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Review Article

Atmospheric-pressure pulsed discharges and plasmas: mechanism, characteristics and applications

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Abstract: Pulsed discharge plasma and its application is one of the promising directions in civilian areas of pulsed power technology. In order to promote the research and development of the theory and application technology for pulsed discharge plasma, in this paper, recent progress on the mechanism of nanosecond-pulse gas discharge and the characteristics and applications of typical pulsed plasma at the Institute of Electrical Engineering, Chinese Academy of Sciences is reviewed. Firstly, progress on mechanism of nanosecond-pulse discharge based on runaway electrons and measurement technology of runaway electrons is introduced. Then, the characteristics of three typical discharges, including direct-driven pulsed discharge, pulsed dielectric barrier discharge and pulsed plasma jet, are reviewed. Furthermore, typical plasma applications of pulsed plasma on surface modification and methane conversion are presented.

1 Introduction

In recent years, atmospheric pressure non-thermal plasma has attracted intensive attentions due to its various applications, such as environmental protection, surface modification, medical application, flow control, ignition and combustion [1–3]. The plasma discharges can be characterised as arc discharge, corona discharge, gliding discharge, glow discharge and dielectric barrier discharge (DBD), and are usually driven by direct current (DC), alternating current (AC), radio frequency (RF) and microwave frequency power supplies [4]. The discharge characteristics of plasma are determined by driven power supplies, discharge modes and applied conditions. The traditional discharges such as DC, AC and shock pulse-driven plasma have been well studied. The reduced electric field intensity (E/N) and overvoltage of these discharges are low and their properties are quite different. Arc discharge is generated under a low E/N condition (1–2 Td). The energy deposition mostly goes into rotational excitation, so the rotational temperature is around 8000 K. The E/N value of microwave discharge is around 5 Td, which is composed with many filaments. The gliding discharge, with an E/N value of 10–1000 Td, is composed with glow discharge and arc discharge. The E/N value of DC glow discharge is close to breakdown threshold (∼100 Td in air). The gas excitation is based on electron rotation and transition. It is usually generated under low pressure and close to room temperature. The E/N for DBD is around hundreds Td. The applied voltage will directly act on gas current. Although these discharges are quite different, all of them can be well explained by traditional Townsend theory and streamer theory.

It is realised that the continuous wave operation we mentioned above (AC, DC, RF and microwave) often leads to problems such as overheating and low energy efficiency. Pulsed power excitation, as one of the alternatives, can provide extremely high instantaneous power density and reduced electric field to accelerate electrons, which enhance the power efficiency [5]. Furthermore, the generation and reaction of plasmas could be controlled. Fig. 1 shows the schematic of pulsed discharge plasma. It can be seen that when the voltage applied, pulsed plasmas are produced. Changing the pulse repetition rate leads to different time interval for plasma reactions. In general, the nanosecond-pulse discharge is produced by an overvoltage (ten times than the breakdown voltage) and develops in the form of a fast ionisation wave (FIW) [6]. In nanosecond-pulse discharge, the streamer development time is shorter than that for photo ionisation in streamer theory, so the discharge is more spatially uniform distributed. Compared to AC or DC discharge, the pulsed discharge is occupied with ‘unconventional’ phenomena, such as high breakdown voltage, high electron energy and multi-channel discharge. The classical Townsend and streamer theory cannot be applied to pulsed discharge. It is generally believed that the high-energy runaway electrons are responsible for the second electrons production and the streamer formation. However, up to now, the data on the investigations of the gas excitation have been solitary and incomplete. The aim of this work is to provide a quick understanding of the concept and progress on the pulsed discharge plasma. This paper is organised as follows:

(i) Describe the pulsed discharge mechanism: high-energy runaway electrons and X-ray.
(ii) Analyse the pulsed discharge characteristics in three types of discharges: diffuse discharge, DBD and plasma jet.
(iii) Summarise the typical pulsed discharge plasma applications on material surface modification and methane conversion.

