

## Review

# Recent progress on non-thermal plasma technology for high barrier layer fabrication

Haibao ZHANG (张海宝), Lijun SANG (桑利军), Zhengduo WANG (王正铎), Zhongwei LIU (刘忠伟), Lizhen YANG (杨丽珍) and Qiang CHEN (陈强)

Laboratory of Plasma Physics and Materials, Beijing Institute of Graphic Communication, Beijing 102600, People's Republic of China

E-mail: [lppmchenqiang@hotmail.com](mailto:lppmchenqiang@hotmail.com)

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### Abstract

This review describes the application of non-thermal plasma (NTP) technology for high barrier layer fabrication in packaging area. NTP technology is considered to be the most prospective approaches for the barrier layer fabrication over the past decades due to unpollution, high speed, low-costing. The applications of NTP technology have achieved numerous exciting results in high barrier packaging area. Now it seemly demands a detailed review to summarize the past works and direct the future developments. This review focuses on the different NTP resources applied in the high barrier area, the role of plasma surface modification on packaging film surface properties, and the deposition of different barrier coatings based on NTP technology. In particular, this review emphasizes the cutting-edge technologies of NTP on interlayer deposition with organic, inorganic for multilayer barriers fabrication. The future prospects of NTP technology in high barrier film areas are also described.

Keywords: non-thermal plasma (NTP), polymer, permeability, barrier layer, surface modification

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

## 1. Introduction

Flexible plastic films, with the features of low-cost, light-weight, transparent, hydrophobic etc, have been extensively used as excellent substitute of glass or metal materials in many applications, including food and medical packaging, liquid crystal displays and organic light emitting devices (OLED) encapsulation and so on [1–3]. However, compared to glass or metal packaging materials, the flexible polymer materials demonstrate relatively low barrier properties towards small molecules like oxygen ( $O_2$ ) or moisture vapors [4], which strongly restrict the their utilization. For example for an encapsulated OLED, the organic materials and electrode metals will be oxidized and led to a decrease in device luminescence. Accordingly, it is very important to improve barrier properties of flexible plastic films.

High barrier means a low gas permeate rate for such as  $O_2$ , moisture vapor, carbon dioxide ( $CO_2$ ) and other gases

through the packed or encapsulated matters. In general, the word ‘barrier’ refers to block  $O_2$  or  $H_2O$  permeability, although other ingredients ( $CO_2$ , product flavors, etc) must also be preserved. Many methods have been developed to improve the high barrier property of polymer webs, for example, multilayer structures using coextrusion or lamination processes in ethylene-vinyl alcohol (EVOH) copolymer or polyamide (PA) resin as barrier layer and middle layer, and polyolefin resin as cover layer or outer layer [5]. Alternatively the polymer web lamination or blending approach, one of the perspective ways of promoting the barrier properties of polymer web is to deposited a thin coating onto the polymer substrate by liquid phase chemical method [6] or vapor phase method, such as physic vapor deposition of metal Al [7] and chemical vapor deposition of metal oxides [8]. Among these methods, the non-thermal plasma (NTP) technology is intensively used in the fabrication of high barrier thin film nowadays [9–11].

As reported, various NTP technology has been used in high barrier thin film areas [12, 13]. With the characterization of high energy electrons, these NTP sources were applied to polymer membranes surface modification, including plasma surface treatment, plasma grafting and plasma polymerization, to improve the polymer surface energy, wettability, and the adhesion between the interface of polymer web and barrier coating. It was reported that the low-pressure NTP treatment was an effective method to modify the chemical and physical structures of the polymer web surface, without influencing its bulk properties [14, 15]. Meanwhile, the NTP generated by a diversity of discharges mode such as the dielectric barrier discharges (DBD) [16, 17], atmospheric pressure glow discharges [18], radio frequency (RF) capacitively or inductively coupled discharges [19], microwave (MW) discharges [20], etc, all of these have their own characteristic properties, will demonstrate different results.

This review covers the recent developments of NTP technology in the field of high barrier layer fabrications on the flexible polymer substrates. The motivations and applications of plasma-based barrier coating depositions are also described in detail. In particular, this review focuses on the different NTP resources applied in the high barrier area, the role of plasma surface modification on flexible polymer film surface properties, and the deposition of different barrier coatings based on NTP. The state-of-the-art of several barrier layers including organic, inorganic and functional multilayer thin films was stated. The future prospects of NTP technology in high barrier film areas are also described.

## 2. Permeability mechanism of high barrier thin film

Along with the progress of society, science and technology, the requirement of high barrier thin film is more and more increasing. The package materials and technologies have developed well beyond its original function as merely a means of product wrapping and protection. For example, in the food packaging areas, besides of the desirable high barrier property for purpose of extending the food shelf-life and maintaining the quality, the polymer packaging materials now play a key role in shelf appeal, providing product information, and establishing brand image and awareness. However, all of these applications are based on the high barrier property of the packaging materials. Regarding the organic electronic devices, it is vital important to encapsulate the devices and to prevent water vapor and O<sub>2</sub> permeation for the purpose of a long lifetime of the organic electronic devices. In past years, these organic materials were protected by using glass or metals. Alternatively, the high barrier, high transparent and flexible plastic webs are another candidates for encapsulation in present time, and their markets are expected to reach over \$550 million by 2025 [21]. For the organic electronic devices, the water vapor transmission rate (WVTR) will be less than 10<sup>-6</sup> g m<sup>-2</sup> day, and O<sub>2</sub> transmission rate (OTR) will be less than 10<sup>-3</sup> cm<sup>3</sup> m<sup>-2</sup> day [21]. Figure 1 shows the schematic diagram of cross-section encapsulated OLED. The application

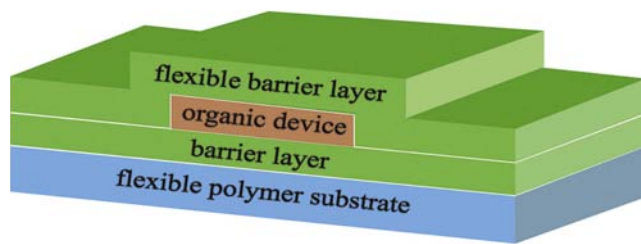


Figure 1. Schematic diagram of cross-section encapsulated OLED.

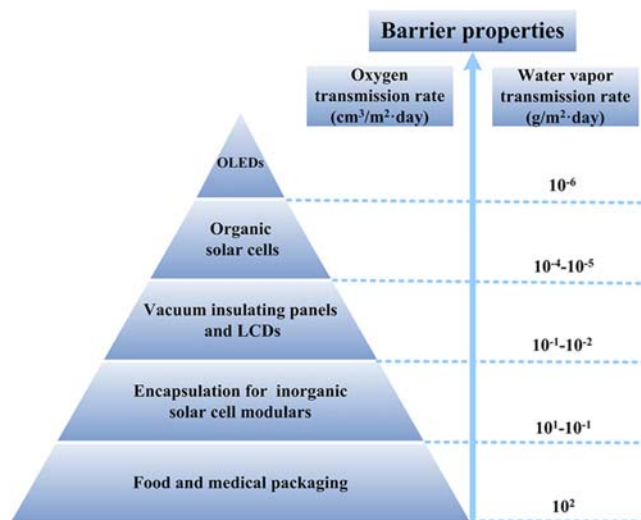


Figure 2. Barrier requirements for different applications.

of high barrier films and the required barrier parameters are shown in figure 2 [22].

It is obvious that the high barrier property is of crucial importance to the packaged foods or encapsulated flexible organic electronic devices in a sufficient shelf-life or a working lifetime. Usually the barrier property is expressed by the water vapor or oxygen permeability or transmission rate (WVTR or OTR), which is defined as the quantification of the gases or vapors permeating transmission through a film [4]. The gases or vapors most often studied are water vapor, O<sub>2</sub>, carbon dioxide, and nitrogen. WVTR and OTR of the barrier films are determined by measuring the amounts of water vapor or O<sub>2</sub> transmitted through the film. WVTR is noted as a gram of water passing through a given area of film in the specified time, the usual units is g m<sup>-2</sup> day atm at a specified temperature and humidity. OTR is usually defined in a cubic centimeter of gas passing through a square meter of film in 24 h, the usual units is cm<sup>3</sup> m<sup>-2</sup> day atm at a specified temperature and humidity.

