



Opto-electronic Polymer Thin Films Deposited by Glow Discharge Plasma Technique: A Review

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ABSTRACT

The technology of opto-electronic polymer thin film deposition has advanced dramatically during the past 20 years. This advancement was driven primarily by the need for new products and devices in the electronics and optical industries. Increasingly complex tasks are performed by computers, requiring more and more memory capacity as well as faster and faster processing speeds. This leads to a constant need to develop high performance opto-electronic thin film materials, which can be used for the preparation of more highly integrated microchips. The rapid progress in solid-state electronic devices would not have been possible without the development of new thin film deposition processes and superior thin film qualities. Among the broad variety of accessible alternatives, plasma organic polymer film has been one of the most widely studied materials due to its outstanding and promising mechanical and physicochemical properties. In this review, the new opto-electronic polymer thin films deposited by glow discharge plasma technique in recent years is introduced and discussed in combination with our research results. In particular, we focus our attention on the opto-electronic properties of these polymer thin films, such as dielectric property, electric conductivity, non-linear optical property, photo(electro)luminescent property and optical band gap. The corresponding deposition methods of the opto-electronic polymer thin films including plasma polymerization deposition, plasma-enhanced chemical vapour deposition are also reviewed within their respective sections. In summarizing the review, the development, potential applications and future directions of opto-electronic polymer thin films deposited by glow discharge plasma technique are discussed, especially the film properties required for applications in opto-electronic devices.

Key Words:

glow discharge plasma;
opto-electronic property;
dielectric materials;
electric conductivity;
thin film deposition.

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INTRODUCTION

With the significant demand increase of the chemical, physical, biological sensors, micro-electronic devices, electro-luminescent devices, non-linear optical as well as molecular devices which are mainly applied in the fields of mechanics, electronics and optics, organic polymer thin films have attracted a great deal of attention from researchers [1]. This advancement was driven primarily by the need for new products and devices in the electronics and optical industries. The rapid progress in solid-state electronic devices would not have been possible without the development of new deposition processes, improved film characteristics and superior opto-electronic polymer thin film qualities. A great deal has been learnt about these novel opto-electronic polymer thin films over the past several years. We have seen that the driving force towards moving to opto-electronic polymer thin film is their superior optical and electrical characteristics. Furthermore, these polymer thin film materials are lightweight, easy to apply, and available from several commercial sources. Although great efforts have been devoted to this area, applications of opto-electronic polymer thin films in commercial processes have been rather slow

and only a few of these organic polymer thin films have been successfully used in electronic and photonic devices due to their poor thermal stabilities, chemical stabilities and bad mechanical toughness [2]. Plasma polymerization deposition or plasma-enhanced chemical vapour deposition (PECVD) is now gaining recognition as an important technique for direct film deposition of entirely new kinds of polymeric films, which are hardly possible to obtain by the conventional methods, and the films obtained by plasma technique are generally of high quality, homogeneous, adherent and pinhole free [3,4].

Compared with other deposition methods, plasma polymerization deposition shows the advantage that the starting feed gases used may not contain the type of functional groups that are normally needed in conventional polymerization. Thus, most of the hydrocarbons without functional groups, such as methane, ethane and cyclohexane, can also be used as the precursor in plasma polymerization [2]. Moreover, plasma polymerization deposition is more easily integrated into existing fabrication processes, and it offers the advantage of solvent-free operation. Thus, there is no solvent to be removed after deposition, and in multilayer deposition schemes, there is no problem of swelling of the lower layer

Table 1. Comparison of the deposition method of polymer films.

Deposition methods	Advantages	Disadvantages
Sol-gel	<ul style="list-style-type: none"> - Prepare solids with pre-determined structure - Lower temperature of preparation - Better purity - Better homogeneity 	<ul style="list-style-type: none"> - High cost of raw materials - Large shrinkage during processing - Residual fine pores - Health hazard of organic solution - Long processing time
Spin-coating	<ul style="list-style-type: none"> - Most polymers can be used - Well-known structures - Specific design 	<ul style="list-style-type: none"> - Multilevel structures - Baking, shrinkage and cracking - New equipment necessary - Health hazard of organic solution
Plasma polymerization	<ul style="list-style-type: none"> - Compatibility with processing equipment - No solvent removal necessary - No swelling in multilevel structures - Chemical inertness, good mechanical properties and thermal stability, weather resistance, and easy shaping 	<ul style="list-style-type: none"> - Deposited structures sometimes uncontrolled - Structure characterization and optimization difficult

during deposition of the top layer. Table 1 compares the three approaches used for the preparation of polymer films.

To prepare a more polar polymer film, hydrocarbons containing more polar groups like pyridine and allyl amine may be needed. In recent years, fluorocarbons have been widely used in plasma polymerization in order to prepare high performance low dielectric constant materials, since the resulting film might show high adherence to the substrate and good thermal stability. Moreover, with higher demand in low dielectric constant materials, some linear and cyclic siloxanes have been also tried in plasma polymerization. At the same time, in order to obtain polymer thin film with better electrical conductivity, volatile organometallic compounds or atomic metal (from an evaporation source or sputtering) have been used as feed gases.

