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Plasmoids for etching and deposition

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Abstract
In this manuscript we show fascinating properties of plasmoids, which are known to be self-sustained plasma entities, and can exist without being in contact with any power supply. Plasmoids are produced in a filamentary discharge in a Ar/CH_4 mixture with a high production rate of about $10^5\,s^{-1}$. It is observed that plasmoids etch the solid amorphous hydrocarbon film with high efficiency. Energy density of the plasmoid, which is estimated on the basis of glowing area of plasmoids in the photographic image and sublimation enthalpy of the etched hydrocarbon film, amounts to about $90\,J\,m^{-3}$. This value is much lower than the energy density of observed ball lightning (natural plasmoid). A very surprising property is an attraction between plasmoids, and the formation of plasmoid-groups. Because of this attractive force, carbon material, which is collected in plasmoids by etching of the hydrocarbon film or by propagation through a methane/argon gas mixture, is compressed into crystals.

Keywords: plasmoids, micro-crystal, etching, plasmoids attraction, plasmoids group, cylindrical plasmoid, torus plasmoid

(Some figures may appear in colour only in the online journal)

1. Introduction

The word 'plasmoid' was proposed by W H Bostick to term a plasma-magnetic entity that can exist without being in contact with any power supply [1]. This concept was used to explain the formation of ball lightning [2–4] and to explain some astrophysical effects [5]. Plasmoids were produced in laboratories in dusty plasmas with dense plasma focus systems [6–8]. Until now, production of plasmoids in laboratories needed extreme experimental conditions (extremely high electric current, high density of high frequency power, etc). Production and properties of plasmoids were studied by applying photography, electro-magnetic probes and etched track detectors, as well as by analysing materials deposited by plasmoids. However, detailed structure and properties of plasmoids have not been clear until now.

In our previous study of filamentary pulsed atmospheric pressure discharge in an argon/methane mixture, a deposition of carbon-based micro-crystals on the inner surface of a closed cavity was observed [9]. It was established that carbon material is collected from an active plasma filament (plasma channel) located outside of the cavity and transported into the cavity through the entrance hole/slit (diameter, 1 mm/ width, 10 μm) of the cavity. The mechanism of this process was not clear. Using microphotography with a high temporal resolution, we establish in the present study that plasmoids are produced in our experimental setup at the end of the plasma channel inside of the quartz tube. These plasmoids touch the surface of substrate and also penetrate into the cavity. We use amorphous hydrocarbon films as etched track detectors to study footprints of these plasma entities. This experimental method provides an opportunity to look at previous experimental results from a different point of view and helps us to explain the deposition of carbon-based micro-balls and micro-crystals in our experimental setup.

2. Experiment

Details of our experimental setup were published in our previous paper [9], hence it is described here only briefly. In a microplasma jet used in this study, a cylindrical tungsten electrode is placed coaxially inside a quartz tube (inner diameter, 6 ± 0.2 mm; length, 20 cm; wall thickness 1 ± 0.1 mm) as shown in figure 1. One end of this electrode is sharpened and the other end is connected to a high voltage power supply (Redline Technologies Elektronik GmbH, Germany).