2. Pulsed discharge mechanism

The mechanism of pulsed discharge is the key factor for the development of pulsed plasma technology. In a pulsed discharge, the electron avalanche time is shorter than the photon life time, so the typical streamer theory no longer valid for pulsed discharge explanation. It is found that the runaway electrons and X-ray play a crucial role in the initiation of sub- and nanosecond discharges. Many hypotheses have been proposed, such as electron avalanche chain model, fast electron and slow electron models, electron multiplication model and FIW model [7]. The electron avalanche model emphasises that the primary electron avalanche developed slowly or suspended when reached its critical value. Then the high-energy electrons (runaway electrons) locate at the avalanche head escape from the avalanche and form secondary electrons. The electron avalanche cannot form breakdown channel due to its small conductivity, and the formation of the breakdown channel needs secondary process, which is determined by photoelectric effect on the cathode. The electron multiplication model believes the E/N in typical streamer theory should have its maximum and minimum values. Fast electrons escape from the avalanche, ionise the gas to

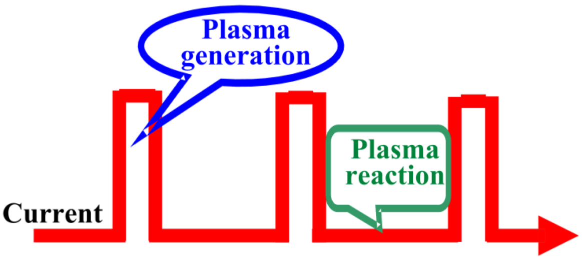

Fig. 1 *Schematic of pulsed discharge and plasma*

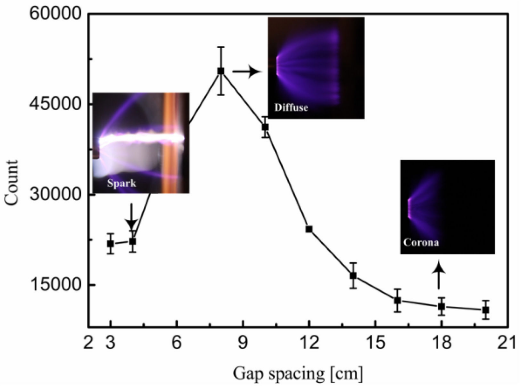

Fig. 2 *X-ray count under different discharge modes [17]*

generate secondary electrons. The number of electrons is multiplied by the above reactions. The key point for these two models is fast electrons. The threshold energy for their escape depends on electric field intensity, gas pressure and gas medium. Most of the work based on rapid ionisation model was finished in gas discharge tube (GDT) at low pressure. The length of GDT is usually several centre-meters, which is suitable for long gap discharge mechanism analysis. Although these hypotheses are different, they all believe that the secondary electrons are generated by high-energy electrons in the avalanche head instead of depending on space photoionisation. Hence, the study of high-energy runaway electrons might be a breakthrough for nanosecond pulsed discharge mechanism. The existence of runaway electron can be detected by two ways: (i) X-ray generated by runaway electrons and gas molecular, atom and anode impaction (indirect measurement) and (ii) runaway electron beams measured by collector (direct measurement). One should notice that the runaway electrons and X-ray are only dominant in nanosecond pulsed discharge up to now.

2.1 X-ray

The concept of runaway electron was first proposed by Wilson (1925) [8]. He believed that after a critical value, the current would not increase with the applied electric field. In this case, the electron energy would keep increase except for limiting by other factors and the drift velocity and conductivity would become very high [8]. However, not until the 1960s, Frankel first observed runaway electron excited X-ray in a helium discharge. Afterwards, Stankevich and Noggle *et al.* further confirmed the above result [9–11]. X-ray photons were generated by fast electron escape, so it is an indirect evidence of runaway electron. Tarasova *et al.* [12] measured the X-ray energy under different gas pressure in air and helium discharge by scintillator detector. Under a pulse voltage of 180 kV and a pulse width of 1.5 ns, the X-ray energy was measured as 15 keV. Byszewski and Reinhold [13] measured X-ray energy in nitrogen and helium discharge by a detector composed with CeI scintillator, Be filter and PMT. Under a pulse voltage of 30 kV and a pulse width of 45 ns, the X-ray energy reached 3 keV. Tarasenko *et al.* [14] measured X-ray by semiconductor and found that the X-ray energy can reach several hundred keV under pulse voltage amplitude of 150–220 kV, pulse rise time of 0.2–1.5 ns and pulse width of 0.5–5 ns. In recent years, many researchers focused on the temporal distribution of X-ray. Nguyen *et al.* [15] studied X-ray distribution in a streamer-corona plasma discharge by $LaBr_3$(Ce) scintillator and PMT. Zhang *et al.* [16] analysed the X-ray energy in pulsed discharge by a low X-ray measurement system composed by NaI crystal, PMT and multichannel analyser. The results showed that the X-ray came from high-energy electrons and anode impact radiation. Compared to other discharge mode, the diffuse discharge showed strongest X-ray intensity (Fig. 2) [17].