The continuous advancement of microelectronics in all fields of technology has become a basic fact of our daily life. Increasingly complex tasks are performed by computers, requiring more and more memory capacity as well as faster and faster processing speeds. This leads to a constant need to develop high performance opto-electronic materials, which can be used for the preparation of more highly integrated microchips. Among the broad variety of accessible alternatives, plasma organic polymer film has been one of the most widely studied materials due to its outstanding and promising mechanical and physicochemical properties. This takes advantage of the unique combination of excellent chemical inertness, good mechanical properties, thermal stability, electrical properties, safety, weather resistance and easy shape formation. Thus, opto-electronic polymer thin films have been considered to be potentially attractive materials for opto-electronic device application. Although intensive research efforts have been devoted to the polymer deposition thin films in recent years due to their potential applications in LEDs, sensors, EMI shielding, photovoltaic devices and dielectric materials on the chips, to the author's knowledge, reviews on the opto-electronic polymer thin films deposited by glow discharge plasma are scanty, especially, reviews on the opto-electronic properties of these plasma polymer thin films, such as non-linear

optical property, photo(electro)luminescent property, dielectric property and optical band gap, have not yet been found in literature. This review focuses on opto-electronic properties of organic polymer thin films deposited by glow discharge plasma technique. The opto-electronic properties of the plasma polymer thin films are discussed as required for the application and to allow a comparison of different polymer thin films. Especially, we focus our attention on the preparation techniques, chemical structures, the related properties and future development directions of plasma polymer thin films materials. The aim of this review is to provide a concise reference and description of the opto-electronic polymer thin films deposited by glow discharge plasma. Emphasis is placed on the most recently developed opto-electronic properties of plasma polymer thin films for applications in high technology.

OPTO-ELECTRONIC POLYMER THIN FILMS

Dielectric Polymer Thin Films

One of the exciting and promising developments in material science today is the design and synthesis of novel low dielectric constant polymer materials, which are found to have potential applications in the field of ultra large-scale integration (ULSI), capacitors and other electronic circuits as insulating and/or dielectric materials [5,6]. With ultra large-scale integration and deep submicron device dimensions approaching 0.13 μm , the performance of microelectronic devices is seriously inhibited by the increase in the resistance-capacitance (RC) time delay, cross-talk noise and power dissipation of the interconnected structure [3,7,8]. It has been reported that the delay, cross-talk and power dissipation all depend critically on the dielectric constant of the separating insulator. Thus, development of new materials with lower dielectric constants is now being considered as one of the most important issues in electronics industry.

Films Made up of Hydrocarbons

Plasma polymer thin films which possess a relatively low dielectric constant value and good thermal stability are now being studied intensively. Jo et al. [9] have tried methylcyclohexane as the precursor in

inductively coupled plasma-enhanced chemical vapour deposition. Methylcyclohexane, with a ring structure and a methyl group, both of which were non-polar and thought to be important in producing thin films with both low k values and high thermal stability. They have investigated the influence of the inductively coupled plasma power (ICP) and the substrate bias (SB) power on the properties of plasma polymerized methylcyclohexane (PPMCHex) thin films, and they found that with the increasing of ICP power or the SB power, the deposition rate and the k value increased, and the lowest k value can reach is 2.63 at 1 MHz, and the thickness of the depositing film can be from 3000 to 5000 Å. When fixing the ICP power, the thermal stability of the PPMCHex films significantly increases with the SB power, however when fixing SB power, the thermal stability did not show such great increase with the ICP power. When the SB power ≥ 30 W while the SB power = 10 W, the resulting films can be stable up to 450°C. PPMCHex with low dielectric constant value and good thermal stability is a promising material used for interlayer by optimizing the plasma power during polymerization.

Other ring containing precursors are also good candidates for making low dielectric plasma polymer thin films. Mitu et al. [10] have successfully deposited parylene-like films by plasma polymerization using di-*p*-xylylene which is a solid dimer as precursor. The research was carried out in a tubular reactor with external electrodes with the radio frequency as 13.56 MHz, a deposition rate of about 4 ~ 250 nm.min⁻¹ can be obtained by changing the RF power and gas flow rate, at the same time, various morphologies and composition layers can be obtained, it can be rough semi-crystalline, smooth amorphous, polymer-like and hydrogenated carbon-like films.

Aside from the above findings, thin polymeric films of biphenyl by plasma polymerization technique using a capacitive-coupled reactor have been also prepared by Chowdhury et al. [11]. In their study, the dielectric properties of as-deposited and heat treated (423 K for 1 h) plasma polymerized biphenyl films from 10¹ to 10⁶ Hz and from 223 to 423 K have been described. They have found that the dielectric constant is dependent on temperature up to 10³ Hz. Moreover, they have also revealed that there

are different relaxation processes in the plasma deposited polymer thin films, for the as-deposited films, the α -relaxation is due to the molecular group motion in the film structure and β -relaxation is related to the pendant group motion at about 300 K on the dielectric loss thermograms, while for the heat treated film, it only has a prominent α -relaxation whereas the β -relaxation is very weak.

Bis-benzocyclobutene (BCB) [12] and siloxane bis-benzocyclobutene (DVS-BCB) are often used as precursors for spinning coating method to prepare low dielectric constant polymer thin film. One great advantage of spin coating is easy to design the chemical structure of a low- k film since the polymerization reaction uses thermal energy; however, it bears a serious concern of poor adhesion to the under-layer film at the same time. Its low adhesion might be caused by the surface contamination of the under-layer film by gaseous molecules or solvent molecules before the monomer polymerization under atmosphere condition. In order to obtain a good adhesion and better stability of the resulting film, Kawahara et al. [13] have made divinyl siloxane bis-benzocyclobutene (DVS-BCB) polymer film for Cu dual-damascene interconnects using PECVD. The process consists of the vapourization of organic monomers, transportation of monomers in the gas phase and polymerization by plasma to make the polymer film. During the polymerization in high vacuum, polymer oxidation of DVS-BCB can be eliminated. The thermal stability of plasma-polymerized BCB (*p*-BCB) with dielectric constant as 2.6 exceeded 400°C under the condition of higher deposition temperature, and had a high resistance to Cu diffusion at 400°C annealing. Meaning while, Trabzona et al. [14] have tried to change the material properties of BCB by plasma treatment, and found that plasma treatment can induce anisotropy in dielectric constant, at the same time, current leakage across the BCB increases substantially with the plasma treatments which is suggested to be caused by the plasma-polymer interaction which resulted in band reorientation as well as band spatial distribution.

