Amorphous carbon film deposition on the inner surface of tubes using atmospheric pressure pulsed filamentary plasma source

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Abstract
Uniform amorphous carbon film is deposited on the inner surface of quartz tubes having an inner diameter of 6 mm and an outer diameter of 8 mm. A pulsed filamentary plasma source is used for the deposition. Long plasma filaments (∼140 mm) are generated inside the tube in argon with methane admixture. FTIR–ATR, XRD, scanning electron microscope, laser scanning microscope and XPS analyses give the conclusion that deposited film is amorphous composed of non-hydrogenated sp² carbon and hydrogenated sp³ carbon. Plasma is characterized using optical emission spectroscopy, voltage–current measurement, microphotography and numerical simulation. On the basis of observed plasma parameters, the kinetics of the film deposition process is discussed.

1. Introduction
Uniform thin film deposition on the inner surface of curved three-dimensional objects is one of the challenging processes in modern plasma technology. Several research groups have reported a systematic development of such film deposition processes as coating of inner surfaces of tubes and bottles [1–11]. Mostly microwave or RF driven ICP, CCP and jet based microplasma or magnetron plasma sources were used for their studies. Generally, in several methods used for coating films on the inner surface of tubes, precursors are decomposed in the confined electrode region where the plasma is active, chemically active species are transported inside a tube and film coating is carried out by gas flow. In this case, because of polymerization and recombination reactions during the transport process, the nature of chemically active species (constituent of polymer film) is different at different places along the axis of the tube. This phenomenon could reduce the film uniformity along the axis of the tube. In our method of film coating on the inner surface of tubes, a long filament of plasma is generated inside the tube in a gas containing a precursor as an admixture [12]. The plasma filament, which is thinner than the diameter of the tube to be coated, is active for long distance in the region of film coating. This plasma filament can ionize and/or dissociate precursor molecules. Using this method, chemically active species can be generated everywhere along the axis of the tube within close vicinity of the inner surface of the tube. In this way, the differences in the nature of depositing chemically active species at different places along the axis of the tube can be reduced and films with better uniformity can be deposited. In addition to this, film deposition is supported by ion fluxes, which results in the formation of high quality film.

In the previous publication [12], we have reported our plasma source characterization and the model used for plasma characterization. In this study, the plasma source has been modified in order to increase the distance between the electrodes as well as to reduce the region which is covered by the grounded electrode. Characterization of deposited film, determination of plasma parameters, and simulation of chemical kinetics are carried out for this modified plasma source. In this paper, we report the following: (1) configuration of our modified plasma source, (2) film deposition with two different positions of driven electrode, (3) characterization of the film deposited on the inner surface...
2. Experimental setup and simulations

2.1. Experimental setup

Experimental setup is similar to one reported previously [12], except for the dimension and the location of the grounded electrode (figure 1). A copper tube (length, 10 mm) is used as the grounded electrode. For all the experiments reported in this paper, the grounded electrode is fixed at 140 mm apart from the spike of the driven electrode. We performed two sets of experiments. The first set of experiments are carried out in argon and methane mixture (Ar, 2.4 ± 0.024 sccm; CH₄, 3 ± 0.03 sccm) to deposit carbon based film on the inner surface of a quartz tube. The discharge runs at low dynamic pressure, 1.8 Pa, because of low gas flow rate. It is carried out at two different positions of the driven electrode. Films deposited under this condition are characterized using various surface analysis techniques. A second set of experiments are carried out with argon, methane and nitrogen gas mixture (Ar, 2.4 ± 0.024 sccm; CH₄, 1.0 ± 0.01 sccm; N₂, 2.5 ± 0.025 sccm) for plasma characterization. Emissions of nitrogen molecules and nitrogen molecular ions are used for the determination of plasma parameters. Plasma parameters determined under this condition are considered to be the same as the plasma parameters during the film deposition process in the first set of experiments. The effect of the absence of nitrogen on plasma parameters is balanced by increasing the methane quantity. This fact (balancing of plasma parameters) is confirmed from the similar simulated electron velocity distribution functions (EVDFs) for both sets of experiments (with/without nitrogen).

It is also confirmed by measuring argon emission spectra at various places along the axis of the tube in both cases. Argon emission intensities are very close to each other in both cases and also have a similar trend along the axis of the tube. Analytical instruments used for the plasma characterization are the same as those used for previous characterization [12], except that the spatial resolution of the CCD camera is about 10 µm for an objective used for the plasma volume measurement in this study.

