SUMMARY OF THE PH.D. DISSERTATION

On the plasma and electrode erosion processes in spark discharge nanoparticle generators

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1. Introduction

Today nanotechnology is undoubtedly one of the most important fields of science and technology. Its significance is well reflected by the fact that it probably doesn't have to be introduced. Most people have heard about "nano" as one of those mysterious things that will save and destroy humanity at the same time. As usually, reality lies somewhere between these two extremes. The ability to manipulate materials on the nanometer scale surely gave us such tools in countless fields of life that were hardly imaginable a few decades ago. Although numerous achievements of nanotechnology and nanoscience have already reached the industrial level and hence became part of everyday life, many breakthrough applications still exist only within the walls of laboratories. Several criteria have to be met until a new technology can break out from the lab, including the supply of affordable base material. The basic building blocks of nanotechnology are the nanostructures, which can be either nanometer thick layers, nanorods or nanowires, or nanoparticles, which are usually referred to as 2D, 1D and 0D nanostructures, respectively. The mass-production of such nanostructures by environmentally friendly and cheap means is a crucial technological bottleneck if nanotechnology-based product development should continue to advance. In the present work I focus on some of the fundamental aspects of spark discharge nanoparticle generation, one of the most promising techniques which are capable of producing nanoparticles (NPs) with controlled properties even on the industrial level.

The spark discharge generator (SDG) has an appealingly simple layout that consists of a leak-tight chamber, housing two electrodes that are separated by a small gap. For creating a spark discharge in between the electrodes, a self-pulsed circuit is typically used, consisting of a capacitor fed by a high voltage DC power supply that is connected to the electrode gap. Each spark is initiated when the gaseous ambient in between the electrodes breaks down, i.e. via the formation of a conducting channel (spark channel) between the two electrodes. The spark plasma erodes the electrode material which results in the formation of an atomic vapor plume in the spark gap. Due to adiabatic expansion and mixing with the carrier gas the atoms cool down and eventually form nanoparticles after nucleation, condensation, coalescence and coagulation.

The potential of spark discharge for mass-production of NPs is only partly based on its relative simplicity. More importantly, the generation process could be easily and controllably scaled up by placing several electrode pairs in parallel at low cost and with minimal impact on the environment. In the BUONAPART-E project, 21 partners from both industry and academia worked on this upscaling approach including our research group at the Department of Optics and Quantum Electronics at the University of Szeged. During the four-year collaboration with researchers from all over Europe we have

investigated several fundamental aspects of spark-based nanoparticle generation and also solved numerous technical challenges along the way. Our team had the opportunity to study the fundamental processes taking place in an SDG, in particular those of which occur in the spark plasma and on the electrodes' surfaces.

Although the main principles of the SDG has been around us since the invention of the spark plug of a gasoline engine, the first use as an intentional NP generator dates to 1988, when Andreas Schmidt-Ott and his colleagues published their first results. Although the design of the SDG is now commercially available, and used by several groups, the very fundamentals of the processes leading to particle formation is not yet fully understood. One reason for this knowledge gap lies in the difficulty of investigating the stages of the inherently multi scale nanoparticle formation process, especially its initial, early phase. The structure of an SDG sets certain limits to the applicable experimental techniques. The common SDG design cannot be altered too much for the sake of experimenting on the plasma, because that would surely alter the NP formation process as well. This limits the potential measurement methods to those which are able to acquire relevant information on the processes taking place in the SDG with disturbing them the least. Keeping these constraints in mind, the core of the investigations presented in this thesis employ non-invasive, *in situ* methods, namely temporally and spatially resolved optical emission spectroscopy (OES) and imaging, complemented with the continuous measurement of the electrical signals (i.e. voltage and current) of the discharge for gaining information on the processes preceding particle formation in the spark without disturbing the examined processes by any means. These techniques allow for the *operando* investigation of the spark plasma with a temporal resolution on the nanosecond time-scale. Optical and electrical methods are complemented with the *in situ* and *ex situ* characterization of the generated particles, and the *ex situ* characterization of the morphology of electrode surfaces subjected to sparking. These experimental techniques allowed me to address the challenge of understanding the peculiarities of the spark based NP formation process from several different viewpoints. Each method was used for gaining insight into the characteristics of the spark plasma and its effect on the electrode material. More specifically, it was aimed to describe the spark plasma, i.e. the source of NP generation, in terms of its composition, concentration, temperature, emission and morphology as a function of time, space and key control parameters. I also aimed to complement these results with investigating the electrode erosion process, including the erosion mechanisms and the role of the electrical parameters of the discharge loop. The careful selection of the above toolbox and the information acquired with them led us to the better understanding of the processes taking place in the spark, and ultimately led to a more deliberate control over the nanoparticle generation in SDGs.