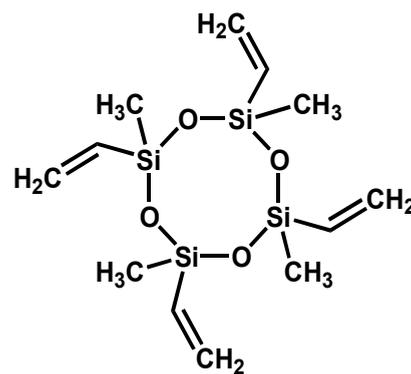
Aside from precursors with ring structure, pure methane has also been used to deposited low dielectric constant amorphous hydrogenated carbon

layers (a-C:H) thin film from discharges in Microwave Multi-polar Plasma excited at Distributed Electron Cyclotron Resonance [15]. Furthermore, the relationship between the physicochemical and electrical properties of the resulting film and process parameter has been investigated. The results show that plasma discharge power is a significant factor influencing the film density and the concentrations of sp^3 - and sp^2 -hybridized carbon atoms which are also influenced by the deposition time. Under the condition of high plasma discharge power and/or long deposition time film with low sp^2 fraction will be obtained, and the density of the film is decreased with the plasma discharge power. Finally, films with different structures, composition and density exhibit a dielectric constant from 2.3 to 3.8 by changing the process parameter-deposition time and microwave power.

Silicon Containing Films

As for interlayer application, the polymer thin films should not only meet the requirement of low dielectric constant, but also need to meet a demanding list of electrical, chemical, mechanical and thermal requirements. In order to balance the process compatibility and the dielectric performance, much effort has been made on preparing polymer thin films with both organic atoms which can provide low dielectric constant and inorganic atoms especially Si which provides mechanical strength [3].

To prepare low dielectric constant polymer thin films, the precursor-containing silicon used most often is siloxane, such as tetraethoxysilane, tetravinyltetramethylcyclotetrasiloxane (TVTMCTS) [16], methyltriethoxysilane [17], etc. Lubguban et al. [16] have synthesized low dielectric constant with the value from 2.5-2.9 using a new liquid precursor, TVTMCTS and H_2 carrier gas under different pressures and temperatures through PECVD. In order to maintain the original ring in the structure, low radio frequency power was used. At the optimum deposition pressure of 1.75 torr and a temperature of 23°C the obtained film showed the lowest dielectric constant of 2.65 which was dependent on the concentrations of Si-CH₃ bonds and of siloxane rings. The films were thermally stable up to 400°C annealing temperature with respect to their dielectric



Scheme 1. Structure of the tetravinyltetramethylcyclotetrasiloxane (TVTMCTS).

and structural properties. Scheme I shows the chemical structure of TVTMCTS.

Meanwhile, Wu et al. [18] have successfully prepared low dielectric films by pulsed plasma-enhanced chemical vapour deposition with the mixtures containing methylsilane (1MS), dimethylsilane (2MS) or trimethylsilane (3MS). They revealed that the refractive index was strongly dependent on methyl content, while relatively independent on the precursor used. The bonding structure of the resulting film was significantly dependent on the precursors used though ^{29}Si nuclear magnetic resonance tests. After annealing under nitrogen performed at 400°C for 1 h, 400°C for 2 h, and 550°C for 1 h and 85% relative humidity treatment for 10 h, all the films which were grown from 1MS, 2MS and 3MS, showed no significant change in the concentration of the CH₃ and Si-CH₃ compared to the as-deposited films, these all indicate that the Si:O:C:H films have high thermal stability and very low moisture uptake. For dielectric constant, it increased with the plasma power, and value of about 2.4-2.6 was obtained for the post-annealed films. With 1MS, 2MS and 3MS alone as precursors for PECVD respectively, under the same condition, films with 3MS showed the lowest dielectric constant which could be related to the increase in Si-CH₃ and decrease in Si-O concentrations in the film.

Hexamethyldisiloxane (HMDSO) is another good candidate for low dielectric constant thin polymers using PECVD. Borvon et al. [19] have prepared ppHMDSO and ppHMDSO(Ar) films with the dielectric constant of about 3 which can be stable to 400°C.

The ppHMDSO showed very weak leakage current density of less than 10^{-10} A/cm² at low electric field. These electric properties of ppHMDSO film make it more promising in interlevel dielectric applications.

All suggested SiOCH films deposited by PECVD using a mixture of a hydrocarbon precursor and a Si-containing precursor can produce films with both low *k* values and high thermal stability, and some researchers have proved this through their results. There are reports that by post deposition heat treatment there is a decrease in *k* value of the films. Yang et al. [20] have investigated the effects of post deposition by in situ heat treatment on the properties of low dielectric constant plasma polymer films deposited using decahydronaphthalene and tetraethyl orthosilicate as the precursors. They have found that after being subjected to in situ heat treatment of 350, 450 and 500°C for 30 min with Ar pressure of 0.3 torr, the dielectric constants of the films have decreased to 2.82, 2.72 and 3.16, respectively, compared to the as-deposited film. The FTIR results show that the decrease in *k* value at 350°C thermally treated plasma polymerized decahydronaphthalene: tetraethyl orthosilicate (PPDHN:TEOS) film compared to that of as-deposited film primarily due to the reduction of O-H and C=O groups, the decrease at 450°C treated was caused by the evaporation of organic species from the film while for 500°C treated, the decrease level of dielectric constant is smaller than that of 450°C, and this is the results of structural change of the bulk film caused by much greater organic species evaporation.