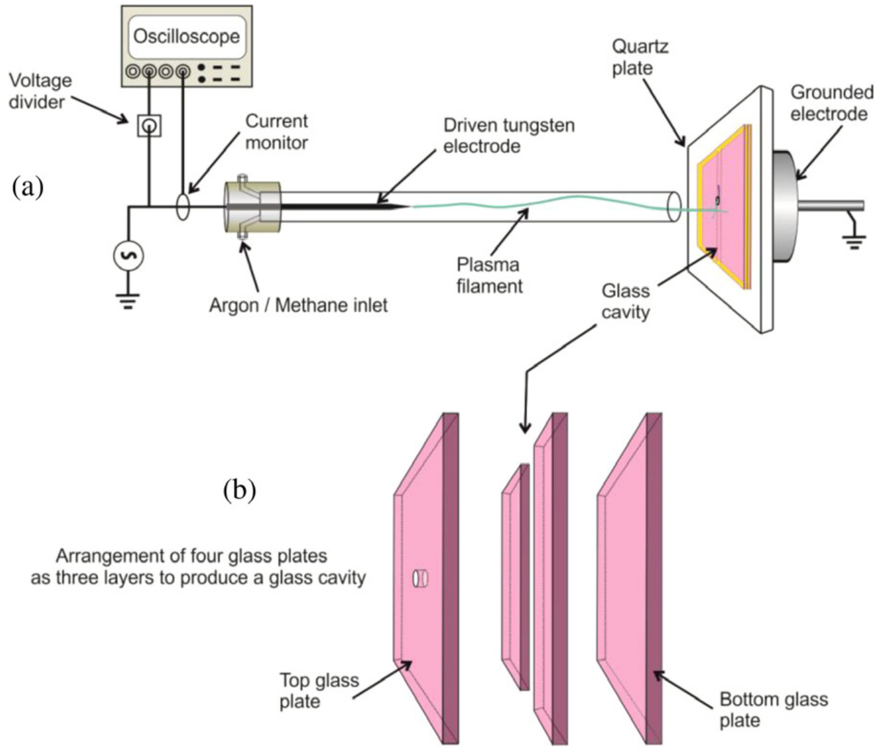

Figure 1. Schematic and rotated (to 90°) view of the microplasma jet used for micro-crystal deposition / a-C:H film etching inside of the cavity. *a*) Overview of the experimental setup. The entrance hole (diameter, 1 mm) of the glass cavity is placed on the axis of the tube. *b*) Exploded view of the arrangement of four glass plates as three layers for the production of the cavity. The cavity (dimension, 1 mm × 1 mm × 76 mm) is produced by keeping one glass plate at the top, one glass plate at the bottom and two glass plates between them. The top glass plate of the cavity is perforated, which acts as the entrance hole of the cavity.

The pulse frequency of the applied high voltage is fixed at 22 kHz (figure 2) for the experiments reported here. Under these conditions, each high voltage pulse exhibits a sequential profile with damped oscillations having a frequency of 200 kHz. An aluminium disc serves as the grounded electrode, which is placed perpendicular to the axis of the quartz tube. The inter-electrode distance is kept as 145 mm and 147 mm for film coating and etching/crystal-deposition studies, respectively. A cavity formed between four glass plates is used as a substrate (figure 1(*b*)), and is placed perpendicular to the tube axis. A gap between the gas exit point of the quartz tube and the substrate surface (top surface of the top glass plate in figure 1(*b*)) amounts to about 1 mm. A quartz plate, as a dielectric, is placed between the grounded electrode and the substrate. Its thickness is 4 mm.

The glass cavity is produced using four glass plates (Thermo Fisher Scientific Menzel-Gläser), as shown in figure 1(*b*). The dimension of the top and bottom glass plates is 26 mm × 76 mm × 1 mm. The middle glass plate's dimension is 12.5 mm × 76 mm × 1 mm. As a result of these values, a gap between the middle glass plates in the cavity is 1 mm. Hence, the dimension of the rectangular cuboid cavity formed at the middle of these four glass plates is 1 mm × 76 mm × 1 mm. Output holes (side openings) of the cavity are closed to prevent any gas flow through the cavity. On the top glass plate, the entrance hole (diameter, 1 mm) for the cavity is perforated (figure 1(*b*)). This hole is aligned along the axis of the tube, and at the centre of the gap between the middle glass plates.

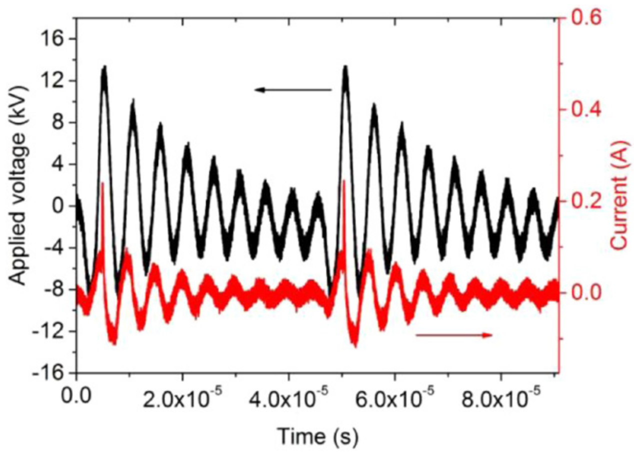

Figure 2. Two sequences of high voltage and current waveforms of the microplasma jet operated in a Ar/CH_4 mixture at atmospheric pressure.

In order to study etching of the amorphous film by plasmoids, a-C:H film is coated on a glass plate of dimension 26 mm × 76 mm × 1 mm. For this purpose, instead of the glass cavity, this single glass plate is used as a substrate in the microplasma jet. Instead of the disc grounded electrode, a ring grounded electrode (outer diameter, 30 mm; inner diameter, 15 mm) is used. Under this condition, mostly neutral species like carbon atoms and hydrocarbon radicals reach the substrate surface in the area covered by the quartz tube. The density of the

