while the amplitude and the period of such fluctuations increase. In the RF discharge, the NPs experience numerous forces. The balance

between the forces may change with the growing size and the amount of NPs present in the discharge [11],[12]. After reaching a certain critical size, the NPs may undergo expelling from the discharge and a NP-free region (void) can be formed. The process then follows the same stages of the NP nucleation, growth to the critical size and the void formation [13],[14]. Such cycling instabilities have been often observed in dusty plasmas. Apparently, similar phenomena occur in the gas aggregation source as well. Under the studied conditions, the ppHMDSO NPs are produced in a cycling regime. The difference is that, in the case of GAS, the neutral drag force is higher, i.e. the pressure difference between the GAS and the deposition chamber provides a continuous flow of the gas along the aggregation chamber. As a result, the NPs produced by the GAS are smaller than those prepared in common dusty plasma reactors.

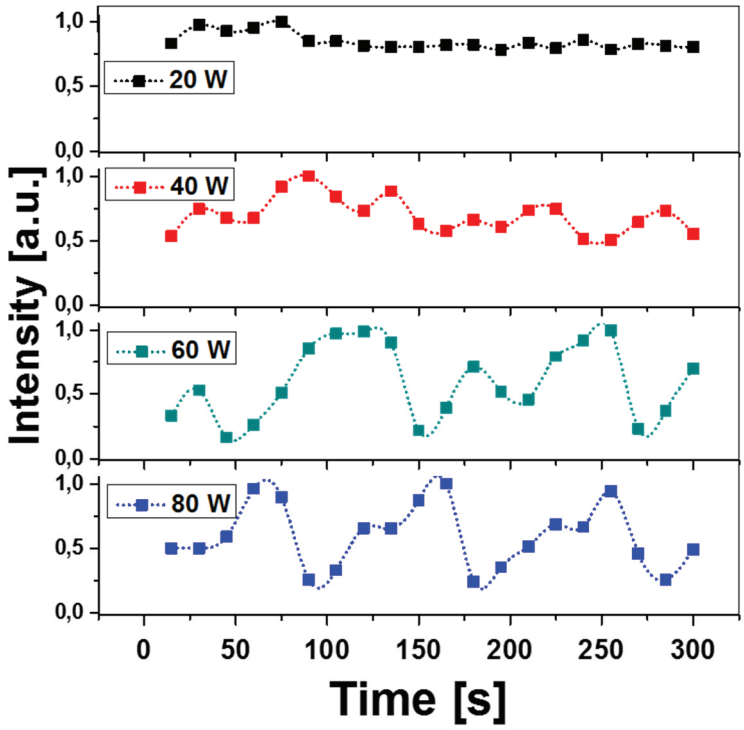

Figure 4 Time evolution of the maximum intensity of scattered light at λ = 446 nm as measured by OES

4. CONCLUSION

In this work, we applied a method of laser light scattering for in situ detection of the organosilicon NPs prepared by GAS. OES in combination with CCD camera was used as detector devices. The analysis of the acquired optical spectral lines revealed that this technique is suitable for in-flight detection of ppHMDSO NPs. It was found that under certain conditions the deposition process of NPs is not stable in time and can be characterized by periodic oscillations of the maximum intensity of the scattered light. Such a phenomenon is associated with a cycling formation and disappearance of the NPs.

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