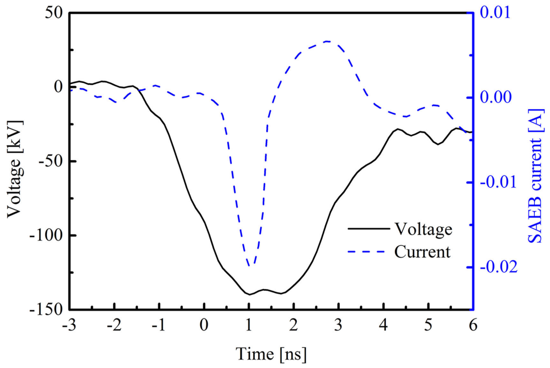

Fig. 3 *Typical waveforms of runaway electron beams [21]*

2.2 Runaway electrons

Runaway electrons were first observed by Tarasova, whom measured the runaway electron beams in a nanosecond-pulse discharge in helium [12]. The low amplitude of runaway electron beams requires high sampling rate of oscilloscope. Benefited from the fast development of pulse power technology, the narrow pulse width and high amplitude voltage generates more runaway electrons with high energy, providing the possibility for direct measure of runaway electron beams. Mesyats *et al.* [18] used time-of-flight method for runaway electron beams measurement and analysed the mechanism for their generation and dissipation. When powered by a sub-nanosecond pulse generator (pulse rise time 100 ps, pulse width 0.5–5 ns, amplitude 220 kV), the width and amplitude of runaway electron beams waveform was measured as ~50 ps and 10 A, respectively. The parameters for runaway electron beams measurement among main research institutions are presented in Table 1. The highest beam amplitude was 100 A with applied voltage of hundreds of kV. The researches on distribution of electron energy were not mature. Recently, Zhang *et al.* [21] measured the runaway electron beams in nanosecond-pulse discharge Fig. 3. The researches on energy distribution of runaway electrons is close related to the high-energy electrons, thus it has attracted much attention. Zhang *et al.* [22] calculated the energy of runaway electron beams in air and SF_6. Fig. 4 shows the reconstructed runaway electron spectra in SF_6 and air at atmospheric pressure [22]. The results showed that the maximum of electron energy was almost the same in these two gases. However, the electron energy range in air was wider than that of SF_6.

3. Pulsed discharge plasma characterisation

3.1 Diffuse discharge

Diffuse discharge is characterised by a large discharge area and high density, so it is also called volume discharge. At the atmospheric pressure, the electron collisions are frequent due to their short mean free path. Hence, the corona discharge easily transits to arc. Different to these two discharge modes, the diffuse discharge is composed with multiple overlapped channels through anode and cathode electrodes, but without sparks. In a diffuse discharge, the plasma is evenly distributed among the discharge gaps. So it is believed to be the ideal discharge mode at the atmospheric pressure [23, 24]. The diffuse discharge is first observed in the 1970s and is usually driven by pulsed high voltage. Ono *et al.* [25] had done a lot of work on the dynamics of pulsed discharges. For example, they observed the first and second discharge processes and obtained the OH density (10^{14} cm^{-3}) by

Table 1 Parameters comparison for runaway electrons among main research institutions

Researcher	Tarasova [12]	Babich [19]	Mesyats [18]	Tarasenko [20]
Institution	Russian Academy of Sciences Irkutsk chemical research institute	VNIIEF Institute of physics experiment	Russian Academy of Sciences Lebedev institute of physics	Russian Academy of Sciences Institute of high current
applied voltage, kV	180	110	220	200
voltage rise time	1 ns	0.5 ns	100 ps	1.5 ns
width of beam	1.5 ns	0.9 ns	50 ps	100 ps
amplitude of beam, A	—	0.1	10	100
electron number	10^9	0.6×10^9	10^{10}	5×10^{10}
highest electron energy, keV	360	300	470	150

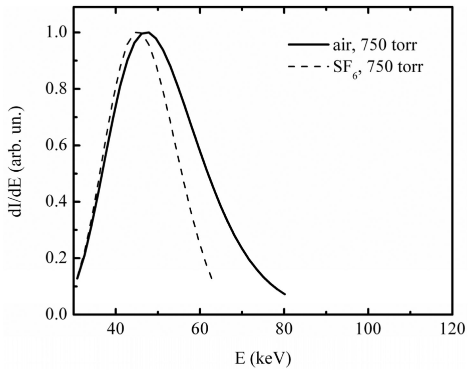

Fig. 4 *Reconstructed runaway electrons spectra in SF_6 and air at atmospheric pressure [22]*