Since the film is coated on the inner surface of the tube, we do not have the possibility of recording FTIR–ATR, XPS and XRD spectra for this film. Hence, the film is coated also on quartz plates as follows. Quartz plates of dimensions 0.1–0.23 mm × 2–3 mm × 25 mm and/or 1 mm × 2–3 mm × 25 mm are placed inside the quartz tube at different places in the region between the powered and the grounded electrodes. Film deposition is carried out on these quartz plates. The film coated plates are used for FTIR–ATR, XRD and XPS spectral measurements. A FTIR spectrometer (BRUKER VECTOR 33) with a resolution of 0.3–1 cm⁻¹ is used. Colour 3D laser scanning microscope (LSM) (Keyence, pitch resolution, 100 nm; Z measurement distance, 13 µm; XY calibration, 46 µm/pixel; Z calibration, 1 nm/digit) is used for surface profile measurement. LSM and scanning electron microscope (SEM) (LEO Gemini SEM 1530 electron microscope) are used to obtain the cross-sectional images of film. Film thickness is determined from the cross-sectional image of the film in the tube [13]. These values obtained from the images of LSM and SEM are in accordance with each other. A few atomic layers of gold film are coated on the samples used for SEM measurements for the electrical conductivity. Information about amorphous nature of the film is obtained using x-ray diffraction analysis (Bruker D8 Advanced AXS diffractometer; Cu Kα radiation (1.5481 Å); position sensitive detector (PSD); films are analysed in the θ–2θ geometry and measured in Bragg–Brentano geometry at room temperature; constant divergence slit is 5 mm; Ni-filter is used; step 0.02°; 90 s per point).

Elements present in the film are determined using EDX spectra. EDX spectra are obtained from the spectrometer attached to the SEM instrument. Chemical nature of the elements is analysed using XPS spectra (Physical Electronics, PHI 5000 VersaProbe, Al Kα radiation). For a survey spectrum, it is scanned in the binding energy range −2 to 1198 eV with the pass energy, 187.85 eV; the energy step, 0.5 eV; number of cycles, 5. For the core level line measurement, the pass energy is kept as 23.5 eV with the energy step of 0.05 eV. Temperature of the tube is measured using digital thermometer attached with K type thermocouple (Greisinger electronic, model GTH 1150). For this purpose, plasma is ignited for 10 min, and then it is switched off. Immediately after switching off the plasma, temperature is measured by keeping the thermocouple in contact with the tube. The error in measurement due to the response time of thermocouple is corrected with the
temperature decay profile. Absorption spectra of deposited films are obtained using a deuterium lamp as a light source. Ocean optics emission spectrometer (QE-65000) is used for transmitted light measurements.

2.2. Determination of gas temperature, EVDF, excitation rate constants and electron density

Optical emission spectroscopy (OES), voltage–current measurement, microphotography and numerical simulations are used for the determination of gas temperature in the filament and the plasma parameters. The details of applied diagnostic methods and parameters used from the literature are described in our previous publication [12]. Therefore, it is described only briefly as follows. Gas temperature in active plasma volume is one of the most important parameters, because of its influence on gas density in plasma and on the rate constants of chemical reactions. It is determined from the rotational temperature of diatomic molecules, namely N2 and CN, from the emissions of N2(3–B, 0–0) and CN(B–X, 0–0).

The relative intensity of N2(3–B, 0–0) with respect to the intensity of N2(3–B, 0–0) is used for the determination of EVDF. For this purpose, the relative intensity of N2(3–B, 0–0) with respect to the intensity of N2(3–B, 0–0) is simulated for various reduced electric fields (E/N) and their corresponding EVDFs for our experimental conditions by numerical solution of the Boltzmann equation in local approximation and varied electric field applying the program code ‘EEDF’ developed by Napartovich and co-workers [14]. Finally, by comparing the experimentally determined relative intensities (I(N2;3–B)/I(N2;3–B)) with the simulated relative intensities (I(N2;3–B)/I(N2;3–B)) for various reduced electric fields and their corresponding EVDFs, the actual EVDF is determined.