2. Experimental setup

Several SDG design exist which may differ in some technical details, but the working principle and the main building blocks are the same. Common parts of all SDGs are the spark chamber and the electrical circuit which feeds electric power into the spark gap. The spark chamber[1] is a stainless steel, leak-tight chamber equipped with several ports for electrical feedthroughs, gas inlet, aerosol outlet and usually have one or several windows to facilitate optical observation. The electrodes are either vertically or horizontally aligned and the gas flow which continuously flushes the inter-electrode gap can be either upward or downward directed, co-axial or crossed. The distance between the facing surfaces of the electrodes (i.e. the size of the electrode gap) can be controlled by one or more positioners. The flow rate of the carrier gas is usually set by a mass flow controller, and atmospheric pressure is kept inside the chamber.

In my experiments the gap size was adjusted by micrometer screws typically in the range from 0.5 to 4.0 mm. The flow rate of the carrier gas was kept in the range of 1-10 l/min. All of my experiments were carried out at atmospheric pressure which was maintained by a vacuum pump and a needle valve and monitored with a pressure gauge. Cylindrical electrodes of 6.35 mm or 3.00 mm diameter were used in two electrode geometries: flat-end and tipped-end (with a 30° apex angle). In the flat-end geometry, electrode erosion is distributed over a larger area (i.e. the entire front surface of the electrode rods), while on tipped-end electrodes erosion is concentrated around the electrode tips. Since high throughput generated NPs needs substantial electrode erosion the flat-end geometry is preferred in SDGs. However, with this electrode geometry, the wandering of consecutive sparks over the electrode surface poses challenges to optical measurements and even the electrical data are less stable due to the positional variation of the surface quality and the concomitant differences in the breakdown voltage. Hence results obtained with tipped-end electrodes provide more reliable information, and more fundamental insight, while observations obtained with flat-end electrodes have more direct relevance to NP production. Therefore, tipped-end electrodes were used in those measurements where high positional stability was required, and in experiments focusing on electrode erosion and NP generation flat-end electrodes were employed.

Energy is fed into the spark gap by a simple capacitor charging circuit. A monolithic capacitor or a capacitor bank (jointly referred to as capacitor) with a total capacitance in the nF range is charged by a high voltage capacitor-charging power supply to a maximum voltage of typically about 10 kV using a charging current of a few or a few tens of milliamperes. Since the capacitor and the electrode gap are connected in series, the

[1] The chamber geometry used in most of our experiments has been developed for the purposes of the BUONAPART-E project, supported by the 7th Framework Programme of the European Union, specifically optimized for NP production purposes, and was manufactured by Pfeiffer Vacuum GmbH.

discharge of the capacitor across the spark gap will commence when the voltage on the capacitor reaches the breakdown voltage of the spark gap. The resulting spark discharge is a bipolar, oscillatory discharge, the damping and the oscillation frequency of which is jointly set by the total capacitance, resistance and inductance of the discharge loop. The discharge of the capacitor via the spark gap is accompanied by the recharging of the capacitor by the charging power supply ("self-pulsed, free running mode"), but since the current in the charging loop is many orders of magnitude smaller than the current in the discharge loop (which is typically a few hundreds of amperes), the two processes can be considered to be practically independent. The repetition of sparking is described by the spark repetition rate, SRR that can be controlled by changing the charging current and the gap size (via the breakdown voltage), assuming that all other experimental conditions are kept constant.

The voltage and current waveforms were routinely measured in the SDG during the characterization of the spark plasma by means of a high-voltage (e.g. Agilent N2771B) and a current probe (Pearson 110). Besides their fundamental relevance, the electrical signals of the spark played an important role in the synchronization of additional instrumentation. Due to the unregulated and transient nature of the sparks, their experimental investigation requires precise synchronization, which was carried out by triggering from the sharp voltage drop or current peak, by using a signal generator (Stanford DG535).