The barrier properties are influenced by many factors, such as the process and materials. The permeation of gas through a polymer is described by a diffusion model [23], which commonly contains three steps: the permeates are adsorbed into the polymer film surface from the high concentration side, the permeates diffuse through the polymer matrix, and the desorption and evaporation of permeates from the polymer film surface on the low concentration side. Several factors in the measurement including the

environmental temperature, pressure differential, and relative humidity, influence the barrier property of packaging films. The diffusion of permeates across the polymer film is influenced by the polymer film chemical structure and physical characteristics, which contains polymer molecular structure, molecular weight, density, defect, pinhole density, degree of crystallinity, orientation, tacticity and cross-linking, and so on [24, 25]. Of course, the penetrating rate also depends on the size, shape, and polarity of the permeant molecules [26]. Generally the permeants mainly refer to those low molecular weight molecules such as aromatic compounds, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and water vapor. All of these affect the penetrating rate and the barrier property.

Based on the diffusive permeation mechanism, many methods have been proposed and adopted for the aim of improving the barrier properties of polymer packaging materials: (1) co-extrusion structure. The polymer films are fabricated by co-extrusion with EVOH or polyvinylidene chloride (PVDC) barrier matters [24]. EVOH copolymers can be easily co-extruded with nylons or laminated with polyolefins, polyesters, and polycarbonates. PVDC is often used as the moisture vapor barrier layer integrally sandwiched between outer layers of polyolefins in pharmaceutical blister packs. This structure satisfies the polyolefin with the performance of barrier properties of PVDC and the machinability, printability, and functionality of polyolefin skins; (2) multi-layer structure. When the specific barrier properties does not meet the requirement by a single layer of polymer film or even with blends of different polymer types extruded in a monolayer film, multilayer structured films are employed to improve the performance of barrier properties, e.g. the polypropylene (PP)/PE or Nylon/PE multilayer films [27]. It can reduce the amount of expensive polymer materials by increasing the amount of less costly polymers such as recycled material, scrap or trim material, or by reducing film thickness and the number of process operations required when several polymers are needed to obtain the desired properties; (3) lamination/deposition with metal barrier layers. Such as aluminum foil-laminated pouches, polyethylene terephthalate (PET)/Al/PP and nylon/Al/PP [28]. Koutchma *et al* [29] reported that the aluminum foil-laminated materials provided shorter preheating time than thinner polymeric materials. The high pressure treatment at high temperatures can increase the seal strength of aluminum foil laminated pouches; (4) plasma polymerization of organic barrier layers on polymer substrate. The common polymer substrates are PET, low density polyethylene (LDPE) and PP. Combinations of organic coating layers deposited on base polymer film greatly improve the barrier properties; (5) deposition of inorganic barrier thin films. Thin inorganic coatings were first commercially applied as gas barrier coating on polymeric substrates for food packaging in the early 1970s [30]. Al foil and vacuum metallized substrates have traditionally been used to provide the necessary barrier properties (0.1–3 cm<sup>3</sup> m<sup>-2</sup> day of OTR and less than 3 g m<sup>-2</sup> day of WVTR for packaging applications) [31]. Nowadays, metallic Al-coated polymer films are widely used as gas barriers in a variety of food and medical packaging applications. Furthermore, many other kinds of

inorganic coatings such as AlO<sub>x</sub>, SiO<sub>x</sub>, DLC, a-C:H, SiN<sub>x</sub>, and SiO<sub>x</sub>N<sub>y</sub> are successfully applied on packaging materials [32]. These advanced functional barrier film, almost are inorganic materials, are deposited by chemical vapor deposition and physical vapor deposition (PVD). Among these methods, the plasma-based techniques are used intensively for polymer surface modification and enhancement of barrier layer deposition.

### 3. NTP resources applied in the high barrier area

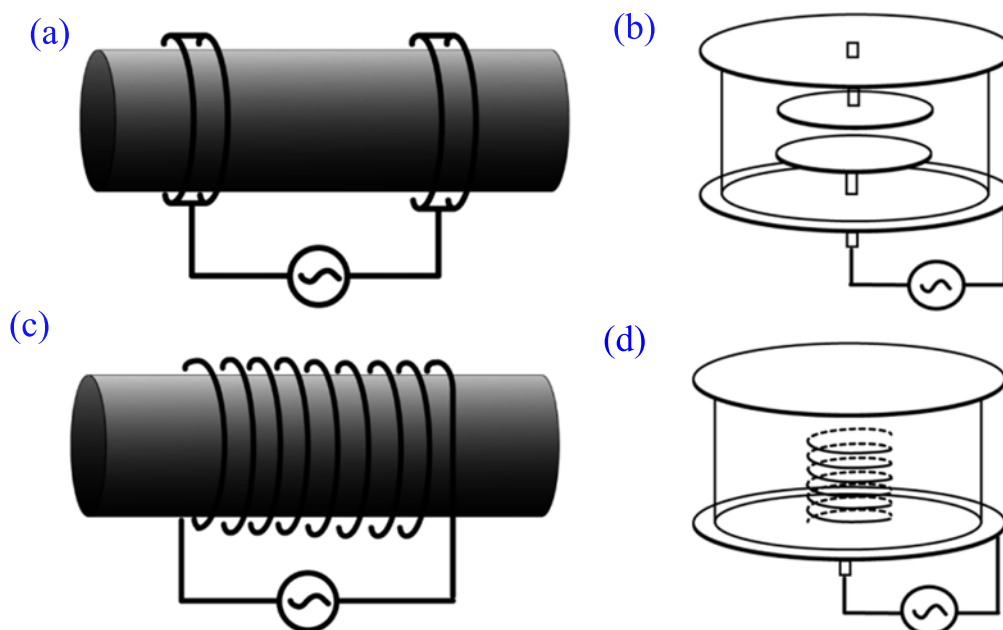
Plasma, which was introduced by Langmuir in 1929 [33], is a partly ionized gas and sometimes can be regarded as the fourth state of matter [34]. The plasma is composed of electrons, ions, highly excited radicals, photons and neutral particles (atoms or molecules). Based on these composed reactive particles, the plasma can provide a reactive chemical environment, in which many plasma-surface reactions can be carried out. Plasma can be generated when molecules or atoms are excited into energetic states, typically by direct-current (DC) [35], RF [36], MW [37], or electrons from a hot filament discharge [38].

Generally, plasmas are classified into non-thermal (or non-equilibrium) and thermal (or equilibrium) plasmas. Thermal equilibrium plasma means that the temperatures of all species, electrons, ions, neutrals, and excited species, are almost same in plasma. The temperature in thermal equilibrium plasma is typically ranging from 4000 to 20 000 K [39–41]. In contrast, in the NTP, the electron temperature is much higher than those heavy particles temperature, for example, ions and excited neutrals atoms. And the gas temperature in the NTP is near room temperature [42]. It is very suitable for the heat-sensitive polymer surface treatment without influence the matrix of polymer materials. Therefore, the NTP sources are widely used in the material treatment, functionalization and coating.

In the following paragraphs, the most typical NTP sources extensively used in the high barrier area are introduced from the discharge mode, experimental setup to some applications.

#### 3.1. Inductively coupled plasma (ICP) and capacitively coupled plasma (CCP)

Plasma can be excited and maintained by DC, RF, MW or other power sources. But in the high barrier area, the RF power supply is used more common than others. Generally, the frequency range of RF frequency is located in 1–100 MHz, most commonly at 13.56 MHz, with the wavelengths of 3–300 m larger than the dimensions of reactor. The RF power supply coupled into plasma can be via two couple modes, oscillating electric fields or oscillating magnetic fields [43], which are named as CCP and ICP, respectively [44, 45]. The schematic of typical RF setup system is shown in figure 3. For CCP discharge, as shown in the figure 3(a), the annular discharge consists of dielectric discharge tube (normally quartz or silica glass) [46], and figure 3(b) for the



**Figure 3.** Schematic of typical RF discharge setup: capacitively coupled plasma system (a) and (b), and inductively coupled plasma system (c) and (d).

parallel plates discharge, is consisted of metal electrodes with a certain gap. For ICP discharge, the induction coils placed outside of quartz tube (figure 3(c)), or placed in the chamber (figure 3(d)) consist of coils to generate the magnetic field. Regardless electrodes in reactor, the electrode located out of the discharge chamber is called as the electrodeless style discharge, as shown in the figures 3(a) and (c). The plasma generated without electrodes in the discharge zone can avoid contaminations originating from the electrodes sputtering.

When the plasma is excited and sustained by high-frequency RF power supply, the heavy species are formed during discharge. The electron temperature is relatively high for a given ion flux to the substrate. This is vitally important for the soft polymer substrates subjected to the plasma treatment.