Using the normalized EVDF and the known collisional cross-section σexc (m²) for electron impact excitation [15], we calculate the rate constants k (m³ s⁻¹) for electron impact excitation of N2, Ar and CH4 using the equation

\[ k = 4\pi \sqrt{\frac{2m_e}{m_e}} \int_0^\infty f_e(E) \cdot \sqrt{\frac{2e}{m_e}} \cdot E \cdot \sigma_{exc}(E) dE, \]  

where \( m_e \) and \( e \) are the mass and charge of electron, and \( E \) is the kinetic energy of electrons (eV). \( f_e(E) \) (in eV⁻³/²) is EVDF, and it is normalized to fulfill \( 4\pi \sqrt{\frac{2m_e}{m_e}} \int_0^\infty f_e(E) \cdot \sqrt{E} dE = 1 \).

The electron density \( n_e \) (m⁻³) is determined using equation (2) from the measured absolute intensity of N2(3–B, 0–0) emission \( I(N_2;3–B, 0–0) \) (phot m⁻³ s⁻¹), the nitrogen density \( [N_2] \) m⁻³, the electron impact excitation rate constant for N2(3–B, 0–0) emission \( k_{N_2}(3–B, 0–0) \), the contribution of excitation of N2(3–B) by collision with argon metastables \( K_{N_2}(3–B) \) [12], the contribution of the quenching of N2(3–B) by argon \( Q_{N_2}(3–B) \), the plasma volume \( V_p \) (m³), the value of fraction of time in which plasma is active \( (\tau) \), and the geometrical conditions during the measurement of emission spectrum \( (g_e) \):

\[ n_e = \frac{I(N_2;3–B)}{[N_2] \cdot (k_{N_2}(3–B) + K_{N_2}(3–B)) \cdot Q_{N_2}(3–B) \cdot V_p \cdot \tau \cdot g_e}. \]  

2.3. Temporal and spatial distribution of the gas temperature as well as fluxes of chemically active species

In order to determine the temporal and spatial distribution of gas temperature as well as fluxes of chemically active species from the plasma filament towards the surface of the tube, we numerically solve the equations for thermal conductivity (3) and diffusion (4) for a cylindrical symmetry [16, 17]:

\[ \frac{\partial T}{\partial t} = \nabla \cdot (\alpha(T) \nabla T) \]  

\[ \frac{\partial[M]}{\partial t} = \nabla \cdot (D(T) \nabla [M]) \]

where \( \alpha(T) = \lambda_{cond} \rho C_p\), \( \alpha(T) \) is the thermal diffusivity, \( \lambda_{cond} \) is the thermal conductivity, \( \rho \) is the density, \( C_p \) is the specific heat capacity and \( D \) is the diffusion coefficient.

3. Results and discussion

The pulsed filamentary discharge is ignited [12] in the mixture of argon and methane. This discharge is similar to a corona discharge in argon [18]. This long filament of plasma generated along the axis of the tube during this discharge has a diameter of about 200 μm. The duration of the discharge is around 160 ns. During plasma operation, the profile and the position of filaments in the tube change with the frequency of several Hz. Because of this fact (profile and position of filaments are stationary for about 100 ms) and the pulse frequency is 22 kHz, about 2000 filaments in series have the same profile and position. Films deposited under this condition are characterized using surface analysis techniques. For the films deposited under both experimental conditions (which differ in the position of driven electrode), nature of the elements, chemical composition and surface morphology are the same. However, variation of film thickness along the axis of the tube is different. The details of film analysis are discussed below.

3.1. Characterization of deposited film

LSM images of the surface of the films deposited on quartz plates show some roughness (Rz = 8 nm) (figure 2, right). Cross-sectional images of the film deposited on quartz tube are obtained using LSM and SEM (figure 2, left). From these images, film thickness is determined at 65 nm distance from the spike. By keeping this value as a reference, film thickness at various places along the axis of the tube is determined using optical density of the film on the basis of Beer–Lambert law. From the known values of film thickness and duration of film deposition, the film growth rate is determined. UV–vis absorption spectra (figure 3, left) of the films in the entire region between the electrodes show similar profiles of absorption with \( \lambda_{max} \) at around 220 nm indicating the uniform nature of the
deposited materials, composed of sp² carbon with a short range of conjugation [19].