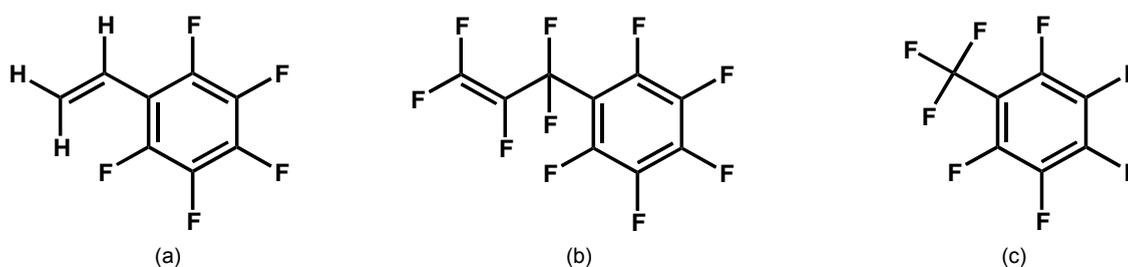
Moreover, as the dielectric constant of the air is only about 1, the introduction of microporous or nanoporous [17,21] is a very effective way to lower the total dielectric constant of the bulk films. Han et al. [22] have prepared low *k* thin films by radio

frequency plasma-enhanced chemical vapour deposition at 400°C using tetramethylsilane (4MS), or the mixture of tetramethylsilane and silane (SiH₄) as precursor and nitrous oxide as the oxidant gas. Two types of films with excellent thermal stability (as high as 400°C) and a constant about 3 have been obtained and characterization results of Fourier transform infrared and X-ray photoelectron spectroscopy show that both films have similar chemical composition and structure. The results also show the Si-O-Si [23] cage structure which can produce microporous structure in films as with further decreases in dielectric constant there would be increases in cage structure and the carbon concentration.

Fluorine Containing Films

It is well known that the incorporation of fluorinated substituents into polymers decreases the dielectric constant due to the small dipole and the low polarizability of the C-F bond. Meanwhile, the advantage of high thermal and oxidative stability, chemical resistance and low moisture absorption make fluoropolymers especially those containing aromatic ring more attractive in the development of dielectric materials. Pentafluorostyrene, perfluoroacrylic benzene (PFAB) and perfluorotoluene have been employed as monomers to synthesize low dielectric constant thin film materials. Their corresponding chemical structures are shown in Scheme II.

Han et al. [24,25] have used above mentioned monomers with a variable duty cycle pulsed plasma for polymerization. After a series of characterizations of infrared and X-ray photoelectron spectroscopy, dielectric constant, thermal stability, as well as surface energy measurements tests, they found that in the case of pentafluorostyrene, a tail-off phenomenon in dielectric constant and thermal stabilities are



Scheme II. The structure of the fluorinated monomers: (a) pentafluorostyrene, (b) perfluoroacrylic benzene and (c) perfluorotoluene.

observed when using pentafluorostyrene as monomer and while using perfluoroacrylic benzene (PFAB) as monomer, the retention of the aromatic ring of the starting monomer is increased with the decreases in plasma duty cycle during polymerization, and the dielectric constants of all the films are below 2.0. One of the serious disadvantages of these films is its bad thermal stability below 300°C which showed a weight loss of above 70%. In order to improve this, annealing has been incorporated, and the resultant annealed films showed negligible weight loss as the temperature was raised to maximum 420°C with only minor increase in the dielectric constant. However, the gain in thermal stability of these films is accompanied by a significant shrinkage in thickness of the dielectric thin films. When using pure perfluorotoluene as monomer, the polymerized films exhibit poor thermal stability as well, and based on this situation, Zhu [26] tried to resolve it by introducing hydrogen or methane onto perfluorotoluene, and found significant improvement in the thermal stability of the resultant films.

To obtain a film which could exhibit good adhesion to a variety of substrates, excellent chemical inertness and high thermal resistance, it is very important to control its chemical structure during polymerization. To better manipulate the structure and properties of the plasma films, Jiang et al. [4] have deposited films from benzene and octafluorocyclobutane (OFCB) by changing the deposition parameter of pressure within the reactor and the monomer feed location relative to the plasma zone to investigate the relationship between chemical structure and dielectric constant. In their research, the two different monomers feed locations were directly in the plasma zone or in the downstream region (DS), the two different pressures, 80 Pa (high pressure) or 6.7 Pa (low pressure), have been used, respectively. After examining the chemical structure of the plasma films by X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy, the dielectric constant and dielectric loss over a range of frequencies up to 1 MHz, dielectric strength (breakdown voltage) by current-voltage method, thickness and index by spectroscopic ellipsometry, they found that plasma polymerized benzene films under high pressure show good dielectric properties and the

resultant film cross-link density was the key factor influencing the breakdown strength, the plasma polymerized benzene films which show a highest value of about 610 V/μm which exhibit high average dielectric strength than that of OFCB. For OFCB molecules are more difficult in terms of reaction initiation, the higher breakdown strength (325 V/μm) only can be obtained under the condition of plasma zone reaction and high pressure environment compared to PP-OFCB films. Furthermore, they also observed that a continuous decrease in dielectric constant and a significant increase in the dielectric loss was a function of applied frequency, and C=O polar content plays a key point in affecting the frequency dependency of both dielectric constant and dielectric loss.

In addition, it has been reported that both silicon and fluorine containing films with a dielectric constant value as low as 2.0 and good thermal stability films [27] have been prepared by PECVD using gas precursors of tetrafluorocarbon as the source of active species and disilane (5 vol% in helium) as a reducing agent to control the ratio of F/C in the films.