Based on the energetic electrons and ions, radicals and energetic neutral species, CCP discharge, in different pressures ranging from a few mTorr to atmospheric pressure, is extensively used as a non-equilibrium plasma processing medium for material modification in many fields [47, 48]. For ICP, it does not depend upon a large voltage to maintain the discharge, the electron and ion energies are considerably lower than those found in CCP [49], especially at high power density condition. Relatively low ion energies in ICP discharges result in a decrease of ion-wall interactions and relatively small ion loss in the sheath. So compared to the CCP, the ICP can efficiently provide a high density plasma.

### 3.2. DBD

DBD has been studied extensively in recent years due to its various applications in ozone generation, CO<sub>2</sub> lasers, thin film deposition and surface treatment [50, 51]. For example, DBD

can be used to treat the polymer webs for the aim of improving wettability, printability and adhesion properties [52, 53]. DBD plasma can avoid spark formation in the streamer channels with help of dielectric barrier in the discharge gap. With the configuration of at least one of the electrodes is covered with an insulating layer, DBD plasma is very suitable for the polymer surface treatment in repetition, uniformity and stability compared to the corona discharge, which is also very popularly used in the polymer web pre-treatment, especially in the industrial scale. In addition, DBD plasma avoids the need of expensive vacuum device and a large amount of pollutable chemical reagents, i.e. the DBD process is a low-cost and green process. Various configurations for DBD are illustrated in figure 4 [54, 55]. The planar DBD plasmas shown in figures 4(a)–(c) are mainly used in the surface treatment [55], while the cylindrical DBD plasmas shown in the figures 4(d)–(e) are mainly used in the waste water treatment [56]. The typical clearance in DBD plasma gap varies from 0.1 mm to several centimetres [57]. The dielectric barrier can be made of glass, quartz, ceramics, polymers or other materials of low dielectric loss and high breakdown strength [50, 58].

In fact, the DBD plasmas are formed by large amount of short-lived filament discharges or sometimes so-called microdischarges, which are caused from the electron accumulation. The dielectrics located in the discharge area can prevent the stream formation from these individual microdischarges. So DBD plasma can obtain a large area uniform discharge. Besides, the microdischarges are established and formed a miniature plasma chemical reactor for some industry applications, for example, polymer surface treatment, dental cavities treatment, bacterial inactivation and environmental treatment [59].

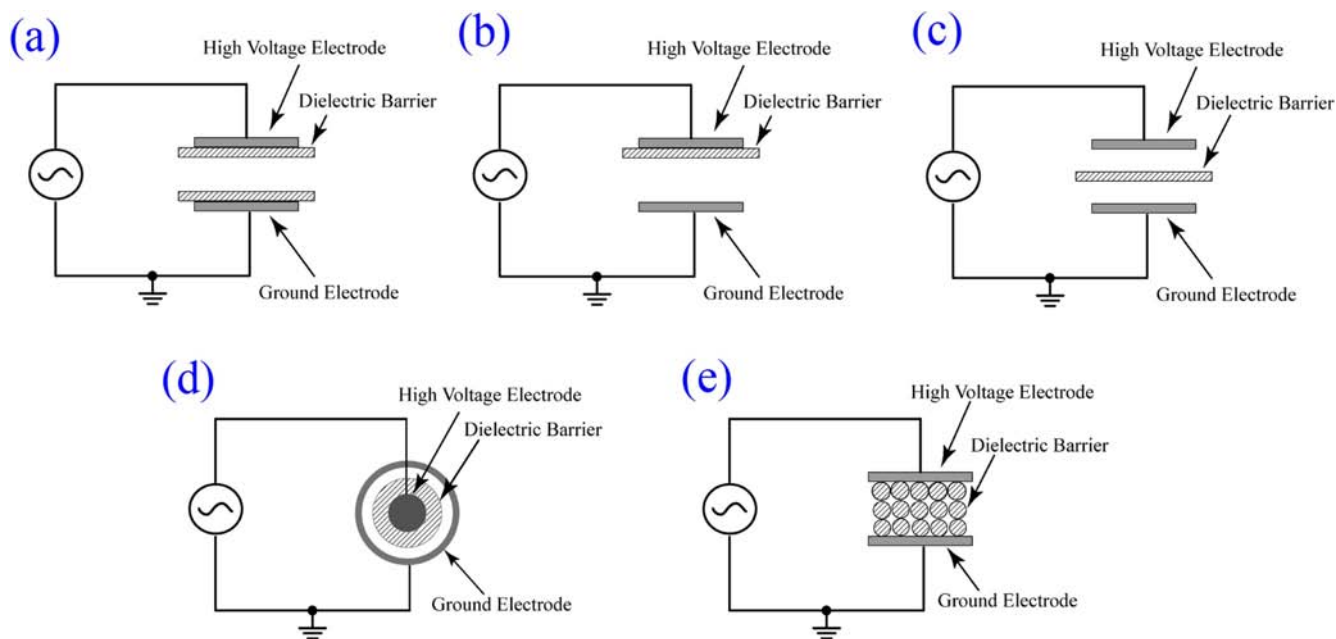


Figure 4. The schematic of various configurations for dielectric barrier discharge.

### 3.3. Electron cyclotron resonance (ECR) and surface wave plasma (SWP)

When the power resource frequency is raised from low frequency ( $\leq 100$  MHz) to high frequency, specially to MW frequency ( $> 100$  MHz), a high density electron density up to  $10^{11}$   $\text{cm}^{-3}$  can be obtained. Therefore, in MW plasma the concentrations of electrons and chemically reactive particles, such as free radicals, are greatly higher than that done in the low frequencies plasma [60]. So it is not surprising that the works done in MW plasma are intensively used in the recent generations of commercial plasma reactor systems. An atmospheric multi-mode MW resource was adopted by Shenton *et al* [61] to generate plasma treating LDPE and PET webs. They reported the enhancement of adhesive strength by 2–10 times. Itoh [62] developed an atmospheric pressure MW plasma using 10 GHz MW power source and produced as high as  $1 \times 10^{15}$   $\text{cm}^{-3}$  of electron density at slots using argon diluted 1%  $\text{H}_2$ .

ECR MW plasma is well known for its high ionization rate with electron density in the order of  $10^{11}$ – $10^{13}$   $\text{cm}^{-3}$  at low pressure of  $1$ – $10^{-3}$  Pa, and controllable and moderate energy of the plasma species, between 10 and 25 eV [63]. This combination of higher ion density and lower ion energy ensures a better surface modification of polymers compared with the conventional plasma surface modification techniques [64]. Moreover, the plasma properties can be controlled conveniently by manipulating the strength and configuration of the magnetic field in the source chamber or by adjusting the MW power [65, 66]. To ignite MW discharges in low-pressure regime, an extraneous magnetic field  $B$  has to be structured to aid the power absorption by rotating electrons in a magnetic field. If the cyclotron frequency equals the MW frequency, the power absorption reaches a maximum. For MW plasma with 2.45 GHz of frequency, the magnetic field

of 875 G can induce the electron cyclotron frequency at 2.45 GHz and the rotational movement of electrons is in resonance mode. The typical values of electron temperatures are near 5 eV [67]. Guruvenket *et al* [65, 66] used an ECR argon plasma to treat polystyrene surfaces, an enhancement of the wettability and the hydrophilicity was achieved.

SWP is another style of high density plasma ( $10^{11}$   $\text{cm}^{-3}$ , approximately two orders higher than that generated in CCP) excited by MW [68]. The MW energy is transferred via antennas, and the wave propagates along the boundary between the plasma column and the dielectric vessel, the MW energy is then absorbed by plasma. SWP, has relatively low electron temperature ( $< 2$  eV), can allow to keep a low substrate temperature [69].

### 3.4. Plasma enhanced chemical vapor deposition (PECVD) and plasma-enhanced ALD (PEALD)

As illustrated in the abstract, some organic or inorganic coatings need to be deposited on the polymer surface for the improvement of the barrier properties. The deposition of inorganic coating with the plasma enhanced technique is addressed as PECVD. As is well known, nano-sized amorphous  $\text{SiO}_x$  coatings with the main advantages of optical transparency, recyclability, and suitability for MW heating have been deposited onto the polymer for excellent diffusion barrier performance [70–72]. The normal deposition technologies for  $\text{SiO}_x$  films are based on PVD and sol-gel technique. The PVD process comprises the evaporation or sputtering of a solid precursor (Si, SiO, or  $\text{SiO}_2$ ). In contrast, PECVD using volatile organic-silicon precursors, which are excited and partially dissociated in plasma, is especially suitable for preparing coatings on temperature sensitive flexible substrates [73–76].