For the determination of optical density with space resolution (∼1 mm), wavelength 350 nm is chosen in order to have both absorbance as well as transmittance for the films in all range of thicknesses. The above figure (figure 3, right) shows the optical density as well as growth rate of the films deposited under two different experimental conditions. Under the first experimental condition, the driven electrode is placed on the axis of the tube at the radial centre. In this case, the filaments ignited from the spike of driven electrode are stochastically distributed in the tube cross-section and touch the tube surface only within the grounded electrode region. This results in maximum film growth rate at the middle region in between the electrodes (figure 3, right, -○-). Under the second experimental condition, the driven electrode with spike is shifted 0.3 mm from the radial centre of the tube towards the surface of the tube. In this case, all filaments approach the tube surface at the same point (at about 20 mm from the spike) and pass on tube surface for a distance of about 20 mm. From this point till the grounded region, the filaments are stochastically distributed around the axis of the tube. This causes an increase in the deposition rate by a factor of about three in the region where the filament touches the surface of the tube (figure 3, right, -■-). Film thickness is almost constant from about 40 to 120 mm from the spike. Under both experimental conditions, the deposition rate is very low shortly before the grounded area. The deposition rate within the grounded electrode region is almost two orders of magnitude higher than the average deposition rate in the area in between the electrodes. The increase in film growth rate near the spike, caused by the contact of plasma filament on the surface of tube, is important for the deposition of film on the inner surface of the tubes of different radii, and will be investigated in future. Also, the position of the filaments in the tube, and therefore deposition rate, can be controlled by placing a grounded conductor (e.g. wire) on or near the outer surface of the tube.

FTIR spectra are measured in the ATR mode with a diamond crystal for the films deposited on quartz plates. Before measurement of the sample, background measurement in atmospheric air is carried out in the ATR mode. After this background measurement, FTIR spectra in the ATR mode are measured for the film coated quartz plates. Background corrected spectrum of the film coated quartz plate is considered as a spectrum of the coated film [20, 21]. FTIR–ATR spectrum of the film on a quartz plate is shown in figure 4. There is a pseudo-high transmittance peak in the background corrected FTIR–ATR spectrum of the film because of the presence of CO₂ in the background air and its absence in the film. Hence, the peak at 2350 cm⁻¹ is not shown in figure 4 for clarity. Analysis of FTIR–ATR spectra of the deposited films indicates the presence of aliphatic C–H groups in the film through their characteristic absorption. All the spectra have peaks at 2954 cm⁻¹, 2926 cm⁻¹ and 2870 cm⁻¹ corresponding to CH₃ asymmetric stretch, CH₂ asymmetric stretch and CH₂ symmetric stretch, respectively [22–25], indicating the presence of hydrogenated sp³ carbon in the film (figure 4). The presence of a strong peak at around 1650 cm⁻¹ shows the presence of double bonded sp² carbon on the surface.
of CO2 in air during the background measurement, is removed for pseudo-high transmittance at around 2350 cm\(^{-1}\) because of strong overlapping of absorption of quartz plate. The region below 1300 cm\(^{-1}\) is not shown because of strong overlapping of absorption of quartz plate. Pseudo-high transmittance at around 2350 cm\(^{-1}\), due to the presence of CO\(_2\) in air during the background measurement, is removed for clarity.

Figure 4. FTIR–ATR spectrum of the film deposited on the quartz plate placed in the middle region in between the electrodes during the pulsed filamentary discharge (Ar, 99.87%; CH\(_4\), 0.13%; total gas flow rate, 2.4 slm). The region below 1300 cm\(^{-1}\) is not shown because of strong overlapping of absorption of quartz plate.

Figure 5. XRD of deposited amorphous carbon film on quartz plate.

of the film [26, 27]. The absence of peak for stretching of (sp\(^2\))\(C–H\) above 3000 cm\(^{-1}\) indicates that sp\(^2\) carbons are not hydrogenated. Hydrogen in the film is mainly attached to the sp\(^3\) hybridized carbon. The relative intensity of ‘(sp\(^3\))\(C–H\)’ absorption with respect to the intensity of ‘(sp\(^2\))\(C=C(\text{or O, N})\)’ absorption varies slightly for the films on the quartz plates, which are placed at different places inside the tube between the electrodes during the film deposition process. Sharp peaks at 1455 cm\(^{-1}\) and 1375 cm\(^{-1}\) are due to the bending vibrations of CH\(_2\) and CH\(_3\) groups, respectively.