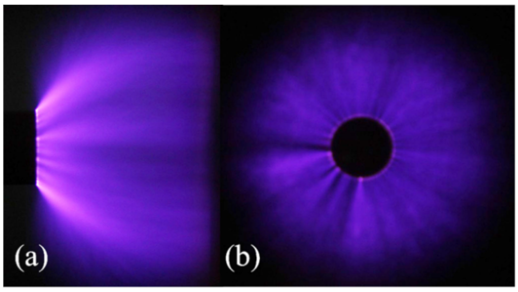

Fig. 5 *Image of diffuse discharge in atmospheric pressure*
(a) Side view, ***(b)*** Front view [36]

ICCD. Laux *et al.* [26–28] studied the nanosecond discharge modes in a pin-to-pin gap structure and their application for combustion by experiments and simulation. Three typical discharges were found: corona, glow and spark discharges. The glow discharge was diffusely distributed between electrodes gap. Tardiveau *et al.* [29] investigated the dynamics of a point-to-plane corona discharge under nanosecond scale high overvoltage. Their results showed that under atmospheric pressure, the discharge exhibits a diffuse pattern. The diffuse regime can exist since the voltage rise time is much shorter than the characteristic time of the field screening effects, and as long as the local field is higher than the critical ionisation field in air. Tarasenko *et al.* [30] applied the pulse with voltage over 100 kV, pulse rise time and full width at half maximum below 10 ns. The results showed the diffuse discharge was more evenly distributed under a higher overvoltage. They also indicated that the diffuse form of discharge at increased pressure is due to the generation of runaway electrons and X-rays [31]. Besides, many theoretical simulations also contribute to explain such volumetric discharges. Sun *et al.* [32–34] used a 3D model to investigate the inception stage of pulsed discharges in atmospheric pressure air. They found that the isolated streamers are inhibited and volumetric discharges showed up if the natural background ionisaiton and electron detachment process are considered in an overvolted discharge.

Institutes and universities in China, such as Institute of Electrical Engineering, CAS, Hua zhong University of Science and Technology and Dalian University of Technology also have done a lot of researches on diffuse discharges. Shao *et al.* [35, 36] studied the diffuse discharge in an inhomogeneous electrical field in repetitive pulsed modes, including pin-to-plate gap, pin-to-pin gap and coaxial electrodes. The typical diffuse discharge image was shown in Fig. 5. Besides, large-scale diffuse discharge was obtained by using multiple pins electrodes and knife shape electrode. Li *et al.* [37] analysed the electrical characteristics of diffuse discharge generated via high-voltage nanosecond pulses with short rise-time and wire electrodes. Experimental results showed the electrode spacing, and the length of wire electrodes can influence the intensity and mode transition of diffuse discharge.

In summary, the advantages of diffuse discharge are homogenously distributed and can work in the atmospheric pressure. Table 2 shows the comparison of typical discharge parameters between diffuse discharge and others. Compared to other discharge modes, diffuse discharge showed a higher average electron energy and electron density. Most of the researches focus on the generation of diffuse discharge and the transition between different discharge modes. Under atmospheric pressure, there are several effective ways to get diffuse discharge, such as pre-ionisation, pre-gas heating and supplement of gas. However, due to the differences of the pulse parameters (amplitude, rise time, pulse width and repetition frequency) and the measurement methods, it is hard to achieve consensus. Further studies should focus on the following questions: the discharge parameters measurement, the discharge mechanism and the applications of large-scale and homogenous discharges.

3.2 Pulsed DBD

Different with diffuse discharge, the DBD discharge is composed with two metal electrodes inserted with dielectric materials. The study of DBD can be traced back to 100 years ago and was initially used for ozone generation. In recent years, the generation of homogenous plasma by DBD at atmospheric pressure has been a hot topic. The homogenous DBD discharge at atmospheric pressure was first observed by Kanazawa *et al.* [38] in a helium mixture gas. After that, a lot of work had been done to study the homogenous discharge under atmospheric pressure. The gas composition, dielectric material and electrode gaps have a significant influence on the discharge stability. However, it is observed that the homogenous DBD discharge was only obtained with noble gas or their mixture. Wang *et al.* [39] have given a review on how to determine, classify and generate a homogenous DBD in noble gases. This is because that the high-energy metastables are only existed in noble gas discharge. These metastables generate a large amount of electrons through penning ionisation, which is the precondition of homogenous discharge.