With the development of organic electronic devices, the demands of superior high barrier and better performances of encapsulation film are increasing. In order to fulfill this requirement, besides the traditional thin film encapsulation (TFE) technologies, such as evaporation, sputtering, many novel methods have been developed and applied in the TFE areas. Atomic layer deposition (ALD), which was developed and introduced worldwide in the late of 1970s, is a widely used method for TFE in nowadays. Compared to the conventional CVD, the coatings deposited by ALD show excellent properties owing to its sequential self-limiting surface reactions and good conformality with atomic-level thickness control [77, 78]. Based on these properties, ALD thin films can provide much lower permeability. Moreover, the NTP can be used to assist the ALD technique, which is named PEALD or plasma-assisted ALD (PAALD), for a lower temperature and a faster deposition rate process [79, 80]. Mourey *et al* [81] had used low-reactivity oxidants ( $\text{CO}_2$  or  $\text{N}_2\text{O}$ ) in PEALD for  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  depositions. The plasma was used to generate a high density of reactive oxide species for a faster PEALD process, where the low-reactivity oxidant could be used as the purge gas when the plasma was off, and as the oxidant when the plasma was on.

### 3.5. Atmospheric pressure plasma (APP) and roll-to-roll (R2R) plasma

NTP is often worked at a low pressure ( $10^{-3}$ – $10^3$  Pa) for a more stable glow discharge, an easily controllable plasma reaction and a low temperature process. However, low pressure discharge needs the vacuum equipment, which increases the process costs and makes the scale up for industrial applications more difficult. Therefore, the NTP discharge in the atmospheric pressure has been paid more attention. The major challenge for atmospheric pressure non-thermal discharge is how to prevent the transition from NTP to thermal arc discharge when the discharge is processing [43]. Many plasma sources have been used to realize discharge at the atmosphere pressure, such as DC [82], RF [83], MW [84], DBD [85], and pulsed corona discharge [57].

For the aim of treating polymer web surface in continuous mode, Bichler *et al* [86] reported a low pressure plasma pretreatment in R2R process. MW plasma was generated with the power between 1.1 and 2.5 kW at a pressure of 2.2 Pa. They found that after this gentle  $\text{O}_2$  plasma pretreatment (low power and low pressure), O atoms were chemically bonded in the surface, as a result the adhesion between polymer and coated Al layers was improved via chemical Al–O–C bonds.

Zhang *et al* [87] used an atmospheric R2R DBD plasma, as shown in figure 5, to modify PE web surface. Three kinds of hydrophilic reactive monomers, allylamine ( $\text{C}_3\text{H}_7\text{N}$ ), ethanol ( $\text{C}_2\text{H}_6\text{O}$ ), and acrylic acid (AAc) were employed, respectively, to pretreat the PE web for the adhesive enhancement of evaporated Al coating. They exhibited that the PE film located in the plasma zone was modified uniformly and continuously in R2R mode.

Although here we only present five kinds of plasma sources used in the high barrier area, it is worth noting that many other types of plasmas sources have also been adopted in the applications of the polymer surface modifications or barrier thin film deposition. It is sure that in the future there will be more novel plasma sources or plasma techniques developed for the increasing demands in the high barrier thin film industry.

## 4. NTP technologies used for the high barrier layers fabrication

The NTP sources have different physical characteristics and can satisfy different demands in the high barrier area. For example, it is very important to pretreat the polymer surface for the improvement of the surface free energy [88]. It will benefit to the strong adhesion between two different polymer films, inorganic coating and polymer surface, and printability of the inks [89–91].

Based on NTP technology, many polymer film surface modification techniques have been developed to improve polymer surface properties, such as inert gas APP treatment, polymers grafting, and the inorganic thin film deposition. Here we will stress the polymer surface modification for the improving performance of polymer surface or interface, while the polymeric bulk performance do not have any change [60]. The limited penetration depth of plasma-based treatment provides the vast improvement of surface properties and preserving bulk mechanical properties.

### 4.1. Plasma surface treatment

The popular discharge used for polymeric web surface treatment in industry is corona discharge. Early than 1960s, the corona discharge surface treatment has been reported [92–95]. The principles of corona discharge surface treatment is to produce active reagent (chemical functionalities) or active sites (free radicals) for reaction on the polymer surfaces, which will be benefit to the subsequent printing, lamination, coating technique and so on. With the development of polymer industry and NTP technology, more and more gases were used as discharging gas for polymer web surface treatments. For example, for the aim of improving hydrophilicity, the discharge gas can be the non-polymerisable gas such as Ar [96, 97], He [98, 99], Air [100–102],  $\text{O}_2$  [103, 104],  $\text{N}_2$  [104, 105],  $\text{NH}_3$  [106],  $\text{CO}_2$  [107, 108], while  $\text{CF}_4$  [109–111] or other CF-based compounds monomers [112, 113] were used to obtain hydrophobic film. Reactive  $\text{O}_2$  plasma is known to introduce a mixture of mainly carboxyl group ( $-\text{COOH}$ ) and hydroxyl group ( $-\text{OH}$ ) functionalities, while  $\text{N}_2$  or  $\text{NH}_3$  plasma introduces amines on the polymeric surfaces. The inert gas, such as He and Ar, used in the plasma surface treatment is due to the effect of ablation/etching, which can form free radicals and more reactive sites on the surface for purpose of recombination, unsaturation, branching

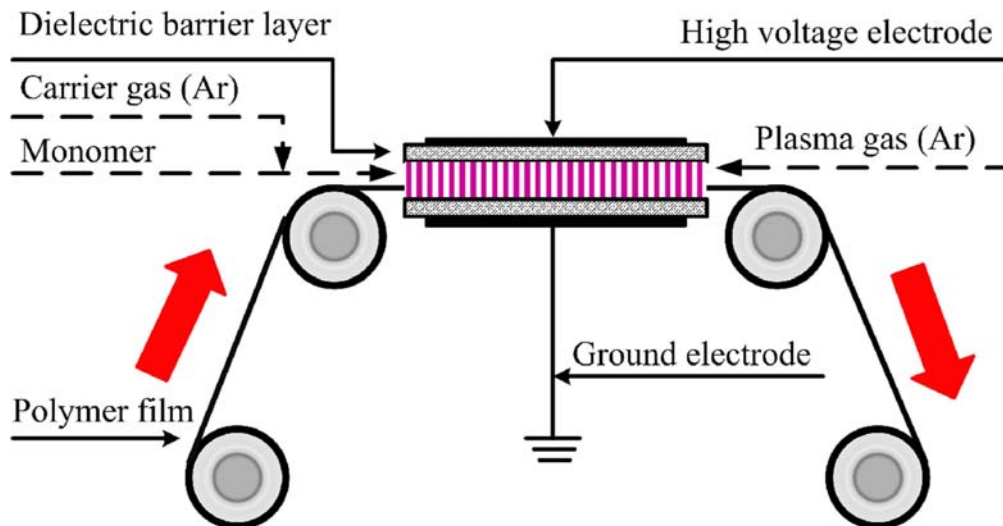


Figure 5. The schematic of the roll-to-roll DBD plasma apparatus.