Heterocyclic Polymer Films

The employment of ac/rf plasma polymerization can produce high quality thin films which are homogeneous, pinhole free and thermally stable. Polyaniline, for their good thermal and electronic properties, has attracted considerable interest due to its potential applications in ultra large scale circuit as interlayer dielectrics. Matha et al. [28,29] have prepared polyaniline using ac plasma polymerization, and investigated the dielectric constant and ac conductivity in the frequency range from 100 Hz to 1 MHz and in the temperature range of 300~373 K. All the dielectric constant values of the resultant films were low in the whole range, and capacitance and dielectric loss decreased with frequency and increased with temperature which fits well with an existing model. Like other plasma polymerized thin films, after annealing in the high vacuum at 373 K for 1 h, the dielectric loss of polyaniline was reduced. Simultaneously, aromatic ring was found retained in the plasma polymerized polyaniline which thought to increase the thermal stability.

Poly(quinoline)s, non-polar, often exhibit very high thermal stabilities with decomposition

temperatures to maximum 600°C even in air. Thus by incorporating functionalized quinoline rings into polymer backbones, desired polymers with high performance can be reached. Recently, Zhao et al. [30] have prepared high quality low dielectric constant plasma-polymerized 1-cyanoisoquinoline (PPCIQ) thin film with a roughness of 0.53 nm by the plasma polymerization technique using 1-cyanoisoquinoline as precursor. PPCIQ thin film deposited at 15 W gives a low dielectric constant (k) of 2.62, probably resulting from lower density of the film due to the higher retention of the aromatic ring (space occupying groups), which might be a potential candidate to be used as intermetallic dielectrics in microelectronics. Furthermore, the variation of dielectric constant with frequency in the range from 100 kHz to 1 MHz, and the variation of the dielectric loss factor ($\tan \delta$) as a function of frequency are also investigated. From the result, it is clear that in the above-mentioned frequency range there is an increase in dielectric constant with a decrease in frequency while the dielectric loss factor increases with increase in frequency.

Poly(nitrile)s synthesized by plasma polymerization are now becoming a class of rising polymers for dielectrics due to their good adhesion to substrate, nice thermal stability, especially low dielectric constant after introducing large occupying groups in their backbone. Zhao et al. [31] reported plasma-polymerized 4-biphenylcarbonitrile (PPBPCN) thin films synthesized by plasma polymerization technique. A uniform and defect-free conjugated polynitrile thin film with a dielectric constant value of about 2.5 can be achieved when a low discharge power of 25 W was used during film formation. The dielectric measurement also shows that the dielectric constant of PPBPCN thin films is decreased with frequency and increased with temperature.

Polythiophene thin films on glass and silicon substrates in the deposition temperature range of 300–673 K using the thiophene precursor by PECVD method for low dielectric and optical devices applications have been reported [32]. The lowest dielectric constant was 2.96 for a thin film grown at 373 K and RF power of 50 W, and the highest deposition rate was approximately 110 nm/min at 300 K and RF power of 100 W, respectively. Under

the condition of Ar:H₂ = 1:1, RF power of 50 W and 300 K, the best leakage current density was obtained to be below 10⁻¹⁰ A/cm² at applied field of 1 MV/cm.

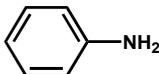
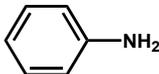
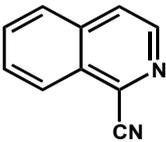
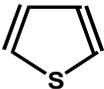
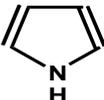
Plasma polymerized thin film from pyrrole is supposed to be another promising candidate as dielectric materials. Kumer et al. [33] have prepared such films by radio frequency plasma polymerization. The dielectric properties of the films were studied in the frequency range from 1 kHz to 1 MHz at various temperatures from 303 K to 423 K, and test results showed that the capacitance significantly increased at low frequency region which is thought to be caused by possibility of an interfacial polarization mechanism prevailing in that region. In the frequency range of 100 kHz to 1 MHz, the dielectric constant is more or less constant with the frequency, and at room temperature, the value can be as high as 3.8, as all these properties together with good stability and chemical inertness made it much more suitable for capacitor material. Table 2 shows the dielectric properties of polymers synthesized by plasma polymerization.

Thin Films with Electrical Conductivity

Conductive polymers are based on conjugated structural systems. Conjugated polymers exhibit insulating or semiconductive properties in their virgin states and become conductive by doping. It has been reported that conductive polymer thin films have great potential for use in opto-electronic devices. Since the conductive polymers with delocalized π -electrons offer unique physical properties which are unattainable in conventional polymers, so development of new π -conjugated polymers films with high conjugation lengths and degree of inter-chain order are strategically possible to attain better materials for the application of conducting or semiconducting material. It has been reported that the plasma-polymerized thiophene, pyrrole and aniline thin films can possess an electrical conductivity of about 10⁻⁴ even 10⁻² $\Omega^{-1}\text{cm}^{-1}$. Thus, a great deal of work has been done in order to better understanding of the conductive property of plasma polymer films.

Polythiophene (PTh) is one of the promising conductive polymers, which is stable in air and can be easily processed. The preparation of semiconductive organic polymer thin film by plasma polymerization

Table 2. The dielectric properties of different plasma polymers.