Recently, the rapid development of pulse power technology, namely the rapid pulse rise time and narrow pulse width, provides a great opportunity for homogenous atmospheric pressure discharge. The results showed that the narrow pulse rise time could suppress the filaments and was beneficial for homogenous discharge [40]. The uniformity of DBD is usually characterised by electrical properties and ICCD camera. Lu and Laroussi [41] observed the first and second DBD discharge driven by a microsecond pulse power by ICCD with an exposure time of 5 ns. Shao *et al.* [42–44] studied the discharge characteristics, optical spectra and applications of pulse driven DBD. They found that the discharge modes were adjustable by modulating the discharge

Table 2 Typical discharge mode and their parameters for non-thermal plasmas

Discharge mode	Pressure, *P*, kPa	Electron concentration, n_e, cm^{-3}	Electron average energy, ε^*, eV	Rotational temperature, T_g, K	Electric field strength range *E*, V/cm
corona	>15	$<10^6$	<3	$<4 \times 10^2$	$<2 \times 10^4$
glow discharge	<15	10^7–10^{10}	2–8	$<7 \times 10^2$	50–10,000
DBD	>15	10^{10}–10^{11}	1–10	$<3 \times 10^2$	10^3–10^5
Arc	>15	$>10^{14}$	>1	$>10^3$	<20
diffuse	>15	10^{10}–10^{13}	>10	$(0.3–3) \times 10^3$	$>10^3$

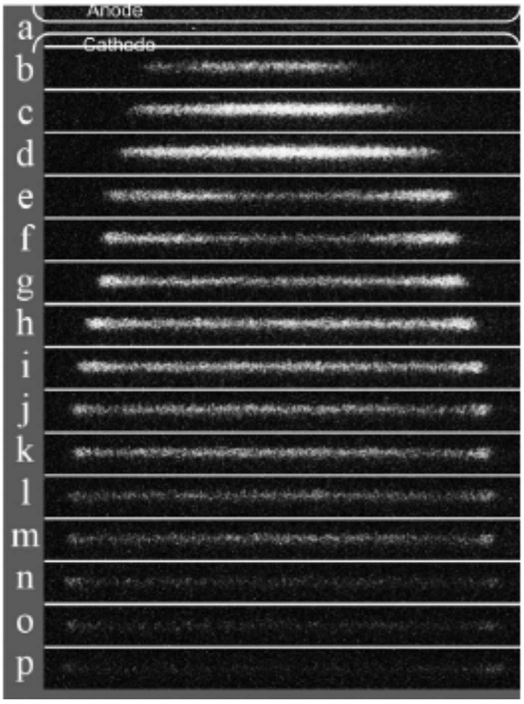

Fig. 6 *ICCD image of nanosecond-pulse DBD in atmospheric pressure air (exposure time: 2 ns) [44]*

gaps, Fig. 6 showed the discharge processes by ICCD with an exposure time of 2 ns. Under a discharge gap of 1 mm, the discharge began in the middle of the gap and travelled along the radial direction of dielectric material. The plasma was evenly distributed in the discharge gap and the discharge intensity was almost the same, showing a homogenous discharge mode.

DBD discharge has drawn intensive attention due to its simple structure and various applications. However, the objects to be treated are limited by its electrode structure. Besides, the discharge mechanism is still unclear. A deep investigation on the micro-parameters such as electron energy distribution, particle movement and transmission of DBD discharge should be performed.

3.3 Pulsed plasma jet

In recent years, atmospheric pressure plasma jets (APPJs) have drawn much attention. The APPJs can be maintained at room temperature while providing abundant active species. Furthermore, APPJs have the advantages of compact size, low cost, high efficiency and flexibility. Furthermore, the APPJs can be generated in open air rather than in confined discharge chambers, and they can be used for direct treatment without the limitation of the object's size.

The research of APPJs can be catalogued into two aspects: (i) device design for various applications and (ii) plasma jet characterisation including plasma bullet and free radicals. The basic configuration of plasma jet includes dielectric-free plasma jet, DBD plasma jet with dielectric materials between two electrodes and DBD like plasma jet, which has been well reviewed in [45]. One limiting factor of plasma jet is the size of its treatment area which tends to be limited to <1 cm^2 [46]. To overcome this challenge, plasma jet arrays consisting of many individual jets placed proximal of each other are considered. Ghasemi *et al.* [46] found that the two adjacent plasma plumes repelled each other and the gas flow rate had a negative effect on the repulsive force. Recent studies have focused on both expanding the number of plasma plumes and on enhancing downstream treatment uniformity. Walsh *et al.* [47] have expanded the number of plasma arrays comprising up to 45 individual jets. Zhang *et al.* [43] found that an amount of oxygen can enhance the uniformity of plasma arrays. Fig. 7 shows the discharge images before and after adding oxygen into a helium plasma jet arrays. The proper amount of oxygen additive enhances the Penning ionisation in the plasma jets, making the plasma jet in the middle of the array no longer substantially affected by the inhomogeneous distribution of the electric field.

