TiO_2 Nanoparticles Detection by Means of Laser Beam Scattering in Hollow Cathode Plasma Jet

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Spatial distribution of TiO_2 nanoparticles that nucleate in plasma plume of hollow cathode plasma jet (HCPJ) was studied in this work. The method of investigation is based on laser beam scattering. Two lasers with wavelength 446 and 661 nm were used. The signal was detected by means photodiode, low resolution optical spectrometer and digital photo camera. Vertical and horizontal polarizations of lasers were used for determination of the scattering type. Maps of the scattering intensity based on photo camera pictures were measured under different discharge parameters. Dependencies of the signal intensity on the O_2 flow rate and wavelength are discussed. Nanoparticles were deposited on the silicon (111) substrate and studied by means of SEM. Aside from nanoparticles we detected TiO_2 columnar structures. Crystalline structure was investigated using XRD.

1. Introduction

In recent years a number of techniques for nanoparticle synthesis have been developed. The most wide-spread techniques of gas-phase nanoparticle synthesis using evaporation of solid material are: pulsed laser ablation, spark discharge generation, inert gas condensation and ion sputtering.

The key part of the HCPJ is the tubular electrode (inner diameter 6 mm, length 40 mm)— a nozzle that works as a hollow cathode — through which the working gas, typically argon flows, and which is attached to a power source. Oxygen is introduced through the separate inlet in a main chamber. Discharge parameters we used in these experiments are given in description of fig.4. The HCPJ utilizes the hollow cathode effects, namely pendulum electrons and the uv-radiation, to create a high density plasma discharge. The deposition of nanoparticles by means of HCPJ is investigated in [1] in details.

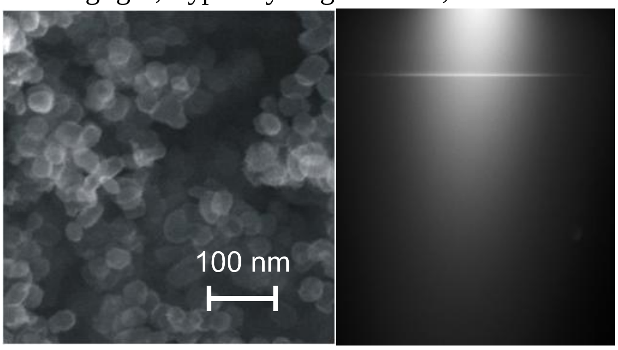

Fig. 1: Nanoparticles deposited on Si(111) substrate (left) and scattered laser beam (right).

The method of nanoparticle detection by means of laser beam scattering is well known and can be described by means of Mie or Rayleigh theory [2]. It is hard to evaluate nanoparticle size from the scattered intensity since such parameter as nanoparticle concentration is not known. Nevertheless, this method gives us instant information about presence of nanoparticles in plasma and makes us able to compare how different discharge parameters affect the scattered signal.

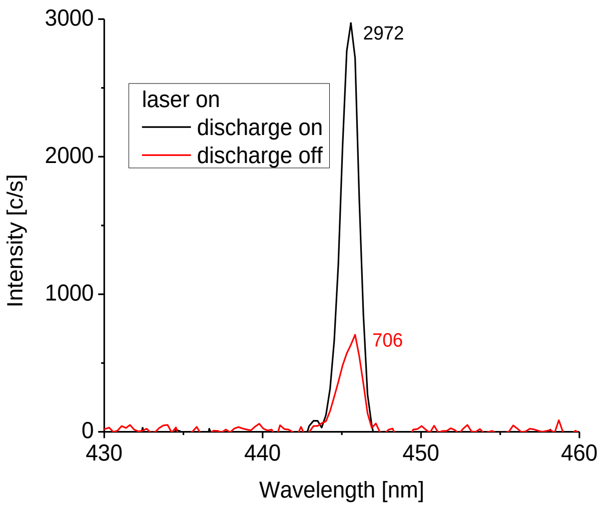

Fig. 1: Nanoparticles deposited on Si(111) substrate (left) and scattered laser beam (right).

2. Nanoparticle detection.

2.1 Detection of scattered laser beam by means of optical spectrometer

We used low resolution optical spectrometer HR4000 (Ocean Optics) as a detector in order to check if the scattered light signal wavelength corresponds to laser beam wavelength. Optical spectra with subtracted background of the scattered signal with and without discharge were compared. In a case when discharge was switched on we used discharge spectrum without laser beam as a background. Results have shown a significant difference of the signal detected at the wavelength 446 nm that corresponds to a blue laser we used. Nevertheless, reflections of the laser beam from the chamber windows and walls caused the presence of the comparably small signal even without discharge.