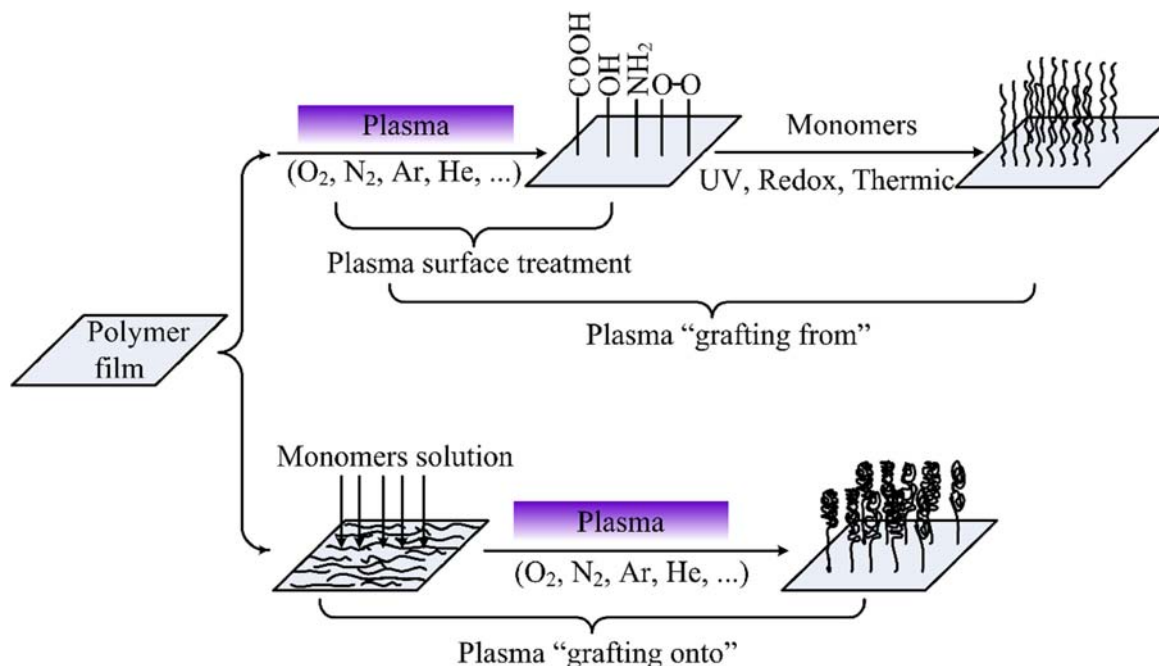
Table 1. The representative NTP treatments on polymer films.

Plasma source	Treatment gas	Polymer	Results	References
DC plasma (400 V, 10 W, 25 mA)	Air	PP	Contact angle (↓) Adhesion strength (↑) Hydrophilicity (↑)	Navaneetha Pandiyaraj (2008, 2009) [118, 119]
DC plasma	N <sub>2</sub>	PAN	Surface wettability (↑) Nitrogen content (↑)	Pal (2015) [120]
RF-ICP (27.12 MHz, 200 W)	O <sub>2</sub> CO <sub>2</sub>	PET	Hydrophilicity (↑) Oxygen-containing groups (↑)	Tkavc <i>et al</i> (2014) [121]
RF-ICP (13.56 MHz, 50–400 W)	O <sub>2</sub>	PET	Contact angle (↓) Oxygen-containing groups (↑) Adhesion energy (↑)	Han <i>et al</i> (2010) [122]
DBD plasma (25 kV, 1 kHz)	Air	PET	Contact angle (↓), Oxygen-containing groups (↑) Surface roughness (↑)	Fang <i>et al</i> (2012) [123]
DBD plasma (3–20 kV, 25–50 kHz)	Air	PP	Contact angle (↓) O/C ratio (↑)	Upadhyay <i>et al</i> (2004) [124]
DBD plasma (AC, 50 Hz, 8 kV)	Air	PP	Surface energy (↑) Surface roughness (↑)	Morsy <i>et al</i> (2006) [125]
DBD plasma (nanosecond pulses, 250 Hz)	Air	PET	Surface contact angle (↓)	Zhang <i>et al</i> (2010) [126]
MW plasma (2860 MHz)	Air	PE PP	Surface roughness (↑) Contact angle (↓)	Kaminska <i>et al</i> (2002) [127]
MW plasma (433 MHz, 0–250 W)	CO <sub>2</sub>	PP	Degradation yield (↑) Roughness (↑) Total surface energy (↑)	Aouinti <i>et al</i> (2003) [107]

or cross-linking on the surface after functional groups are grafted [114, 115].

Post-induced grafting onto the polymer surface is very popularization used in Ar plasma treatment [116, 117]. Some works reported on the ‘inert gases’ discharge for polymer surface treatment are listed in the table 1. The plasma surface

treatments obviously improve the polymer web surface properties, e.g. surface energy, hydrophilicity, surface roughness, adhesion strength. The influence of inert gas discharge on the polymer web properties is due to the activating and etching effect of energetic particles bombarding to surfaces. The activation can induce active site of reaction on the



**Figure 6.** The strategy of plasma grafting for modification.

polymer surface. The etching can fabricate nano-scale structure, which is benefit to the adhesion of inks, adhesives, and coatings onto the polymer surface.

However, there are some limitations for the non-thermal inert gas plasma used in polymer surface treatment. One of the most serious problems is relatively unstable of treated surfaces. The hydrophilicity/functionalities generated on the polymer surface as a result of plasma surface treatment are temporary and will lose with storage time, which is named as 'ageing effect' [126]. Normally the treated surface energy will recover to the original status after several days later in the open air. It is serious on the reliability of product applications. It will affect the quality of the printing, adhesive, coating because the treatment effect is weaken or failure.

#### 4.2. Plasma grafting

As a kind of the most common use in polymer surface modification technologies, surface grafting has been widely used in various fields [128, 129]. Surface grafting refers to the addition of polymer chains onto a surface or in some case a small molecular chain is grafted on the surface. The added small molecular chains are connected to the original surface by chemical bonds in surface grafting process. The chemical bond can be produced by chemical treatment [130–132], high-energy radiation technique [133–136] or NTP treatments [137, 138]. The surface active groups or free radicals are vital important for subsequent grafting or polymerizations [139, 140].

Generally the strategy of plasma grafting modification can be classified to two kinds of different processes, which are termed as 'plasma grafting from' and 'plasma grafting onto', as shown in figure 6. In the 'plasma grafting from' model, a polymer chain is grafted on the surface, which has functional groups (such as  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ , and  $-\text{O}-\text{O}-$ ) or active

sites introduced by plasma treatment. Sometimes the 'plasma grafting from' model is called 'surface-initiated polymerization process' [141–143]. The longer chain and the higher graft density are the most obvious features of the 'plasma grafting from' process. In general, the 'plasma grafting from' technique can produce polymer brushes [144, 145].

Navaneetha Pandiyaraj *et al* [146] reported a cold APP assisted polymerization process. An AC potential (14 kV) Ar plasma was used to induce chain scission and surface roughness of PP film. Then  $\text{O}_2$  was fed into the chamber in the absence of plasma to create oxygen containing polar group formations onto PP surface. In the later, Ar plasma was ignited again and the AAc vapors were fed into the plasma regime for grafting process.

Wang *et al* [147] proposed a plasma grafting technique for polytetrafluoroethylene (PTFE) film modification. The PTFE film was pre-treated by remote argon RF plasma (13.56 MHz, 30–180 W) [148, 149]. Subsequently the plasma-pretreated PTFE film was exposed to air forming peroxides, which were used as the initiator for the grafting of AAc. They found that the hydrophilicity of the PTFE film surface was greatly enhanced after plasma initiated grafting of AAc. And the time-dependent activity of the AAc-grafted surface was better than that of the only inert gas plasma treated film.

Vasilets *et al* [150] adopted a  $\text{CO}_2$  MWP to activate the PTFE, which was subsequently exposed to AAc vapor for grafting. The operating frequency of  $\text{CO}_2$  MWP was 2.45 GHz and the output power was 250 W. They found that the formation of  $\text{O}=\text{C}-\text{F}$  and  $-\text{C}=\text{C}-$  groups after  $\text{CO}_2$  plasma treatment, and the formation of  $-\text{COOH}$  groups after AAc grafting, which were attributed to the gradually decrease of water contact angle on the PTFE surface.

In the so-called 'plasma grafting onto' model, 'mushroom' regime polymer are grafted onto a surface by



**Table 2.** The representative overview of monomers in NTP polymerization.

Monomers	Plasma source	Film	Key findings	References
AAc	DC plasma (3 kV, 1 A)	LDPE	Hydrophilicity (↑) Aging effect (15 d)	Navaneetha Pandiyaraj <i>et al</i> (2015) [166]
AAc	ECR MW plasma (2.46 GHz, 300 W)	PP	Adhesion (↑)	Dayss <i>et al</i> (1999) [170]
AAc	RF plasma (30–180 W)	PTFE	Water contact angle (↓) Hydrophilicity (↑) Ageing effect (↑)	Wang <i>et al</i> (2007) [147]
Acrylamide	RF plasma (13.56 MHz)	PE	Water contact angle (↓) Antithrombogenicity (↑)	Zhao <i>et al</i> (2007) [171]
<i>n</i> -Butylamine Allylamine	MW plasma (2.45 GHz, 60 W)	Polysulfone (PSU)	Hydrophilicity (↑)	Gancarz <i>et al</i> (2002) [172]
C <sub>2</sub> H <sub>2</sub>	RF-CCP (13.56 MHz, 20 W)	Biodegradable polyesters	Coating adhesion (↑) Oxygen barrier permeability (↑)	Bélar <i>et al</i> (2013) [173, 174]
Glycidyl methacrylate	RF plasma (35 W, 40 kHz)	PTFE	Adhesion property (↑)	Zhang <i>et al</i> (2001) [175]
AAc Ethanol Allylamine	DBD plasma (RTR, 40 kHz)	PE	Al coating adhesion (↑)	Zhang <i>et al</i> (2016) [87]

pre-adsorption of monomers solution and then following by plasma treatment. Due to the large volume of the coiled polymer and the steric hindrance effect, the grafting density is small in ‘plasma grafting onto’ model compared to ‘plasma grafting from’ model [151, 152].