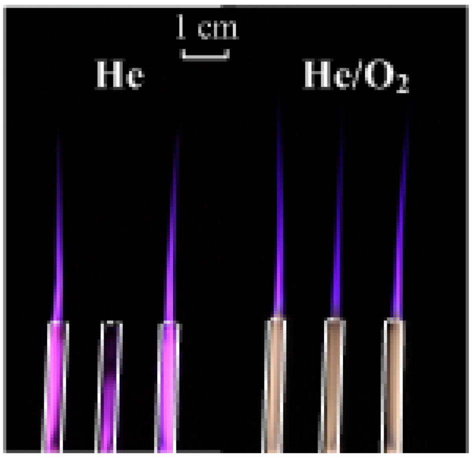

Fig. 7 *Improvement of spatial uniformity of pulsed plasma jet array in helium before and after oxygen additive [48]*

The physical properties of APPJs should be well understood in order to improve their performance. Recent research focused on the discharge mechanism of sub-microsecond, microsecond and nanosecond pulsed plasma jets. It is found that the electron density and oxygen atom density of pulsed driven plasma plume was 3.9 times and 3.5 times than that of AC power, respectively [49]. Under the same pulse parameters, the nanosecond pulse-driven plasma showed a longer plasma plume, a higher discharge current and more reactive species than that of microsecond pulse [50]. Lu *et al.* [51] studied the effect of the pulse width on the plasma plumes. They found that the plasma plume length increased with the pulse width and reached its maximum at 1 μs. Experimental research showed that the APPJs are typically composed of discrete plasma bullets, which propagates with velocities on the order of 10^4–10^6 m/s [52, 53]. Wang *et al.* [54] investigated the spatial and temporal distribution of N_2, N_2^+, O and He emission in a pulse-driven helium plasma jet. The N_2 and N_2^+ emission plume travelled at a faster speed and located in the plume front while He and O emission travelled at a slower speed and only located in the nozzle exit. It should be noticed that, the properties of plasma jets driven by different polarity pulses were totally different. The dynamic development of plasma jets showed a dark space appeared behind the plasma bullet head driven by positive pulse polarity, while the plasma bullet driven by negative pulse polarity moved forward continuously (Fig. 8) [55].

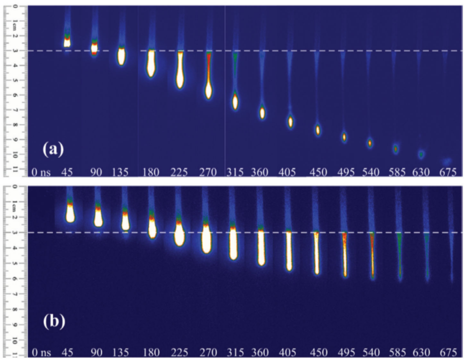

Fig. 8 *Evolution of plasma jet at different polarities [55] (exposure time: 5 ns)*

The pulsed-driven plasma jets have been a promising area in recent years. The intensive applications of APPJs rely on the optimisation of the reactive species density, large area discharge and the reaction efficiency enhancement. Besides, the development of portable APPJs for medical and environmental applications has a vast promising prospect.

4 Pulsed plasma applications

4.1 Surface modification

As an environmentally friendly method, the application of low-temperature plasma for surface modification of polymers has been well studied. The high-energy electrons (>1 eV) in low-temperature plasmas can induce molecule excitation, ionisation and dissociation, hence, resulting in the chemical bonds breaking and restructuring. It has been considered of an ideal method for surface modification due to its easy operation, moderate working conditions, low-energy consumption and highly reactive reaction. In addition, since the reactive species in low-temperature plasma possesses a small penetration depth on the order of only tens to hundreds nanometres, plasmas are capable of conducting surface modification without changing their bulk properties.

The plasma modified materials include polymers, fibre, metallic and biological material. Plasma treatment can change materials' surface energy, electricity properties, hydrophilicity and hydrophobicity. To get a uniform modification, homogenously discharged plasma is needed. Compared with the common plasma using AC or DC power source, pulse powered plasma can avoid the local overheat of micro-discharges, and improve discharge efficiency. Under certain conditions, homogenous DBD was achieved in atmospheric pressure when powered by bipolar pulse. Besides, the pulse interval is in the order of 1 s, while plasma generation is in the order of several nanoseconds, which insures full reaction between reactive species and materials. By changing the pulse repetition rate, the plasma chemical and material treatment processes can be precisely controlled. Walsh and Kong [56] applied 10 ns pulsed atmospheric air plasma for polypropylene surface modification. The SEM result showed small bumps appeared on the polymer surface after 300 s plasma treatments. Shao *et al.* [2] studied the modification effects of filament discharge and homogenous discharge on PET and PI. They found homogenous discharge was more effective for material modification (Fig. 9). Zhang *et al.* [57] applied pulse-driven diffuse discharge on copper surface modification. After plasma treatment, the copper surface was oxidised and its surface hardness was enhanced.