2.2 Scattering type determination by means of photodiode

Photodiode (Siemens BPW 34) performed several advantages as a detector in comparison with optical spectrometer. The most important are: shorter measurement time, higher sensitivity in red range of

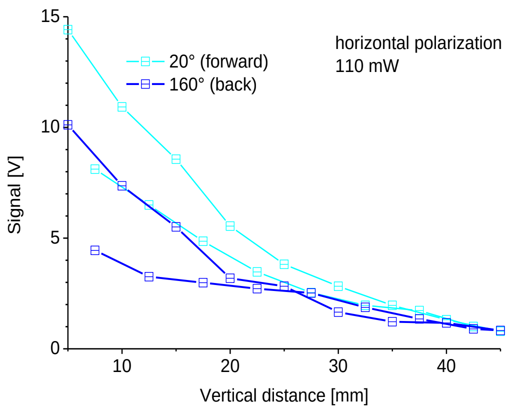

Fig. 3. Dependence of scattered signal (mV) on the vertical position of the laser beam (446 nm) in the discharge for 20º and 160º (horizontal polarization).

wavelengths and wide range of magnitude of detected signal. Laser was operated in pulsed regime (50% and 70% duty cycle, frequency 1 kHz) with the mean laser power of 110 mW. Detected signal was amplified by means of two narrow bandwidth amplifiers connected in series. The AC signal was measured by means of oscilloscope in mV (peak-to-peak). The main interest for us was the impact of different sputtering parameters on the scattered signal. We used red (661 nm) and blue (446nm) lasers to investigate the wavelength factor. It was not possible to measure the whole polar diagram of the scattered signal because of the construction of the vacuum chamber. We chose angles 20º and 160º for comparison of the forward and backward scattering. Laser polarization was horizontal. Scattering intensity at the angle of 90º was measured with both horizontal and vertical polarizations. These measurements give us information about scattering type and the range of nanoparticle sizes. Experiments were carried out under the same discharge conditions as we used for nanoparticle deposition.

2.3 Scattered signal profiles measured by means of photo camera

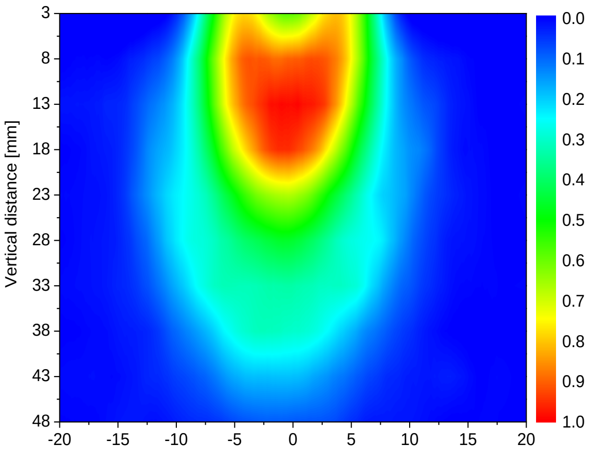

Fig. 4. Example of nanoparticle distribution map measured by means of photo camera. Discharge current 175 mA, argon flow 200 sccm, oxygen flow 3.5 sccm, pressure 60 Pa.

We used digital photo camera Nikon 5100 with KIT objective for the nanoparticle spatial distribution measurement. Narrow interference filter was attached to objective of photo camera in order to dump the discharge radiation. The discharge photos with laser beam on and off were subtracted, see Fig. 1 (right). The pixel line along the laser beam was extracted from the photo and combined with the similar lines from other photos with different laser beam vertical position. Nanoparticle distribution maps based on

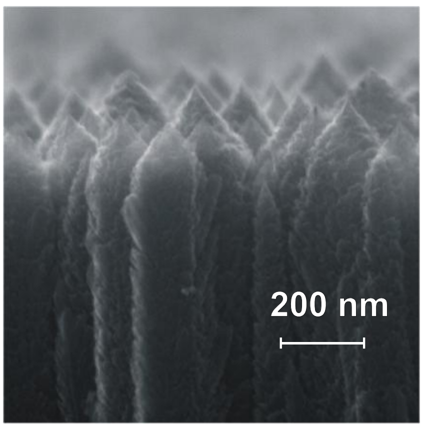

Fig. 5: TiO_2 columnar structures.

these data were plotted as it shown in fig. 4. We used different discharge parameters in order to know the complex information about nanoparticle distribution in plasma.

3. TiO_2 columnar structures

We deposited several samples under the conditions used in previous experiments in order to measure nanoparticle sizes directly on the substrate. Deposited thin films do not completely reflect the distribution of nanoparticles in plasma since they were affected by the supersonic or near-supersonic plasma flow that blows nanoparticles away from the centre of the sample to the periphery. Gas flow velocity was measured in [3] under similar conditions and experimental setup. In a centre of the sample we found TiO_2 columnar structures (fig.5) that show themselves in a case when the substrate was close to the nozzle. The crystalline structure of the films was studied by means of XRD.

References

[1] R. Perekrestov, P Kudrna and M Tichý: *Plasma Sources Sci. Technol*. (2015).

[2] MiePlot v. 4.5, http://www.philiplaven.com/mieplot.htm.

[3] L. Bárdoš and I. Štěpanek, *Neutral gas flow velocity profiles in jet plasma-chemical reactor*, Vacuum **40** (1990), 449.