The optical emission and morphology of the spark was investigated by an intensified CCD (ICCD) camera (Andor iStar 734-18F-03), with a temporal resolution in the range of 50-500 ns. In the plasma morphology studies, photographic lenses were used with the ICCD camera, while for measuring the spectrally resolved optical emission of the spark plasma the camera was complemented by an Andor Mechelle 5000 fiber coupled spectrograph. Spatially integrated measurements were carried out by collecting the light of the spark plasma by a lens, while spatial resolution have been achieved by imaging the spark and using an optical fiber for collecting light from distinct points of the plasma image. The spectrograph was wavelength-calibrated and allowed for spectral data collection in the 300-800 nm wavelength range with ~0.125 nm resolution (at 435 nm). The spatial resolution of emission spectroscopic measurements was about 50 μm. The spectral sensitivity of the optical system was corrected by using a NIST-traceable deuterium-halogen calibration lamp (Model DH-2000-CAL, Ocean Optics, Inc.). The correction was checked before each experimental run and repeated if necessary.

The nanoparticles produced in the SDG were sampled and deposited onto TEM grids for *ex situ* electron microscopic analysis by using a home-built low pressure impactor and an electrostatic precipitator. The size distribution of the generated nanoparticles

have also been characterized *in situ*, by using either a Grimm Aerosol Technik GmbH SMPS-C or a home-built scanning mobility particle sizer (SMPS) system.

For studying the effect of erosion on the surface morphology, electrodes were exposed to sparking in a well-controlled manner. For the initiation of a single or a few sparks in the SDG (which is primarily designed for continuous operation) custom circuitry was developed for the power supply, which allowed for either manual or electrical triggering of the spark. Polished electrodes were used to study the changes of surface morphology, which were characterized by optical microscopy (OM), confocal laser scanning microscopy (CLSM), and atomic-force microscopy (AFM) with the instruments Nikon Optiphot 100S, Keyence VK-X100K, and PSIA XE-100, respectively, before and after the initiation of a single spark or a controlled number of sparks. The electrode surface morphology was also characterized after prolonged sparking (hundreds of thousands of sparks) by using a CLSM (Keyence VK-X100K).

The processing and evaluation of the large amount of experimental data as well as the plasma diagnostic calculations were carried out by using Origin (Originlab Corporation) and by purpose-made scripts written in Python 3.5 programming language and MATLAB (MathWorks, Inc.).

3. Results

In the present work, experimental investigation of the spark discharge plasma and the electrode erosion processes was carried out under the conditions of nanoparticle generation, with concomitant characterization of the produced nanoparticles. *In situ*, non-invasive methods were developed and applied which do not disturb the particle formation process. The temporal and spatial evolution of the spark plasma was examined by means of fast imaging. Images taken with temporal resolution on the nanosecond timescale were used to follow the changes of the plasma morphology, commencing as a confined quasi cylindrical channel and proceeding towards a more diffuse, irregular shape. The variation of the width and the expansion speed of the plasma channel, as well as the spatially resolved and spatially integrated light emission of the spark were also determined. In order to gain information on the species present in the spark gap, optical emission spectroscopy was employed. The acquired emission spectra were used to determine the excitation temperature and the electron concentration of the spark plasma at different temporal and spatial domains. With the help of a semi-empirical plasma model developed, the concentration of the metal vapor in the spark gap was also estimated. The temporal evolution of the excitation temperature and the electron concentration was also elucidated via acquiring and processing temporally resolved atomic emission spectra. In parallel with the optical

investigations of the spark plasma, current and voltage waveforms were also continuously monitored, and via *in situ* aerosol based sizing the size distribution of the generated nanoparticles was also determined. Correlation was found between the electrical and optical signals and the particle properties. Last, but not least, the effect of sparking on the electrode surface, i.e. the role of the material erosion process was also investigated by characterizing the changes of electrode surface morphology as a result of either a single spark or prolonged sparking. On one hand, complex morphological changes were observed even on electrodes exposed to a single spark discharge, while on the other, the development and characteristics of self-ordered patterns were revealed after intense sparking.