As we discussed above, pulsed discharge plasma is an effective method for material surface treatment. However, there are still some questions to be resolved. The mechanism of plasma surface modification is still unclear, especially the interaction between plasma parameters, material surface parameters and their properties. The development of large area and evenly distributed plasma for surface modification is a challenge. In addition, the aging effect of plasma treatment needs to be improved.

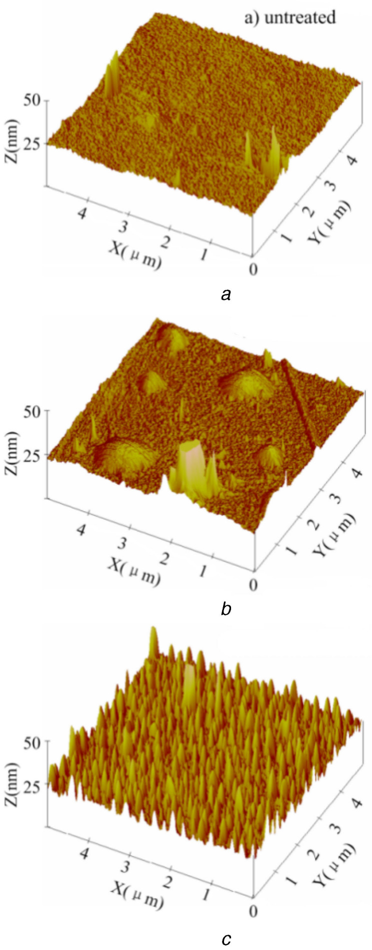

Fig. 9 *AFM observation of PI before and after surface treatment by nanosecond-pulse DBD*
(a) Untreated, ***(b)*** Filamentary DBD treated, ***(c)*** Homogeneous DBD treated [2]

4.2 Methane conversion

The study of plasma for methane conversion is one of the important applications of plasma technology in the energy chemical engineering field, which has been investigated by many researchers in the world. From 1990s, researchers from Japan, Iran, Russia, UK, China etc. have carried out a series of research on plasma methane conversion. The key of plasma methane conversion is how to improve the conversion rate, increase energy efficiency and control product selectivity. Kado *et al.* [58] utilised DBD, corona discharge, and spark discharge cracking methane at atmospheric pressure. The results show that the methane conversion rate is highest at spark discharge at the same input energy. Thanyachotpaiboon *et al.* [59] investigated the effects of voltage, residence time, and added gases on the methane conversion to heavy hydrocarbons and the results proved that the methane conversion rate increased with the increasing of voltage and residence time but the product selectivity was not affected by these factors. Tu *et al.* [60] performed methane dry reforming in DBD reactor with Ni/Al_2O_3 catalyst and it showed the catalyst could improve the ratio of H_2/CO. Liu *et al.* [61] used glow discharge to produce high efficient catalysis to lower ignition temperature and increased the methane conversion rate. The research results have already demonstrated plasma has positive effect in methane conversion and methane reforming hydrogen production. However, for industrial application, it is necessary to optimise the plasma methane conversion processing and solve some problems, such as the uneven of the electron energy and density in the discharge area, the lack the methods to control the product selectivity and repeatability, the removal of carbon deposition in the discharge area, and the low energy efficiency etc.

The plasma source is one of the key factors of methane conversion, which determines the methane conversion rate, energy efficiency, and the product components and selectivity etc. Therefore, recently, more and more researchers adopt nanosecond pulsed discharge plasma to convert methane. Compared with DC or AC discharge, the nanosecond discharge has a higher *E*/*N*, energy efficiency and chemical reaction rate due to its short rising time and short duration time. In addition, it is easier to control repetition rate and pulse parameters of the nanosecond discharge to monitor the plasma generation and chemical reaction precisely. Ghorbanzadeh *et al.* [62] utilised pulsed discharge plasma to reforming methane and carbon dioxide and got 50% hydrogen production rate. Taghvaei *et al.* [63] investigated the effect of carrier gas and hydrocarbon type on the cracking of methane and the results showed the increase of the ratio of methane in the mixture of argon and methane would lower the conversion rate and energy efficiency.