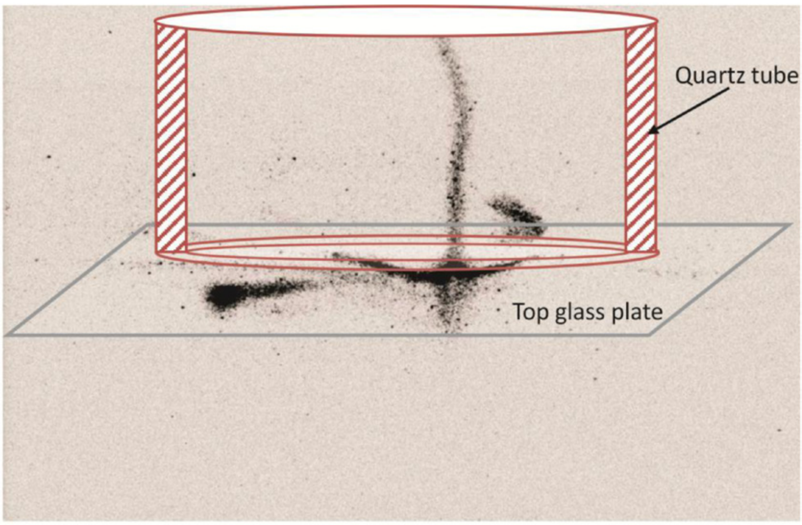

Figure 3. Negative of an image showing filamentary discharge in pure argon at the end of the quartz tube near the glass cavity (substrate). This image is obtained using a microphotographic ICCD camera with an exposure time of 30 ns. Schematics of the quartz tube and glass plate (not to scale) are superimposed on this image for the sake of clarity.

deposited micro-balls is reduced and a relatively smooth amorphous hydrocarbon (a-C:H) film disc is deposited [9]. Outside this circular a-C:H film disc the film thickness is much less.

A Pearson current monitor (model, 6585; output, 1 V = 1 A) is used for plasma current measurement. A cable connecting the transformer and the tungsten electrode is passed through this current monitor. The output of the current monitor is connected to an oscilloscope (LeCroy *Wave Runner* 204MXi-A). The actual voltage applied for the plasma generation is measured by connecting the output of the transformer to the oscilloscope through a capacitive voltage divider with a dividing factor of 2000 (PULS-PLASMATECHNIK-GMBH). The hydrocarbon films and the micro-crystals deposited on the substrates are characterized using a scanning electron microscope (SEM) (JEOL, model: JSM6510). Using SEM images, we determine dimensions of micro-crystals and plasmoids-etched hollows. From the cross-sectional SEM images, the thickness of the deposited a-C:H film is determined. A few atomic layers of gold film are coated (using JEOL JFC-1200 FINE COATER) onto the samples used for SEM measurements to provide electrical conductivity. Microphotography using an intensified charge-coupled device (ICCD) camera (PCO dicam PRO) allows for studying the spatial and temporal behaviours of the plasma filament and plasmoids. Exposure time can be varied from 3 ns to 1 s. For producing the image of the plasmoids shown in figure 3, a 30 ns exposure time is used. The camera is synchronized with the highest voltage peak of the pulse sequence, and image recording is carried out for each half period of the oscillating voltage for a complete voltage sequence by appropriately adjusting the delay time of the recording with respect to the highest voltage peak in the voltage pulse sequence.

3. Results and discussion

A filamentary discharge is ignited on the sharp point of the driven tungsten electrode while argon (2400 sccm) or argon/methane (2400 sccm /2 sccm) gas flows through the quartz tube. Chemically active neutral hydrocarbon radicals are produced in the plasma filament ignited in the Ar/CH_4 mixture. These radicals flow together with the working gas and reach the outer surface of the top glass plate [9]. As a result of the flux of neutral hydrocarbon radicals, a homogenous hydrocarbon film is deposited in the region covered by the quartz tube end. Radicals can also reach inside of the cavity by penetration through the entrance hole. But the gas flow through the closed cavity is prevented, and diffusion under atmospheric pressure conditions is slow. Therefore a very thin film is deposited inside of the cavity near the entrance hole.

Based on space- and time-resolved microphotographic analysis, we conclude that the plasma filament is a long, narrow, spatially- and temporally- (about 100 ms) stable plasma channel located inside the quartz tube between the driven electrode and the quartz tube end (figure 1). Its diameter is about a few hundreds of micrometers. Microphotographic images recorded for each half period of oscillating high voltage for the complete voltage-pulse sequence reveal that one ionization wave is propagated in this plasma channel for each half period of applied voltage [10]. Therefore more than 10^4 ionization waves are propagated through the same plasma channel, since the voltage oscillation frequency is about 200 kHz (figure 2). Based on microphotography with a high temporal resolution (Δt = 30 ns), we find that each ionization wave is transformed into several (3–5) self-sustained micro-plasma entities, namely plasmoids, near the tube end.