X-ray diffraction analysis is carried out in order to find out the crystallinity of the film. It does not show any characteristic diffraction for the graphene or diamond form of carbon. It only shows diffraction pattern characteristics for quartz substrate as shown in figure 5. It clearly indicates that the film is highly amorphous [28].

The nature of the elements present in the film at various places along the axis of the tube is determined using EDX measurement. It shows that the film is mostly composed of carbon with traces of O and N elements (also contains hydrogen, on the basis of FTIR–ATR spectra). Oxygen, water and nitrogen molecules are the impurities in the supplied gas mixture, Ar/CH\(_4\). The presence of trace of W element in addition to the traces of O and N elements has been observed for the film deposited near the spike. In order to investigate the chemical nature of these elements and their composition, XPS measurements are carried out. It also indicates that the film is mostly composed of carbon with traces of O and N. Chemical nature of the carbon is analysed using curve fitting procedure (figure 6, left). It shows that the film is mostly composed of sp\(^2\) carbon bonded to other sp\(^2\) carbon with less quantity of sp\(^3\) carbon bonded to other sp\(^3\) carbon [29]. It also shows that some quantity of carbon is attached to O as well as to N. This fact is also supported by the presence of characteristic peaks for O and N in the XPS spectrum.

The film has two phases as shown in figure 6, right. One phase in the film has large area with smooth surface, as also shown in figure 2, right. The secondary phase in the film has hemispherical top faces, which are occupied in a small area of total film surface. Preliminary chemical inertness test shows that the deposited film is stable against brushing with water, iso-propanal and soap solution.

3.2. Characterization of plasma conditions

To study the mechanism of film deposition, we characterize plasma conditions (gas temperature in plasma, electron density, EVDF, etc), calculate production rates of atoms and excited molecules, simulate fluxes of excited chemical species to the inner surface of the tube, and simulate the chemical kinetics. OES, microphotography and current–voltage measurements are used for the characterization of plasma conditions. In the following section, gas temperature, reduced electric field and electron density in the plasma are discussed. Because of the high neutral gas temperature in pulsed plasma filament, the tube is also heated. Since the temperature of tube will influence the film growth process and film properties, tube temperature is also determined. It is discussed along with the gas temperature in plasma and its fluxes towards the surface of the tube.

The gas temperature in the plasma filament is about 1000 K. Although it is high (figure 7(a)), duration of the discharge pulses is short, of about 160 ns. Therefore, the actual (stationary) temperature of the tube will be much lower than the gas temperature in the plasma filament. The actual temperature of the tube during the discharge is measured using a thermocouple. It shows that tube temperature is less (about 330 K) close to the spike and it reaches about 400 K close to the grounded electrode (figure 7(b)). Gas flow could be one of the reasons for this trend in tube temperature, since the gas mixture at room temperature is entering the spike region and relatively hot (or warm) gas mixture is entering the region close to the grounded electrode. With these data, equation for thermal conductivity is numerically solved to simulate the gas temperature in afterglow phase with temporal and spatial resolution.

The results of this simulation presented in figure 8 show that the steady-state conditions in the tube will be reached after...
Figure 6. XPS of carbon (left) and SEM image (right) of the film at the middle region in between the electrodes.

Figure 7. Gas temperature in the plasma filament obtained using CN (B–X, 0–0) and N2(C–B, 0–0) emissions (a), and tube temperature (b) along the axis of the tube during the pulsed filamentary discharge (Ar, 99.85%; N2, 0.11%; CH4, 0.04%; total gas flow rate, 2.4 slm).

Figure 8. Spatial distribution (in the radial direction) of the gas temperature from the plasma filament towards the surface of the tube. The filament diameter, 200 µm, is used for the simulations on the basis of micro-photographic images of the filaments.

Figure 9. Variation of the reduced electric field along the axis of the tube during the pulsed filamentary discharge (Ar, 99.85%; N2, 0.11%; CH4, 0.04%; total gas flow rate, 2.4 slm). Standard deviation in the reduced electric field is estimated by considering the fluctuation in the intensity of emissions of N2(C–B, 0–0) and N2⁺ (B–X, 0–0).

The electron density is almost constant (1.7 × 10¹⁸ to 2.8 × 10¹⁸ m⁻³) in most of the region in between the electrodes (figure 10). The filament propagates far outside the grounded...
region during the discharge with much less intensity of emission compared with the region in between the electrodes. Investigation of this process is in progress.