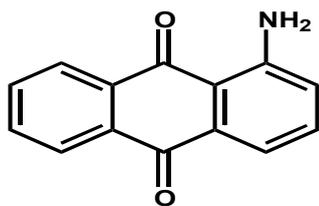
Plasma polymers	Chemical structure of monomers	Dielectric constant	Reference
Polyaniline		1.18~2.90	[28]
Polyaniline		1.20~1.45	[29]
Polyquinoline		2.62	[30]
Polynitrile		2.50	[31]
Polythiophene		2.96	[32]
Polypyrrole		3.80	[33]

of 1-benzothiophene has been reported. Lately, Bhat et al. [34] have fabricated plasma-polymerized thiophene films at high radio frequency (rf) flux density region near the monomer inlet within a tubular reactor, the glow discharge was obtained at low pressure (0.5 torr), using a 13.56 MHz rf source. However, the electrical conductivities of the highly cross-link thin films with different thicknesses were very low (between 10^{-15} - 10^{-10} S/cm) compared to conventional methods. The electric conduction of the films with morphology of globular was found to be space charge-limited current. Meanwhile, plasma-polymerized thiophene thin film, with a high retention of the conjugated monomer structure or less fragment during deposition is thought to demonstrate a higher electric conductivity. To better understand the influence of the substituents on fragmentation during deposition, Groenewoud et al. [35] chose methylated and halogenated thiophenes as monomers and used them to prepare the conductive polythiophene thin films by means of plasma polymerization technique. They found that methylated thiophenes show a low degree of fragmentation during deposition, whereas for halogenated thiophenes a high degree of fragmentation was observed, besides, another interesting

finding is that substitution on the 2-position results in less fragmentation compared with substitution on the 3-position for a specific substituent. Furthermore, they obtained a series of films with high electric conductivity through iodine doping, and after that a higher conductivity was found for the methyl-substituted thiophenes compared with non-substituted thiophene and halogenated thiophenes.

John et al. [36] and Cruza et al. [37] have investigated the electric property of plasma-polymerized and iodine-doped polypyrrole (PPy). According to their studies all the films undoped or doped show a hygroscopic behaviour and consequently the conductivity is increased at relatively higher humidity. In addition, PPy films show higher absorption than iodine-doped PPy films; however, iodine-doped PPy films displayed a big increase in conductivity when the films absorbed enough water.

Like pyrrole, aniline has also being used as precursor in iodine-doped plasma polymerization for semiconducting application [38]. Sajejev et al. [39] have prepared pristine and in situ iodine-doped polyaniline thin films by ac and rf plasma polymerization techniques. The conductivity measurements show that films deposited from rf plasma



Scheme III. Chemical structure of 1-amino-9,10-anthraquinone.

polymerization show a higher value than that from ac plasma polymerization, and also, the value of conductivity increased after doping by iodine, which is thought to be caused by lowering of binding energy of the polymer after the introduction of iodine in its backbone.

Besides doping with plasma-polymerized pyrrole and plasma-polymerized aniline alone, efforts have been also made to investigate the effect of

iodine-doping on conductive property of the plasma-polymerized copolymers composed of aniline and pyrrole [40,41]. Also, the humidity sensitivity rule has been found for these plasma-polymerized copolymers.

Drachev et al. [42,43] have deposited thin films with 1-amino-9,10-anthraquinone in a direct current discharge plasma polymerization technique. The chemical structure of monomer 1-amino-9,10-anthraquinone is shown in Scheme III. The results show that the film deposited on the cathode with a polyconjugated structure show the electric conductivity of 10^{-5} - $10^{-4} \Omega^{-1}\text{cm}^{-1}$, while the layers deposited at anode show low dielectric constant properties.

Plasma polyfurfural film is another good candidate for semiconducting material. Plasma-polymerized furfural thin films with different thickness values were prepared by ac plasma polymerization technique

Table 3. The electric conductive properties of different plasma polymers.

Plasma polymers	Chemical structure of monomers	Electric conductivity (current density)	Reference
Polythiophene		10^{-15} ~ 10^{-10} S/cm	[34]
Polythiophene derivatives		1.78×10^{-7} ~ 5.62×10^{-4} S/cm	[35]
Polyaniline		10^{-8} ~ 10^{-5} A/cm ²	[39]
Copolymers of aniline and pyrrole		10^{-12} ~ 10^{-9} S/cm	[40]
Polypyrrole		10^{-11} ~ 10^{-6} S/cm	[41]
Polyaniline		10^{-11} ~ 3×10^{-9} S/cm	[41]
Polyfurfural		2.0×10^{-10} ~ 1.2×10^{-9} A/cm ²	[44]
Polypyrrole		1.0×10^{-7} ~ 8.5×10^{-7} A/cm ²	[45]

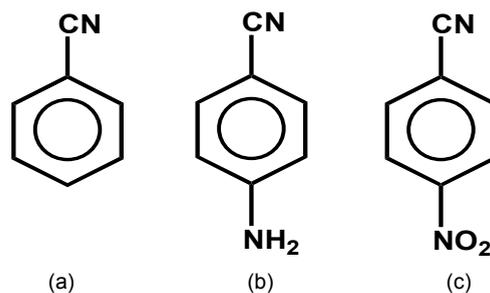
[44]. It was found that the conduction is an activated process with activation energy decreasing from 0.54 to 0.50 eV as the bias voltage is increased and Schottky type conduction is dominant in plasma-polymerized furfural thin films. Table 3 shows the electric conductive properties of polymers synthesized by plasma polymerization.

Thin Films with Non-linear Optical Property

Since the advent of non-linear optics, there has been a long and sustained interest in organic and polymeric materials with significant non-linear optical (NLO) properties. The interest is driven by the need for devices for optical signal processing, all-optical switching, optical computing, bi-stable elements, logic devices and sensor protection [46,47]. The criteria for practical applications and device fabrication include high non-linear susceptibility, fast response times, adequate optical transparency, excellent environmental stability and good processability for multilayer integration into large-area devices. Plasma polymerization is gaining recognition as an important technique for direct film deposition of entirely new kinds of NLO polymeric materials. In recent years, interests have been transferred to improve the non-linear performance by structure modification while not simply lengthening the conjugated structure. As the conjugated structure cannot only be formed by carbon atom, but also some other atoms, attempts have been made to prepare heterocyclic polymer thin films with good NLO property.