In figure 3, it is clear that glowing plasma entities (moving parallel to the glass plate) near the end of the plasma filament are not in any visible contact with the latter, and therefore they are not in contact with the driven electrode through any self-sustained plasma region. These plasma entities are plasmoids, as defined by W H Bostick [1]. On this basis and other photographic images, we conclude that plasmoids are produced at the end of the plasma filament. Possibly, these plasmoids are slightly charged, because they follow the electric field.

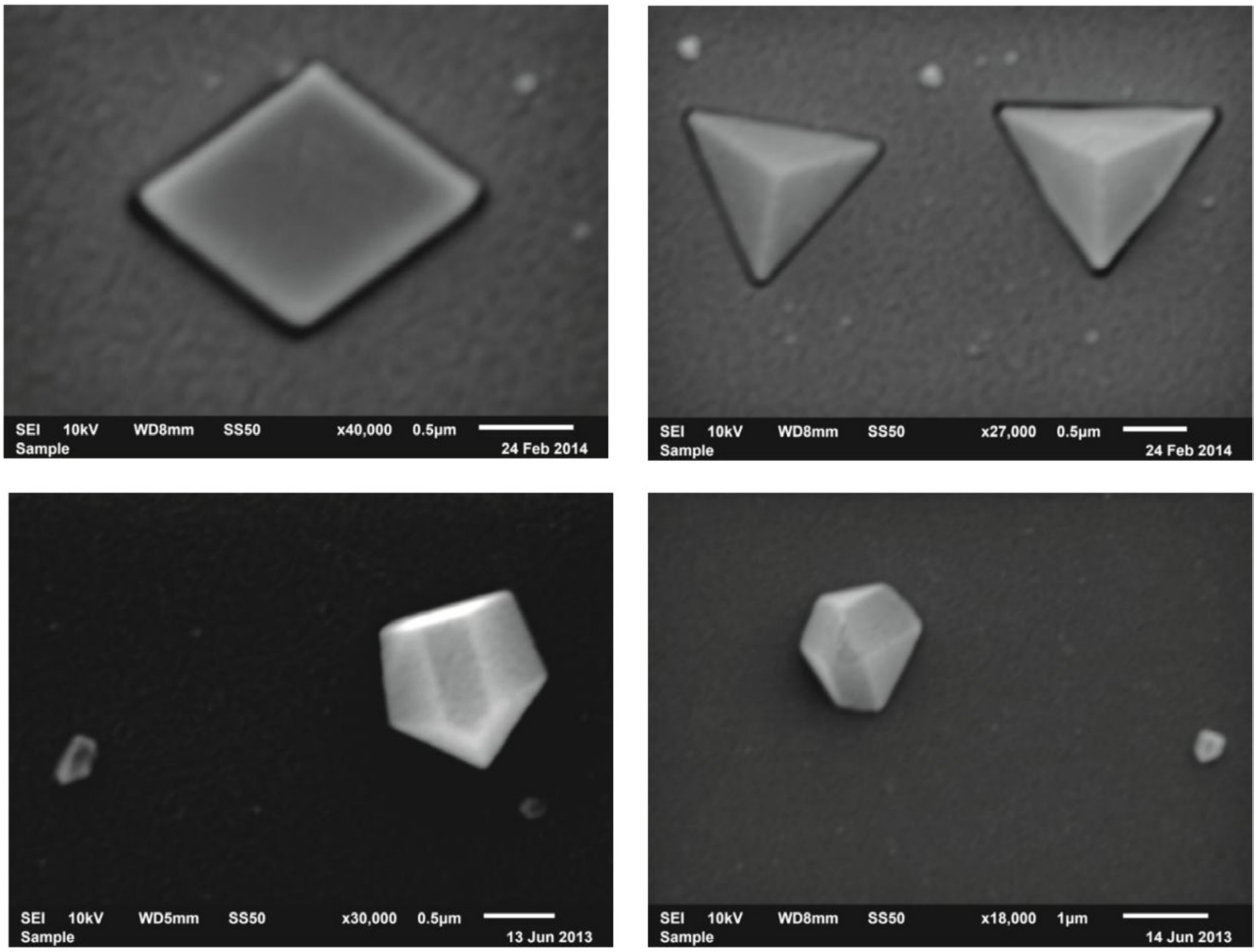

Figure 4. SEM images illustrating different geometric forms of single microcrystals deposited inside of the closed cavity by plasmoids produced in the microplasma jet operated in the Ar/CH_4 mixture under atmospheric pressure.