The main scientific results of my work are the following:

Thesis I. I have employed fast *imaging* for investigating the temporal evolution of the morphology of a spark plasma produced between copper electrodes under nitrogen atmosphere in a spark discharge nanoparticle generator. I have shown that the spark channel retains its relatively confined, cylindrical shape throughout the duration of electrical current between the electrodes. The channel width expands in time at supersonic speeds, which scale quasi-linearly with the spark energy. I have found that the light emitted by the spark has an uneven spatial distribution, and identified the existence of an axial "hot spot", that is the position of highest emission intensity within the spark gap. I have proved that the position of this spot oscillates synchronously with the instantaneous current, and is always situated in the vicinity of the momentarily negative electrode **[T1]**.

Thesis II. I have applied temporally and spatially resolved *emission spectroscopy* in order to characterize the spark plasma produced in a spark discharge nanoparticle generator during the generation of copper nanoparticles under argon atmosphere without disturbing the operation of the generator. I have determined the temporal variation of the excitation temperature and electron concentration in the arc stage of the spark. Temperatures in the range of 16600-20000 K and electron concentrations of $\sim 2\times10^{17}$ to $\sim 7\times10^{17}$ cm^{-3} were found. For the characterization of the afterglow stage a semi-empirical equilibrium plasma model was developed. The model was used to derive the temperature and electron concentration and also to give an estimate on the number concentration of copper atoms and ions generated in the nanoparticle generator. Number concentration of copper atoms and ions was found to be in the order of 10^{14} cm^{-3} **[T2]**. I have derived the rate of change of the plasma temperature in the afterglow stage, i.e. the cooling rate of metal atoms from the emission spectra, which was found to be in the order of 10^{8} Ks^{-1} both in argon **[T2]** and nitrogen atmospheres **[T3]**.

Thesis III. I have investigated the *electrical properties* (i.e. voltage, current, total resistance, instantaneous dissipated power and energy) of a spark discharge generator. I proved that only a fraction of the electrical energy stored in the capacitor is dissipated in the gap. The ratio between the (dissipated) spark energy, calculated from the instantaneous current, and the stored energy was found to be about 80% in the particular generator studied **[T1]**. My results also prove that the mass loss of the electrodes correlates with the spark energy, calculated from the instantaneous current, and not the energy stored in the capacitor, as is generally assumed in the literature. The stored energy is only proportional to the spark energy calculated from the current, when the electrical parameters of the discharge loop (i.e. resistance, inductance, capacitance) are fixed. Therefore both quantities can be used to describe the erosion processes in a given spark discharge generator, but only the current-based quantity should be used for comparing different generators **[T4]**.

Thesis IV. I have investigated the changes of the *surface morphology* of metal electrodes (predominantly Ni and Cu), exposed to a controlled number of spark discharges, ranging from a single spark to several hundreds of thousands of sparks. I have proved that important information can be gained by the analysis of surface morphology of electrodes used in spark discharge generators. I have shown that even a single oscillatory discharge event (a so called single spark) creates complex surface morphology dominated by hundreds of craters and also featuring undulated areas and dendritic structures. I have also shown that the number and size of craters depend on the electrical current measured in the spark gap **[T5]**. By increasing the number of sparks delivered to the electrodes, the formation of closely packed, self-ordered patterns were found on nickel, gold and silver electrode materials **[T6]**. My results indicate that the spark energy, i.e. electric energy pumped into the electrode gap, is mostly used for melting and redistributing the electrode material over the electrode surface and only a small fraction of it is utilized for material release, and hence nanoparticle generation **[T5].**

Thesis V. I have investigated the effect of two of the main control parameters of a spark discharge generator, namely the gap size and the charging current on the size distribution of copper and gold *nanoparticles* generated in nitrogen atmosphere. I have found that by increasing the electrode gap and hence the spark energy the size of the generated nanoparticles varies via a maximum. I have shown that this behavior correlates with the variation of the integrated emission of metal atoms acquired during the afterglow stage of the spark plasma. The observed tendencies indicate that the concentration of metal atoms generated by a single spark cannot be increased monotonously beyond a certain level by simply increasing the spark energy. I have

explained the results by the competing processes of spark channel expansion and electrode material erosion and their dependence on spark energy **[T3]**.

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