In comparison with other conjugated polymers, polynitrile has been found to be an unusual class of polymers with good environment stability, optical transparency, large second-order hyperpolarizability as well as excellent and reproducible electrical bistability property. Wang et al. [48] have studied the non-resonant optical non-linearity of the polybenzotrile at a wavelength of 647 nm using the sub-picosecond time-resolved optical Kerr effect, and investigated the relationship between the second-order hyperpolarizability (γ_{1111}) and the average-polymerization-degree (m) of plasma-polymerized benzotrile.

The results show that the linear fit corresponds to $\gamma_{1111} = m^{2.4}$, when $m < 12$.



Scheme IV. Chemical structures of monomers: (a) benzonitrile, (b) aminobenzotrile and (c) nitrobenzotrile.

At the same time, Zhao et al. [49-51] have successfully prepared plasma-polymerized benzonitrile (PPBN), plasma-polymerized aminobenzotrile (PPABN) and plasma-polymerized nitrobenzotrile (PPNBN). The chemical structures of three monomers are shown in Scheme IV. Their results revealed that smooth and homogeneous plasma-polymerized polybenzotriles films with strongly delocalized electrons along the backbones could be obtained at the relative lower discharge powers. In the case of higher discharge powers, some distinct folds were formed on the surface of plasma polymer films owing to the higher film deposition rate. All the deposited polynitrile thin films show fast response speed and large non-linear optical susceptibility.

In succession, the second-order hyperpolarizabilities (γ) of poly(*p*-methylbenzotrile) and poly(*p*-hydroxybenzotrile) (PHBN) measured by femtosecond time-resolved optical Kerr effect at 820 nm have been reported. The results show that these polynitriles have large non-resonant third-order optical non-linearities, the non-resonant γ as large as 4.8×10^{-32} esu can be obtained for PHBN with only eight conjugated bonds [52]. These polynitriles show higher γ compared to the structure of similar material with the same conjugation length.

Wang et al. [53] have developed a newly plasma-polymerized polynitrile derivative thin film, poly(1-isoquinolinecarbonitrile) (PPIQCN). Their results show that a transparent, smooth and homogeneous PPIQCN film with a large π -conjugated system can be formed at low plasma discharge power of 10 W; a high discharge power of 30 W can bring about more severe molecular (aromatic ring) fragmentation, and thus, the conjugation length of PPIQCN film decreases due to formation of a non-conjugated

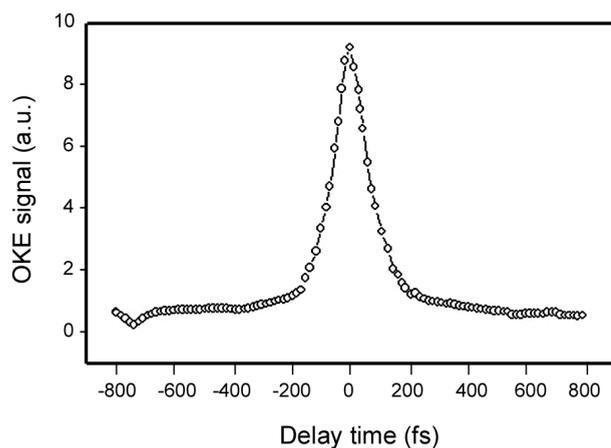


Figure 1. The ultrafast OKE response signals of PPIQCN10 thin film.

polymer. The third-order non-linear susceptibility ($\chi^{(3)}$) of PPIQCN10 film in the non-resonant region is as large as 8.8×10^{-12} esu, larger than that of plasma-polymerized benzonitrile films. This indicates that the delocalized electrons of the quinoline ring would contribute more to the main chain than the benzene ring. Moreover, the ultrafast response was observed in PPIQCN10 film and the time constant was found to be approximately 130 fs. The temporal evolutions of optical Kerr effect (OKE) response of PPIQCN10 film is shown in Figure 1.

Lately, Zhao et al. [54] reported the preparation and NLO property of plasma poly(4-biphenylcarbonitrile) (PPBPCN) thin films. The results show that a large π -conjugated system can be formed in the PPBPCN thin films at low plasma discharge power of 30 W, and the plasma polymerization of 4-biphenylcarbonitrile monomer took place mainly through the opening of the π bonds of $C\equiv N$ functional group. A high discharge power of 50 W

brings about more severe molecular (aromatic ring) fragmentation, and thus, the conjugation length of PPBPCN films decreases due to forming a non-conjugated polymer. The third-order non-linear susceptibility ($\chi^{(3)}$) of PBPCN30 thin film in the non-resonant region is 6.2×10^{-12} esu, larger than that of plasma-polymerized benzonitrile. This indicates that the electron cloud of the biphenyl ring would contribute more to the main chain than the benzene ring. Table 4 shows the NLO property of different plasma-polymerized nitriles.

Optical Band Gap

Fluorinated amorphous carbon film has become a promising candidate in large scale integrated circuits for its low dielectric constant. In the mean time, it has been discovered to be a good optical material with low index and small dispersion which is very critical for practical applications. There are many parameters which influence the optical band gap such as fluorine concentration, concentration of aromatic (sp^2 bonded) carbon, the degree of conjugated $C=C$ bonds or graphite-like sp^2 structures in the films. Lately, Ye et al. [55] have measured optical band gap of fluorinated amorphous carbon films by electron cyclotron resonance plasma chemical vapour deposition using trifluoromethane (CHF_3) and benzene (C_6H_6) as the source gases with the parameters as follows: input microwave power of 140–700 W, pressure of 0.1–1.0 Pa and CHF_3/C_6H_6 flow ratio of 1:1–10:1. The optical gap (E_g) of the a-C:F films was studied in the range of 1.76–3.98 eV. The results show that E_g increases with the amount of fluorine while decreases with the increased amount of $C=C$ bonding.