3.3. Chemical kinetics

The rate constants for electron impact methane dissociation, argon ionization and argon metastables formation are determined (figure 11) using equation (1), from the known values of cross-section for the corresponding process [30–33] and the determined EVDFs.

Electron impact dissociation rate constant of methane molecules is higher than the electron impact ionization rate constant of argon atoms (figure 11). Despite this fact, because of the higher concentration of argon than methane in the supplied gas mixture, electron impact argon ionization rate is much higher than the electron impact methane dissociation rate. Since the charge exchange reactions of argon ions with hydrocarbon molecules (methane) have big cross-sections [34], mainly these reactions are involved in the ionization and dissociative ionization of hydrocarbon species. Hence, argon ion plays a dominant role in the methane ionization, dissociation and consequent film deposition processes. This is in contrast to the low pressure plasma chemical kinetics, where electron impact plays a dominant role in methane ionization, dissociation and consequent film deposition processes [35–37].

Since the exact density of various chemically active species and their diffusion coefficients are not known, methane diffusion in argon is simulated in order to have some hints about the diffusion of various chemically active species. Simulated results for methane diffusion in figure 12 show that it takes about 10 to 20 ms for a chemically active species generated in the filament, which is approximately placed at the middle of the tube, to reach the tube surface. During this transport process, it may undergo several chemical reactions. Gas velocity is 1.4 m s⁻¹ for the gas flow rate of 2.4 slm. Hence, in the duration of 10 to 20 ms, neutral radicals will be moved to a distance of 1.5 to 3 cm along the axis of the tube.

On the basis of densities of argon, methane and electron, as well as rate constants of various processes determined from the plasma parameters [38–44], most probable reactions among others are calculated using equation (5),

$$\tau = P^{-1} = [M] \cdot k$$

where $[M]$ is the density of argon or methane or electron (m⁻³), $P$ is the probability and $k$ is the rate constant (m³ s⁻¹). The possible important chemical reactions with the inverse of their probability ($\tau$, lifetime of active species concerning the corresponding reaction) are shown in the following scheme (figure 13). The high probable reactions among others are shown in thick arrows in the scheme. Because of high electric field in active plasma volume, argon ion formation is more probable than argon metastable formation. Under atmospheric pressure conditions, Ar⁺ ion produces molecular ion, Ar²⁺ through a three particles’ reaction. This is in contrast to the low pressure plasma, where the probability for three particles’ reactions is very low [35–37, 45–47]. Lifetime of this molecular ion in argon–methane mixture is very short because of effective charge transfer reaction with methane [37]. This reaction produces CH₂⁺ ion. This ion undergoes further reaction with CH₄ to produce CH³⁺ ion and CH₃ radical. These chemically active species on further reaction with electrons present in the afterglow phase leads to the formation of CH₃ radical. Although this methyl radical is mostly produced through the above stated mechanism, it is also produced by direct reaction of argon metastables with methane as well as...
Figure 13. Chemical reactions involved in the film growth process. Thick arrow indicates high probable reaction. Emissions of active species in thick frames are observed in the measured emission spectrum.

Figure 14. Emission spectrum measured at 70 mm from the spike using echelle spectrometer during the pulsed filamentary discharge ignited at total gas flow rate of 2.4 slm (Ar, 99.87%; CH4, 0.13%).

by electron impact dissociation of methane. Electron impact dissociation of methyl radical ultimately leads to the formation of carbon atom through CH2 and CH species. The presence of C and CH are confirmed through their characteristic emissions (figure 14) [48–50] measured using echelle spectrometer. In addition to the production of molecular argon ion (Ar+) through termolecular reaction,argon ion (Ar+) also produces CH+ ion through a high probable reaction with methane. The further reaction of CH+ ion with methane and electron leads to the formation of diatomic molecular carbon C2, which has been observed through emission spectrum. The C2 molecule on further reaction with electron leads to the formation of atomic carbon and its presence has also been observed through its emission. Since the electron density in the afterglow phase is not known, probability for the electron impact reactions in the afterglow phase could not be calculated.

To determine the lifetime of positive ions in the afterglow phase of the discharge, the measured current is compared with the displacement current ($I_{disp}$), which is calculated as $I_{disp} = dV/dt$ and normalized to the measured current immediately after the discharge.