Therefore they propagate into the cavity or end on the outer surface of the top glass plate of the glass cavity (figure 3). Even by applying a high temporal resolution of 30 ns, images of plasmoids consist only of the head and tail. For this reason, in a previous study [9] with a low time-resolved analysis (Δt = 500 ns), we interpreted the traces of the plasmoids as thin filaments. Details about the dimensions of the plasmoids are discussed below.

As was partly shown in [9], if touch points of plasmoids (produced in Ar/CH_4 mixture) are protected from ambient air by argon flow, for instance in the area of the substrate surface covered by the quartz tube end, micro-balls are produced. Micro-crystals are deposited at touch points of plasmoids inside of the closed cavity, where the air admixture is high. In the latter case, plasmoids collect carbon material from the plasma filament, transport them through the entrance hole of the cavity, and deposit them as micro-crystals on the walls of the cavity. Different geometric forms of crystals are deposited inside the cavity (figure 4) in the argon/methane discharge. Near the entrance hole inside of the cavity (within a distance of several mm), an amorphous film and flake like carbon based material are deposited [9]. Except for this region, the number density of crystals deposited in the cavity is approximately constant in all the areas covered by the grounded electrode (diameter of 30 mm), and decreases rapidly outside of this area. Total deposition rate in our experiment is about 1500 crystals per second. In this estimation, only crystals with a dimension bigger than 0.5 μm are taken into account. No crystal or any other carbon-based material is deposited in the pure argon discharge.

Diamond microcrystals and a diamond-like carbon (DLC) film were also produced under atmospheric pressure thermal plasma conditions in various plasma torch experiments [11]. To form diamond crystals in a plasma torch, high densities of hydrogen and carbon atoms are needed. These conditions are sustained by a very high gas temperature (about 4000 K) in the effluent of the arc discharge that is blown out with the gas flow. Therefore the substrate, where diamond crystals or the DLC film are to be deposited, is placed in these experiments at some defined distance from the plasma jet nozzle. Energy density in the arc discharge is extremely high. Discharge conditions in our experiment are much milder, and the applied current only amounts to about 100 mA. In addition to these, the substrate in our experiment can even be placed at a distance longer than one meter from the driven electrode to receive similar experimental results as that of short distance. This is possible as plasmoids can propagate to a long distance in an inert gas atmosphere without visible losses. Certainly, in this case we