Kuzuya *et al* [153–155] proposed a novel strategy for fabrication of durable hydrophilicity on several hydrophobic polymer (polyethylene-naphthalate copolymer, nylon-12 and LDPE) by plasma treatment (ICP, 13.56 MHz, 40 W). The main 3-steps method involved: sorption of vinylmethylether-maleic anhydride copolymer (VEMA), plasma inducing cross-link reaction to generate maleic anhydride-containing polymer onto hydrophobic polymer film, and hydrolysis of the maleic anhydride moiety to form hydrophilic –COOH groups on the hydrophobic polymer surface. Sasai *et al* [156] adopted this method to modify LDPE. The VEMA was firstly soaked into LDPE surface using a mixed solvent cyclohexanon/*p*-xylene, and then the adsorbed VEMA was covalently grafted to LDPE surface by an ICP at 13.56 MHz with applied power of 20 W, following by a hydrolysis of VEMA, –COOH was generated on the LDPE surface for the subsequent fabrication of polyglycidyl methacrylate (pGMA) through an atom transfer radical polymerization process [157].

#### 4.3. Plasma polymerization

As plasma grafting, plasma polymerization also uses monomers for surface modification. Plasma polymerization often means that via plasma the vapor monomer can form coating by polymerization on the polymer surface. It can be traced to the second half of the 19th century that polymer polymerization occurred in organic vapor plasma (ionized gas) [158, 159]. And the NTP polymerization has been practically utilized to make a special coating on metals in 1960s

[160, 161]. The coatings by plasma polymerization have many advantageous features, e.g. flawless microstructure, good adhesion to the substrate, chemical inertness, and low dielectric constant. Many applications concerning to the plasma polymerization process were reported [162–165]. The flawless, homogeneous coatings in very thin deposited onto appropriate membrane substrates demonstrated a low permeability, which would provide a means of preparing high barrier membranes.

It is vital important to select proper polymerization monomers for desired hydrophilic/hydrophobic surface functionality. Navaneetha Pandiyaraj *et al* [166] adopted DC excited low-pressure plasma *in situ* grafting AAc onto LDPE. The modified LDPE films demonstrated a good hydrophilic behavior compared with the unmodified one. The plasma treated surface did not show significant change after stored in air for 15 d. Zhang *et al* [87] studied the adhesion between PE and Al in atmospheric DBD plasma R2R process by polymerizing 3 different active monomers, i.e. allylamine, ethanol, and acrylic acid. They found a high remained surface energy of PE even over three-month ageing because of the polar groups. They deduced that the plasma-grafted high concentration oxygen-containing functional groups played a critical role in the improvement of the adhesion between Al coating and PE substrate via chemical Al–O–C bonds.

The active monomers, NTP techniques and their corresponding efficiencies on the plasma induced polymerization are shown in table 2. Common monomers, such as C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, styrene, acrylonitrile, ethanol, acrylic acid, allylamine, acrylamide, have been used for the plasma polymerization [167–169]. One can see that the common monomers used in the NTP induced grafting process are those organic monomers with unsaturated bonds (–C≡C–,

–C=C–), carboxyl (–COOH), amino (–NH<sub>2</sub>) or hydroxyl (–OH).

Plasma polymerization of organic or hybrid coatings as adhesion promoters and primers is an essentially plasma treatment method for polymer surface modification in adhesion applications [176–178]. Petersen *et al* [177] reported an APP polymerization of allylamine to form amine-rich coatings on Al surface. The adhesion strength of Al-epoxy assemblies could be greatly increased in regulating plasma power parameters.

#### 4.4. Inorganic thin film deposition

The polymer surface modification by plasma is for the aim of improving the surface properties, so as to facilitate the subsequent process. But at the early stages, in order to improve the barrier properties of films, the polymer webs are metallized, which means some metals or metal compounds deposited on the polymer surface. The earliest adopted metal deposited on the polymer surface is Al, which is evaporated in vacuum to form Al-coated polymers [179–181]. Sometime Al foil is sandwiched between polymer films as a barrier layer [182]. While the major inorganic materials deposited onto the polymer surface are AlO<sub>x</sub> [183–186], SiO<sub>x</sub> [187–189], SiN<sub>x</sub> [190–192], SiO<sub>x</sub>N<sub>y</sub> [193], TiN<sub>x</sub>O<sub>y</sub> [194], and DLC or a-C:H [195–197], etc. Some inorganic coatings by plasma processes as barrier layers have been summarized in table 3.

The main advantages of depositing inorganic barrier coatings on polymer surfaces are: (1) great improvement of barrier properties; (2) high flexibility; (3) low cost. Compared to the Al metallized barrier coating, oxide layers like SiO<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub> are the better choice due to they are transparent, colorless, microwaveable and good barriers properties [203, 204].

Hegemann *et al* [205–207] studied the roles of etching, cross-linking, and activating as well as coatings in surface properties of polymers like PC, PP, PE, PS, PET and PMMA through a RF discharge of Ar, He, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, or hexamethyldisiloxane (HMDSO), respectively. They illustrated some conclusions on the plasma surface treatments: (1) plasma treatment in different gases had different effects on the aging. They observed the lowest aging effect was on PC in the situation of N<sub>2</sub> plasma treatment. However, a more stable and permanent hydrophilic effect on PC was yielded by an ultra-thin plasma-deposited layer like SiO<sub>x</sub> than a plasma treatment with non-film-forming gases like N<sub>2</sub>. No aging effect was observed for siloxane films after storage for 1 year in air at ambient conditions [208]; (2) the adhesion strength of plasma-deposited coating was subject to aging, which depended strongly on the polymer component, the internal stresses of coating, and the storage conditions; (3) the deposition of graded layers or ultra-thin films like 1.5 μm thick SiO<sub>x</sub> coatings on PC generally improved adhesion. Starostin *et al* [209] demonstrated an atmospheric pressure DBD plasma *t* for deposition of thin silica-like moisture barriers films on polyethylene 2, 6 naphthalate webs in R2R process. They reported that a dense, uniform, smooth and well adherent inorganic silica-like coating at 100 nm thick could

be deposited on polymer surface, as a result the WVTR of  $1.8 \times 10^{-3} \text{ g m}^{-2} \text{ day}$  (at 40 °C, 90% RH) was achieved. Scopece *et al* [8] presented results of SiO<sub>x</sub> thin layers deposited by APPJ on PP films. Monomer HMDSO was vaporized for the deposition of SiO<sub>x</sub> thin film. The results revealed that SiO<sub>x</sub>C<sub>y</sub>H<sub>z</sub> coatings with good controlled thickness and better barrier properties were deposited on PP substrates.

Besides silicon oxide, aluminum oxide is another important transparent barrier coating to fulfill recent packaging requirements, such as visibility, microwaveability and retortability. There are main two method of preparing aluminum oxide coating as the barrier layer in recent year. One is reactive thermal evaporation technique, based on the traditional vacuum R2R metallizer. Other technique for preparing aluminum oxide coating is ALD technique. Struller *et al* [210–212] prepared aluminum oxide coated BOPP and PET barrier films via reactive thermal evaporation using a high-speed R2R process. The metal aluminum wire was continuously evaporated via resistively heated evaporation [213], and the transparent aluminum oxide coating was formed when the O<sub>2</sub> was introduced into the aluminum vapor stream. Their results demonstrated that the adhesion of AlO<sub>x</sub> coating on BOPP film exceeded the BOPP tension strength. The surface energy of AlO<sub>x</sub> was considerably higher (63–66 mN m<sup>-1</sup>). During process, the in-line plasma pre- and post-treatments were applied by magnetically enhanced plasma. The plasma treatment was generally accompanied by a chemical modification and cleaning effect, which were benefit to the improvement of the coating barrier properties. In fact, the plasma pretreatment mentioned in here was different from the inert gas plasma treatment, plasma grafting, or polymerization surface treatment illustrated in this paper. Here the plasma treatment was performed by a magnetron sputtering with metal targets. In other works, PET substrates had been pretreated by magnetically enhanced glow discharges powered using either medium frequency pulse DC or low frequency high power pulse (HIPIMS) sources with Cu or Ti sputter targets [214].