From the progresses of plasma methane conversion, it can be seen that the researches focus on the conversion rate and selectivity of the methane conversion and reforming hydrogen production by adjusting discharge parameters. Little has been done about the mechanism of the plasma physical chemistry reactions and the synergistic effect of plasma and catalyst, especially in nanosecond pulsed discharge, the adoption and desorption reaction on the catalyst surface is unclear. It is important to reveal the relationship between the plasma parameters, active radicals, reaction channels and product selectivity etc. for the practical industrial application.

5 Summary

In recent years, plasma discharge as a new type of energy carrier is in according with the national energy saving strategy. It has been found tremendous potential applications in the fields related with national economy, construction of national defence and social development, such as biomedical applications, solar cell film, nano-optoelectronics, flexible thin film circuit board, free electron laser, plasma propeller and environment protection. Along with the development of new applications, the traditional subject-plasma discharge, with over 100 years history, has been introduced new vital factors. The research of nanosecond pulse gas discharge belongs to the integration of pulse power technology and plasma technology. The nanosecond pulse with high-power density, high *E*/*N* and high-energy electrons, can effectively generate highly reactive plasma under atmospheric pressure. The pulse power-driven plasma and their applications is an international research hotspot. The domestic correlated research on plasma discharge has been developed rapidly, including atmospheric pressure DBD, nanosecond-pulsed discharge and plasma jet. In recent years, new applications of plasma discharge have been discovered. The plasma discharge has been applied in material surface modification, biomedical application, water waste treatment and even national defence, such as flow control and combustion. However, the fast development of plasma applications also brings big challenges for pulse plasma discharges.

(i) The mechanism of pulse plasma discharge. Although it is believed that the runaway electron breakdown theory is more reasonable for nanosecond pulsed discharge explanation, the micro-processes of runaway electrons on second electrons avalanche and streamer development still needs further investigation. Besides, the rapid ionisation wave and shock wave have been discovered on pulsed discharge applications, which needs further study base the mechanism of pulsed discharge.
(ii) Large area and homogenous plasma generation under atmospheric pressure. The rapid pulse can inhibit arc discharge and generate homogenous plasma under atmospheric pressure, which is beneficial for many applications such as material surface modification. Homogenous plasma discharge has been obtained by pulse-driven DBD with small discharge gap, diffuse discharge with rapid pulse rise time or direct gas heating. However, the large area homogenous discharge is very hard to maintain when increase the discharge area. Hence, the scale effect of plasma discharge needs further study.
(iii) Plasma diagnosis technology. The diagnosis of the pulsed plasma demands higher requirements on the diagnostic devices, such as faster transient response, protection against severe electromagnetic interference and more precise signal synchronisation. Besides, when it comes to atmospheric pressure discharge, many diagnostic methods are no longer applicable.

Recently, the pulse plasma discharges and their applications have been well developed. As research continues, new scientific problems have been introduced, as named below:

(i) *Nanosecond pulse mechanism*: runaway electron beams measurement devise with high resolution; runaway electron beams and X-ray analysis; electron energy distribution in electron avalanche; establishment of rapid ionisation wave measurement and theoretical model; establishment of high-energy electron breakdown model.
(ii) *Nanosecond pulsed discharge characterisation*: the measurement and diagnosis of pulse plasma under multiple parameters and transient response; the generation of pulse homogenous discharge with large discharge areas; reactive species generation and dissipation processes; pulse plasma characterisation in gas–liquid interphase; generation of highly reactive pulse plasma.
(iii) *Nanosecond pulsed discharge applications*: compact repetition rate pulse power technology, the interaction between pulse plasma and subjects, high electron energy transfer, the combination of plasma and fuel and efficiency optimising.

In this paper, we summarised recent progresses in the pulsed discharge plasma mechanism, characterisation and its applications on material surface modification and methane conversion. The following conclusion can be made:

(i) The measurement of runaway electrons and X-ray is an important way for high-energy runaway electrons behaviour analysis. An in-depth study on temporal resolution of collector, runaway electron beams and high-energy electron spectra is helpful for nanosecond pulsed discharge mechanism understanding.
(ii) The pulse power is beneficial for homogenous plasma generation under atmospheric air. The discharge mode includes diffuse discharge, DBD and plasma jet. The diagnosis of reactive species inside of plasma is significant for pulsed plasma development.
(iii) Pulsed discharge plasma has been found an effective method for material surface modification and methane conversion. However, the superiority of pulse power is doubtable, making it a long way to go from industrial application. Therefore, it is very important to discover the individual advantages of pulsed plasma for specific applications.

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