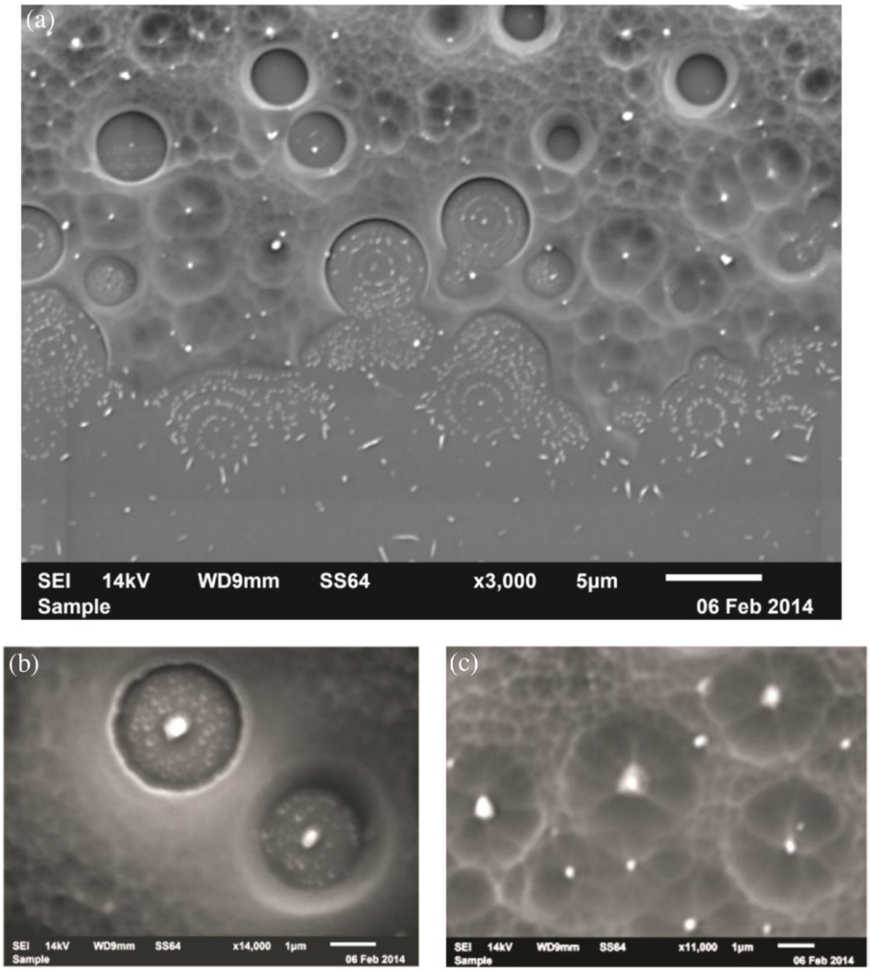

Figure 5. (*a*) An amorphous hydrocarbon (a-C:H) film is deposited at the bottom surface of the closed cavity, and then it is treated with the filamentary pure argon discharge. Plasmoids produced in the pure argon plasma etched or perforated the a-C:H film. (*b*) Hollows formed as a result of etching by cylindrical plasmoids. (*c*) Hollows formed as a result of etching by toroidal plasmoids. In the middle of the etched hollows, crystals are formed.

have to use a long tube (made of glass or plastic) between the driven electrode and the substrate to protect the working gas mixture from ambient air.

To investigate properties of plasmoids, which are formed in the plasma filament and moved into the cavity, we study traces of plasmoids on the wall of the cavity. For this purpose, we deposit the amorphous hydrocarbon film (a-C:H film) on a glass plate by using the flux of neutral radicals. This film serves as the etched track detector, since it is etched by the plasmoids. The thickness of this hydrocarbon film amounts to about 1 μm. We mount this film on the bottom surface of the closed cavity, and treat it with the discharge in pure argon. In this experiment, we observe numerous traces of plasmoids on the surface of the hydrocarbon film (figure 5(*a*)). The solid hydrocarbon film is etched (milled) very effectively. In some areas of the cavity, the film is etched completely during a 10 min treatment. Based on forms of perforations in the hydrocarbon film (figure 5(*a*)), we conclude that each perforation is milled-through during one contact with plasmoids. The diameter of milled holes in the hydrocarbon film amounts to 0.5–5 μm. This value is much lower than the diameter of glowing plasma entities (about 0.5 mm) presented in figure 3. Analogously with results presented in [10] we assume here that plasmoids have in reality a smaller diameter than can be estimated using microphotography, and the dimension of plasmoids corresponds to the etching pattern. At the same time it produces excited atoms and molecules in the surrounding area by emitting photons and electrons, and this area is detected with an ICCD camera. Other possible explanations for the difference in the dimension of plasmoids observed over the top surface of the substrate and milled traces of plasmoids inside of the cavity is the similarity of the structure of plasmoids in our experiment to the ball lightning (natural plasmoid). According to [12], a ball lightning consists of a large number of fractal nanoclusters, which can be disintegrated under certain conditions. Validation of these assumptions will be carried out in our forthcoming investigations.

The averaged etched volume in one perforation is equal to about $3 \times 10^{-18}\,m^3$ because the film with the thickness of 1 μm is milled through down to the glass surface. In assumptions that density and sublimation enthalpy of the deposited hydrocarbon film are similar to those of the acrylic polymer (PMMA), namely $1190\,kg\,m^{-3}$ and $1.62 \times 10^6\,J\,kg^{-1}$,