ALD is a powerful nanofabrication technique for the preparation of uniform, conformal, and ultrathin films with accurate controllable composition and thickness at the atomic level [215, 216]. ALD technique can be classified to thermal ALD and PEALD, sometimes called as PAALD. With the high energy species, the PEALD, which can enhance the reactivity at low temperatures, is suitable for the temperature-sensitive deposition process. Now PEALD has been applied to prepare high-quality ultrathin films for microelectronics, catalysis, and new energy applications [217, 218]. Lee *et al* [219] reported a low frequency plasma assisted ALD technique to deposit Al<sub>x</sub>O<sub>y</sub> layer on polyethylene naphthalate substrates as barrier layer. Trimethylaluminum and O<sub>2</sub> plasma were used as precursor and oxidant, respectively. The best WVTRs of the Al<sub>x</sub>O<sub>y</sub> layer could reach  $8.85 \times 10^{-4} \text{ g m}^{-2} \text{ day}$ . Li *et al* [220] presented a novel magnetized RF PEALD technique for the deposition of Al<sub>2</sub>O<sub>3</sub> thin film. The deposition rate of prepared ALD Al<sub>2</sub>O<sub>3</sub> was more than 3 Å/purging cycle without extra heating. Langereis

**Table 3.** The representative overview of inorganic barrier layers deposited by NTP.

Inorganic film	Plasma source	Polymer film	Key findings	References
Al	MW plasma (O <sub>2</sub> , 1.1–2.5 kW)	BOPP	Oxygen groups improved the adhesion of coated Al layers via chemical Al–O–C bonds	Bichler <i>et al</i> (1999) [86]
Al	DBD plasma (60 kHz)	PET Polyvinyl chloride (PVC) BOPP	Al coating adhesion was increased by plasma treatment	Langowski <i>et al</i> (2012) [7]
SiO <sub>x</sub>	VHF plasma (150 MHz, 40 W cm <sup>-2</sup> )	Polycarbonate (PC)	SiO <sub>2</sub> -like film was obtained with high deposition rate of 33 nm s <sup>-1</sup>	Kakiuchi <i>et al</i> (2012) [198]
SiO <sub>x</sub>	Atmospheric plasma jet (APPJ, 315 V, 21 kHz)	PP	Gas barrier properties of PP improved by APPJ deposition of SiO <sub>x</sub> C <sub>y</sub> H <sub>z</sub> coatings	Scopece <i>et al</i> (2009) [8]
DLC	PECVD (RF, 13.56 MHz, 250 W)	PTFE	No cracks were observed and CO <sub>2</sub> gas permeation decreased drastically with increasing film thickness	Ozeki <i>et al</i> (2009) [199]
DLC	PECVD (RF, 13.56 MHz, C <sub>2</sub> H <sub>2</sub> )	PET	OTR: 13.7 cm <sup>3</sup> m <sup>-2</sup> day	Zhang <i>et al</i> (2011) [200]
DLC	PECVD	PET and PC	WVTR 0.0316 g m <sup>-2</sup> day	Abbas <i>et al</i> (2005) [201]
a-C:H	PECVD (RF, 13.56 MHz, 0–90 W)	PET	Increased film density and relatively low thickness in the range of 7–120 nm be benefited for the barrier properties	Polonsky <i>et al</i> (2013) [202]

*et al* [221] showed a PAALD technique to deposit  $\text{Al}_2\text{O}_3$  moisture permeation barrier layer at low substrate temperature (from RT to 100 °C) in short cycle times. A good WVTR of  $5.0 \times 10^{-4} \text{ g m}^{-2} \text{ day}$  was obtained for a 20 nm thick film deposited at room temperature in a cycle time of 17 s. The high energetic radicals in plasma enable the deposition at room temperature without requiring long purging times. Kim [222] fabricated an  $\text{Al}_2\text{O}_3/\text{TiO}_2$  nanolamination (NL) corrosion-resistant passivation film by using a PEALD technique. The  $\text{Al}_2\text{O}_3/\text{TiO}_2$  NL films deposited at low-temperature processing (<100 °C) were found to exhibit excellent anticorrosion and low gas permeation.

#### 4.5. Inorganic and organic multilayer film deposition

As reported by Groner [223], almost defect-free single layer ALD  $\text{Al}_2\text{O}_3$  showed excellent barrier properties. He had reported a WVTR of  $1 \times 10^{-3} \text{ g m}^{-2} \text{ day}$  in single-sided ALD  $\text{Al}_2\text{O}_3$  PET at low deposition temperature. However, the ALD deposition rate was small for inorganic barrier layers, such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , the defects and cracks always limit their barrier performance [224]. For the aim of solving these disadvantages, a multilayer barrier structure consisting of inorganic and organic layers is constructed. The inorganic layers act as barrier layers, and the organic layers decouple the defects in the barrier layers and extend the permeation path for water molecules in the barrier film [225, 226]. Based on the NTP technique, many researchers have fabricated the high quality multilayer structure barrier films. Tashiro *et al* [227] prepared DLC coating with organosilane interlayer onto PP film, which showed remarkable improvement in the gas barrier property. Hwang *et al* [228] demonstrated an organic–inorganic multilayer structures composing of plasma-polymerized *n*-hexane and ALD  $\text{Al}_2\text{O}_3$  layers. The organic–inorganic multilayer structures showed about 35% better moisture-barrier property than those obtained from individual organic and inorganic layers. Seo *et al* [229] also presented a organic–inorganic multilayer moisture barriers composing of plasma-polymerized *n*-hexane and ALD aluminum-oxide layers. Lim *et al* [230] presented a multilayered barrier composing of a ALD  $\text{Al}_2\text{O}_3$  layer and flexible plasma-polymer layer polymerized by ICP plasma using three monomers, HMDSO, *n*-hexane and furan. The bending property of the as-prepared films could retain the initial barrier property even after 10 000 times of bending at a radius as small as 3 mm. Furthermore, some researcher had simplified the fabrication process of the multilayer barrier structure in a single-chamber system. Bülow *et al* [231] reported a PEALD  $\text{AlO}_x$  and PECVD polybenzene multilayers coating on polyethylene naphthalate substrates in the same reactor. Patelli *et al* [232] developed a single step vacuum PECVD technique for the deposition of  $\text{SiO}_x$ -based multilayer barrier coatings. The ‘ceramic’ or ‘polymeric’ layers were modulated by  $\text{O}_2/\text{HMDSO}$  ratio, which was controlled only by pumping speed. Wu *et al* [233] also reported an organosilicon/silicon oxide ( $\text{SiO}_x$ ) multilayered barrier structure, which was consecutively deposited onto PET substrate by PECVD using same monomer in one chamber.

## 5. Applications of high barrier thin film based on NTP technologies

As illustrated above, polymer surface modification by NTP technology is benefit for the improvement of the polymer surface properties, and then enhancement the adhesion between polymer substrate and others laminated polymers or deposited coatings. Meanwhile, barrier thin films deposited by NTP onto the polymer substrate improve the barrier properties of the polymer membrane directly. It is obvious that the NTP is an essentially important technology for the preparation of high barrier film. And many high barrier film or products based on NTP technology have been researched and developed for specific applications.

### 5.1. High barrier laminated polymer film

Compared with metals, glasses and other packaging materials, polymers demonstrate poor barrier properties. Both of lamination of EVOH, PVDC, or PA and deposition of organic or inorganic coating onto polymer membrane as barrier layer are perspective in promoting the barrier properties of polymer web. However, the low surface energy of the polymer substrates often results in the delamination problem in composited multilayer structure, which seriously influences the barrier properties. Plasma surface treatment, has been introduced in detail in section 4, is one of the most commonly used polymer surface modified technique. As reviewed in above, many researchers studied the NTP surface treatment of polymer film. And furthermore, the NTP pretreated polymer films have been used in lamination or deposition of barrier layers for the enhancement of adhesion properties and barrier properties. Besides commonly used inorganic or organic polymer coatings, many sustainably-produced biopolymers, such as whey protein isolate (WPI) and corn–zein, can be used as novel biopolymer barrier coating for food packaging applications. Hong and Krochta [234] investigated the oxygen permeability of the WPI coated PP films pretreated by corona discharge ( $25\text{--}30 \text{ kV cm}^{-1}$ , 4–5 MHz). The corona discharge was used to pretreat the nonpolar surfaces of PP film for the aim of enhancing the adhesion of WPI coating. Their results illustrated that the oxygen permeability of PP with WPI coating drastically reduced more than 4-fold in the temperature range of 15 °C–40 °C. Schmid *et al* [235] described a similar whey-protein-based barrier coating layer included in an laminated multilayer structure (PET/Wheylayer/Adhesive/PE). The developed whey protein formulations based on PET film pretreated by corona discharge had excellent barrier properties with an OTR of  $<2 \text{ cm}^{-3} \text{ m}^{-2} \text{ day}$  and WVTR of  $<3 \text{ g m}^{-2} \text{ day}$  when normalized to a thickness of 100  $\mu\text{m}$ , almost comparable to the EVOH barrier layer conventionally used in food packaging composites. Tihminlioglu *et al* [236] fabricated a novel corn–zein coating on corona-discharged-treated PP for flexible packaging industry. The water vapor and oxygen barrier properties of uncoated PP films were significantly improved with corn–zein coating. The improved OTR value of plasticized corn–zein coating on PP films reduced nearly more than 3 orders.