Figure 15. Voltage and current profiles during the pulsed filamentary discharge (Ar, 99.87%; CH4, 0.13%; total gas flow rate, 2.4 slm). The pulse frequency is 22 kHz. The voltage frequency of each pulse sequence is around 200 kHz. Displacement current is calculated as $I_{disp} = dV/dt$ and normalized to the current measured immediately after the discharge.
3.4. Mechanism of film deposition

On the basis of (i) plasma parameters determined applying optical emission spectroscopy and simulation, (ii) rate constants calculated using plasma parameters, (iii) voltage–current measurements and (iv) characterization of the film deposited inside the tube between the spike and the grounded area, it is concluded that the hydrocarbon ions produced in the charge exchange reactions of argon ions with hydrocarbon molecules play a dominant role in the film deposition process. Under steady-state conditions, methane, which is a part of gas mixture flows through the tube, is fully ionized and dissociated in the tube at the distance of approximately 20 mm from the spike. However, the film deposition rate has sharp maxima under the grounded area, which is 140 mm away from the spike. The film deposited in the area between the spike and the grounded electrode has different thicknesses at different places, but with similar properties and components. This film is dense and amorphous; has a smooth surface and low content of hydrogen. We suppose that this film is deposited during ion fluxes [45] on the wall after ambipolar diffusion and drift. In the frame of this assumption, we can explain different observed facts such as (i) increase in deposition rate in the region where filament passes on or near the wall because of small distance to the wall, (ii) higher deposition rate in the region under grounded electrode because of higher drift velocity in comparison with the velocity of ambipolar diffusion, and (iii) low deposition rate near the grounded area because of the high axial component of electric field in this region. The hydrocarbon film deposited in the region beyond the grounded area differs strongly from the film deposited before and under the grounded area. This film is soft, rough and of low density. This film may be deposited by flux of neutral hydrocarbon species which are produced by collisions of hydrocarbon ions with the surface of the tube under the grounded area. The kinetic energy of these ions is high enough for their partial dissociation. The neutral hydrocarbon species formed in this process flow with gas along the tube and deposit on the wall after diffusion.

The mechanism of ions’ transport from the spike area to the grounded area is under investigation. The steady-state conditions of this filamentary discharge depend on the distance between the electrodes as well as the amplitude and the frequency of applied voltage. For longer distance between the electrodes, lower voltage frequency requires higher applied voltage for steady-state discharge. We suppose that the residual charged species produce the electric field near the propagated head of the filament, and stimulate the propagation to a long distance. As mentioned above, the lifetime of the ions in the tube is about 30 µs, which is comparable to the pulse duration (45 µs). During this period, the charged species diffuse from the plasma channel and also undergo electron–ion recombination reaction; hence density of these species is reduced. The average density of these charged species during the initiation of next discharge is about 10^{15} m^{-3} at the steady-state conditions. On the other hand, very high density of charged species also hampers the ignition of the filamentary discharge, as discussed in the previous publication [12].

The facts discussed above show that plasma conditions in our experiment are different along the plasma channel. To make plasma conditions more uniform along the axis of the tube, the applied voltage with frequency of several tens of kHz can be modulated with sufficiently low frequency (pulse package modulation frequency) for filling of all tubes with fresh gas mixture between the plasma treatment phases. These experimental conditions will be used and studied in our forthcoming investigations.

4. Summary

The pulsed filamentary plasma source has been constructed to produce a long filament of plasma inside a tube for film deposition on the inner surface of tubes. FTIR–ATR, XRD, SEM, LSM and XPS analyses give the conclusion that deposited film is amorphous, composed of non-hydrogenated sp\(^2\) carbon and hydrogenated sp\(^3\) carbon with traces of O and N. UV–vis absorption spectra of the film deposited on the inner surface of the tube also confirm the presence of doubly bonded sp\(^2\) carbon, which are shortly conjugated. Optical emission spectroscopy, voltage–current measurement, microphotography and numerical simulations are used for the determination of the plasma parameters and the gas temperature. With these data, the equation for thermal conductivity is numerically solved to simulate the gas temperature in the afterglow phase with temporal and spatial resolution. The rate constants for argon ionization and methane dissociation are almost constant in the entire region in between the electrodes although it is slightly higher close to the spike. Based on the analysis of kinetics of deposition processes, it is concluded that ions play an important role in the deposition of amorphous carbon film.

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