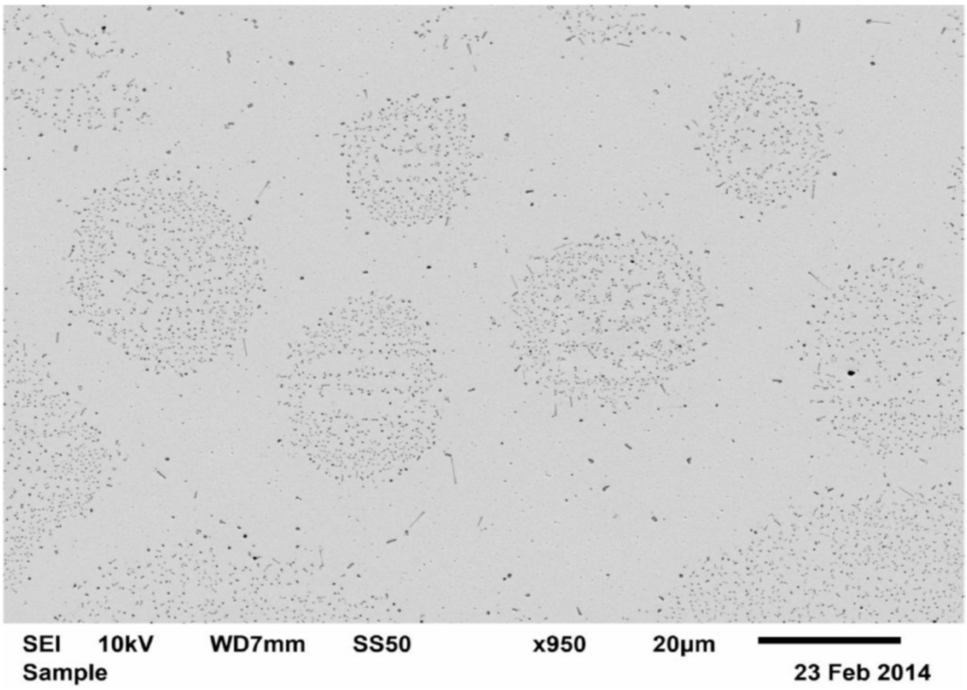

Figure 6. Negative of an SEM image showing groups of crystals deposited inside of the closed cavity that testifies the formation of groups of plasmoids. Plasmoids are produced in the filamentary discharge in the Ar/CH_4 mixture.

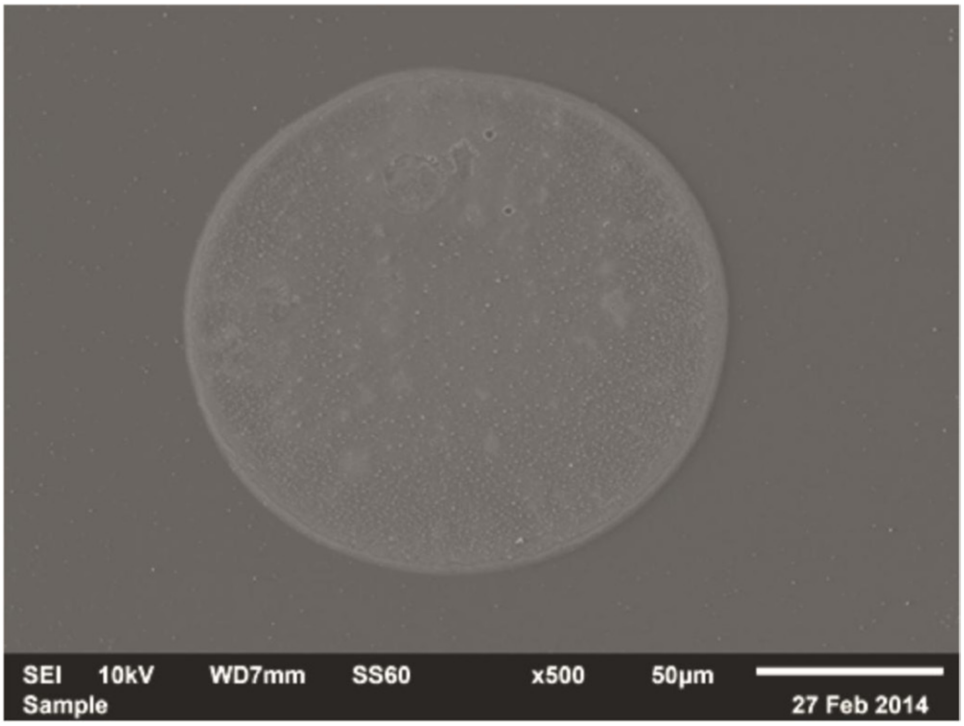

Figure 7. A carbon based solid entity deposited by a large plasmoid, possibly formed as a result of merging of a group of plasmoids, in the facial-gap between two glass plates. The diameter of this solid entity amounts to about 150 μm.

respectively [13], we estimate the energy necessary for etching of one perforation in the hydrocarbon film to 5.8×10^{-9} J. Under the assumption of a spherical form of plasmoids with an apparent diameter of 0.5 mm, the volume of plasmoids is 6.55×10^{-11} m^3, and the energy density amounts to about 90 J m^{-3}. This value is about two orders of magnitude lower than the expected energy density of ball lightning having a diameter of 0.5 mm [14, 15].

By analysing SEM images of plasmoids traces in figure 5, we establish two geometric forms of plasmoids, namely cylindrical and toroidal plasmoids. In the cylindrical plasmoids, the milled surface is parallel to the substrate surface and