### 5.2. Packaging bottle with high barrier coating deposition

The use of plastic PET bottles for packaging oil, milk, beer, mineral waters, fruit juice, and carbonated soft drinks are still growing in worldwide [237–240]. However, the PET bottle owns limited barrier properties against gas permeation [241]. Many methods have been applied to improve the PET bottle barrier properties and to suppress the permeation of CO<sub>2</sub>, O<sub>2</sub>, and water vapor. In principle, there are two methods to deal with the poor barrier performance of conventional PET bottle. The first one is to cope with a barrier enhancement during the plastic production process, such as blending of melted PET resin before the shaping process with oxygen scavenger additives to reduce ingress of oxygen into PET bottles [242, 243], while the second method is coating a barrier film on the plastic product after the production process, e.g. depositing a DLC barrier coating onto PET foils or bottles [244–246]. Li *et al* [247] demonstrated an ICP enhanced RF CCP source to deposit DLC coating onto PET bottles for reducing OTR. It revealed that the OTR value was decreased over four times compared to non-coated PET film. Deilmann *et al* [248–250] developed a MW driven low pressure plasma reactor for plasma processing of PET foils and bottles. They deposited SiO<sub>x</sub> films onto PET foils as a permeation barrier coating. And good residual permeation as low as OTR of  $1.0 \pm 0.3 \text{ cm}^3 \text{ m}^{-2} \text{ day}$  for SiO<sub>x</sub> coated PET foils was observed. Moreover, they deduced that the critical thickness of SiO<sub>x</sub> coating act as a permeation barrier was about 50 nm. Naima Boutroy *et al* [251] deposited 100 nm thick, transparent, a-C:H films onto inner surface of PET bottle by a plasma-assisted deposition process. A high deposition rate of  $60 \text{ nm s}^{-1}$  can be obtained which was necessary for industrial process. And the deposited a-C:H films provide a 50-fold reduction of OTR.

### 5.3. Electronic encapsulation superhigh barrier films

Organic electronic devices are extremely sensitive to moisture and oxygen. Packaging for any type of organic electronic device is critical important to influence the device's reliability and service. The encapsulation limits are commonly set at  $\text{OTR} < 10^{-4} \text{ cm}^{-3} \text{ m}^{-2} \text{ day}$  and  $\text{WVTR} < 10^{-6} \text{ g m}^{-2} \text{ day}$  proposed by Buows *et al* [252], respectively. For the aim of fulfill the encapsulation requirement, many complex multilayers superbarrier films have been developed and applied in the electronic encapsulation fields [253].

Charton *et al* [254] reported a synergetic effect from the use of the hybrid polymers film in combination with sputtered Al<sub>2</sub>O<sub>3</sub> films. Furthermore, a flexible OLED test device based on the inorganic organic hybrid polymer barrier film was assembled. They demonstrated that lifetime of only one day for test devices encapsulated with uncoated PET, while a lifetime of 2–3 months for encapsulated test devices. Kim *et al* [255] determined relationship between the barrier film performance and shelf lifetime of organic solar cells encapsulated by multilayer barrier films consisting of SiN<sub>x</sub> and parylene. SiN<sub>x</sub> inorganic barrier layers were fabricated by PECVD configured with two parallel plates in a RF supported

plasma to deposit the materials. The parylene organic layers were produced by vapor-phase deposition in a vacuum chamber. By alternating the deposition of organic and inorganic layers, multilayer structures were fabricated. The barrier performance of multilayers was measured through WVTR by Ca corrosion tests [256, 257]. Based on experiment, the organic solar cells encapsulated with three dyads of barrier films consisting of SiN<sub>x</sub> and parylene were predicted to maintain performance for at least 13 500 h.

### 5.4. Anti-transition barrier thin films

Plasticizers in the packaging polymers may damages human body with a variety of adverse outcomes, for example, di-(2-ethylhexyl) phthalate (DEHP), which is one of the most frequently used plasticizers for soft and flexible in PVC film, is not stable and can easily migrate from PVC matrix into foods and food stimulants [258–260]. For the aim of prevention the immigration, Fei *et al* [261, 262] reported a flexible SiO<sub>x</sub> barrier layer deposited onto PVC surface to block the DEHP migration. The SiO<sub>x</sub> coatings deposited by PECVD (CCP, 40 kHz, 20% duty cycle) process were hybrid components of organic and inorganic. Significant improvement of the barrier property to protect against DEHP migration was obtained as the DEHP migration rate was decreased to as low as 3.72 wt% (<5% in regulations of 82/711/EEC). Furthermore, the experimental results indicated that the process parameters had a critical influence on the SiO<sub>x</sub> barrier properties. For example, a smooth surface was crucial for barrier property. Wang *et al* [187] prepared a nano-scaled SiO<sub>x</sub> barrier coatings on PET webs by MW surface-wave assisted PECVD (2.45 GHz). HMDSO and O<sub>2</sub> were used as precursor and oxidant gas, respectively. The optimized OTR value of  $3.69 \text{ cm}^3 \text{ m}^{-2} \text{ day}$  was obtained in  $12 \mu\text{m}$  PET web. For the aim of suppressing the migration of post-consumer compounds from the PET bottle wall into packaged food, Welle *et al* [263] deposited SiO<sub>x</sub> onto the inner surface of PET bottles using an impulse plasma chemical vapor deposition process. They demonstrated that the SiO<sub>x</sub> coating was an efficient barrier layer to post-consumer compounds with maximum surrogate concentrations in the bottle wall corresponding to a migration limit of  $10 \text{ mg l}^{-1}$ .

## 6. Conclusions and future outlook

Since introduced by Langmuir in 1929, plasma technology has become a versatile tool for substantial applications. In the high barrier packaging or encapsulation field, NTP also play an irreplaceable role in improvement of polymer surface properties, enhancement the adhesion of coating or lamination, and the deposition of a lot of functional coating. Mang NTP sources and plasma techniques, such as ICP, CCP, ECR, SWP, DBD, PECVD and PEALD, have been applied into this field. And a large amount of applications associated high barrier packaging is researching and developing more and more, for example, high barrier bottle, electronic encapsulation, and anti-transition barrier thin film etc. This situation has

stimulated the NTP technology to provide more efficient and novel work in high barrier fields. Here we highlight several major trends, which have appeared and will develop in the future based on the NTP technology. (1) The development of flexible transparent barrier film, such as PECVD-SiO<sub>x</sub> or PEALD-Al<sub>2</sub>O<sub>3</sub> barrier film will become more important in the near future. The transparent high barrier film with the excellent performance will gradually replace the traditional Al coating, which is now used widely and everywhere. (2) Novel high barrier, bio-degradable polymers can be realized based on low temperature NTP technology. Some bio-sourced materials, e.g. polylactic acid, whey protein and corn zein, with specific interest, regarding the environment pollution, have merged into the high barrier packaging field. (3) The R2R APP processes, e.g. R2R PECVD and R2R PEALD, have been attempted to realize the production of high barrier thin film in a continuous and large scale process, which is a prerequisite for large-scale packaging application, especially for food and beverage industries. (4) PEALD technique, owing to its self-limiting surface reactions and good conformality with atomic-level thickness control, has been developed for the superhigh barrier encapsulation of flexible organic electronic devices. (5) Fabrication of inorganic/organic multilayer structure is under research for the encapsulation of flexible organic electronic devices. The use of innovative barrier systems will be more and more important and widely.

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