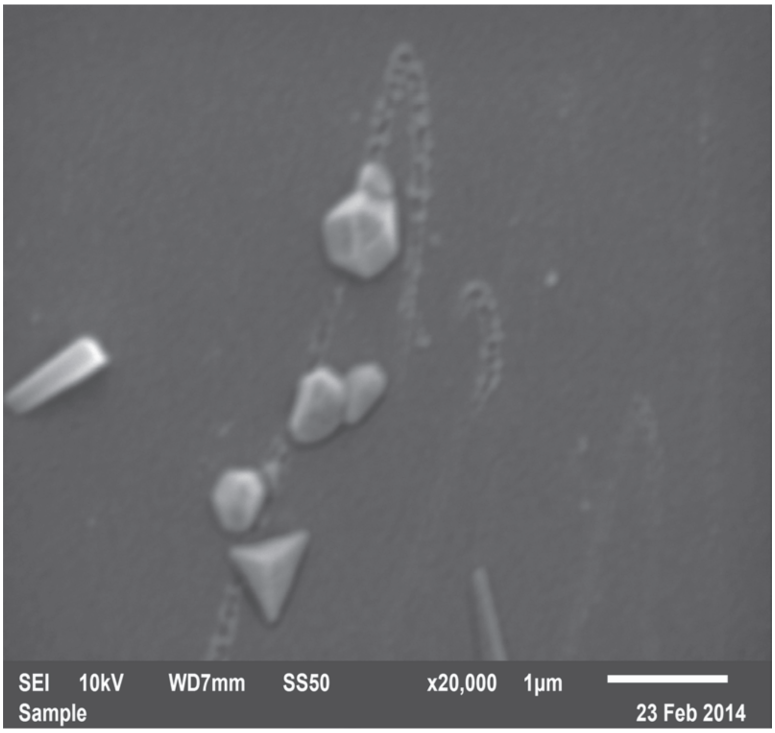

Figure 8. Traces of plasmoids observed inside of the closed cavity. Plasmoids are produced in the filamentary discharge in the Ar/CH_4 mixture outside of the cavity, and reach the inner volume through the entrance hole. Plasmoids deposit crystals on the inner-surface of the cavity, where a very thin a-C:H film was pre-deposited to act as the track detector.

perpendicular to the plasmoids axis; that is the 'milling tool' is perpendicular to the substrate surface (figure 5(*b*)). In the toroidal plasmoids, several 'milling tools', with rotational axes parallel to the substrate surface, are placed around the main axis (figure 5(*c*)). The etched material is collected inside of plasmoids. Pressure and temperature inside of the plasmoids are sufficient for the production of carbon based crystals from the collected material. In the middle of the etched hollows, we found crystals. Moreover small solid particles (with diameter of about $0.1\,\mu$m) are observed inside of the etched hollows of the cylindrical plasmoids (figure 5(*b*)). Until now, we could not report all geometric forms of these particles because the resolution of the microscope was limited. On the basis of better zoomed-in images, we conclude that at least some of these particles are of a crystal form. Based on these results of a group of voids as well as a group of crystals (figures 5 and 6), we suppose that despite the hypothesized Coulomb repulsion between charged plasmoids, they can form groups, attract each other, and possibly merge into the plasmoid with a larger dimension. Conditions inside of the merged plasmoid are sufficient for the formation of crystals from the collected carbon material. Interesting evidence for the presence of a large, possibly merged, plasmoid is presented in figure 7. The big solid entity is deposited by this plasmoid at the bottom glass plate in the region covered by the middle glass plate in the cavity. This large plasmoid penetrates a gap between two glass plates arranged one over the other (middle and bottom glass-plates in the cavity). The diameter of this entity amounts to about $150\,\mu$m. The gap distance between these glass plates amounts to about 10–20$\,\mu$m. The traces of similar large plasmoids are observed inside of the cavity region too. The formation of a group of plasmoids was also suggested in [12] to explain the production of ball lightning. For this reason, the electrostatic attraction between fractal cluster dipoles was assumed.

The results received by applying the etched track detector are very helpful for interpreting the deposition of crystals in the closed cavity in the argon/methane filamentary discharge [9]. Plasmoids are effectively produced in the plasma filament under our experimental conditions. When they are produced in argon with the methane admixture, plasmoids collect carbon material. Parts of the plasmoids go into the cavity through the entrance hole, and transport the carbon material to inside of the cavity. Carbon based micro-crystals are formed after compression of the material. A very thin amorphous hydrocarbon film pre-deposited on the walls of the cavity, as a track detector, help us to observe gliding of plasmoids on the substrate surface before depositing crystal (see figure 8). Here one can also observe that the diameter of plasmoids is much lower than the diameter of the glowing area of plasmoids observed in figure 3.

4. Conclusion

Plasmoids are produced at a high rate (about $10^5\,s^{-1}$) in the filamentary discharge of the argon and argon/methane mixture under our experimental conditions. By propagation through the Ar/CH_4 mixture as well as by etching of the hydrocarbon film, plasmoids collect carbon material. The energy density of the plasmoids is about two orders of magnitude lower than the energy density of ball lightning that has the same glowing volume. Conditions inside of the plasmoids are sufficient for the production of crystals from their collected material. Plasmoids can form groups and therefore the dimension of etched hollows and deposited crystals can be varied in a broad range (from 0.1 μm up to 5 μm under our experimental conditions).

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