As mentioned above, we all know that iodine-doping has been used to enhance the conductivity of

Table 4. The non-linear optical (NLO) property of polynitriles synthesized by plasma polymerization.

Polynitriles	Monomers	NLO property (esu)	Reference
PPBN	Benzonitrile	$\chi^{(3)} = 3.0 \times 10^{-12}$	[49]
PPABN	Aminobenzonitrile	$\chi^{(3)} = 3.3 \times 10^{-12}$	[50]
PPNBN	Nitrobenzonitrile	$\chi^{(3)} = 3.8 \times 10^{-12}$	[51]
PHBN	<i>p</i> -Hydroxyl-benzonitrile	$\gamma = 4.8 \times 10^{-32}$	[52]
PPIQCN	1-Isoquinolinecarbonitrile	$\chi^{(3)} = 8.8 \times 10^{-12}$	[53]
PPBPCN	4-Biphenylcarbonitrile	$\chi^{(3)} = 6.2 \times 10^{-12}$	[54]

the plasma-polymerized pyrrole (PPPy) and plasma-polymerized aniline (PPAN). It has been found recently that the iodine-doped PPPy [56,57] and PPAN [58] thin films show a lower band gap energy. Kumer et al. [56] have prepared undoped and doped PPPy films with band gap energies of 1.3 and 0.8 eV, respectively. Comparing the IR and SEM test results of the doped and undoped films, they found that the doping iodine is not bonded in any manner to the polymer chain of PPPy. However, it does make the surface morphology of the PPPy film smoother. John et al. [57] have carried out such research as well and found that the aromatic ring from the monomer retained in the resulting films as well as the optical band energy decrease after doping. Mathai et al. [58] have prepared pure and iodine-doped polyaniline by ac plasma polymerization, and the doping is being carried out in situ by employing iodine chamber methods. From structure analysis of FTIR and optical band gap evaluation from UV-vis of these films, they discovered that the aromatic ring in the monomer is retained in the resulting film and the band gap of the iodine chamber doped samples show a great reduction but increase to the undoped value after heat treatment while for the in situ doped polyaniline thin films, the band gap is only lightly changed with heat treatment. Therefore, an in situ doping method is more reliable than chamber doping for a permanent band gap.

Besides, *Lavandula angustifolia* essential oil [59] has been used to prepare transparent plasma polymerized thin films under varying RF power levels. UV-Vis spectroscopy in the wavelength range of 200~1000 nm (6.199~1.239 eV) has been used to

investigate the optical properties. The results show that the film with the polymerization degree of 3 is the best density state distribution for optical band gap tests, and the optical band gap decreases with the increase of RF power, the value at 10 W is 2.75 while at 75 W is 2.34.

Recently, a new monomer named non-synthetic terpinen-4-ol [60], has been used to prepare plasma polymer thin films with optical property by plasma polymerization technique. Films with smooth, homogeneous and defect-free surfaces can be obtained when the discharge power is 25 W. The results of optical studies in the wavelength range of 200~1000 nm show that the optical band gap of the fabricated film is about 2.67 which makes it a promising candidate for electronics, optics and biomedical industries applications. Table 5 shows the optical band gap of different plasma polymers.

Thin Films with Photo(electro)luminescent Property

The designs of new conjugated polymers with high conjugation lengths and degree of inter-chain order are a possible strategy to attain, through a reduction of the competing non-radiative decay processes, better materials for light emitting diode (LED) and photodiode applications [62]. Plasma-polymerized conjugated thin films with extensively delocalized π -electrons along the backbones have been proven to be a kind of optical materials with applications as the molecular photonic, electronic and electroluminescent devices due to their strong delocalization of electrons contributing to a large and fast optical response [63,64]. The interesting optical properties of

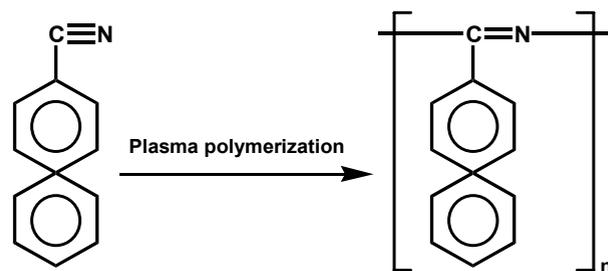
Table 5. The optical band gap (E_g) of plasma polymers.

Monomers	Optical band gap, E_g (eV)	Reference
Trifluoromethane, benzene	1.76~3.98	[55]
Pyrrole	1.3 (Undoped)	[56]
	0.8 (Iodine-doped)	
Aniline	3.04 (Pure polyaniline)	[58]
	1.80 (Iodine-doped polyaniline)	
<i>Lavandula angustifolia</i> essential oil	2.34	[59]
Terpinen-4-ol	2.67	[60]
Thiophene	2.2	[61]

plasma-polymerized thin films critically depend on the conformation of the π -conjugated chains in both the ground and the excited states and on the inter-chain orientation. Several recent reports demonstrate that chain structures exert a considerable effect on the nature and radiative properties of excited states in π -conjugated polymers [65]. Controllability and reproducibility of the surface composition of plasma deposition thin film are of utmost importance to achieve superlative performance. It is well known that several plasma reaction parameters like power input, monomer flow rate and substrate temperature influence the structure and the composition of plasma thin films [66]. It is now recognized that under low discharge power input conditions, a plasma polymer is created which retains more of the aromatic ring structures of the starting monomer and resembles a more conventional polymer [67,68].

Zhao et al. [69] have prepared plasma-polymerized 4-phenylbenzotrile (PPBPCN) by plasma polymerization and investigated the photoluminescence property of the obtained plasma thin films. The results show that a transparent, smooth and homogeneous PPBPCN thin film with a large π -conjugated system can be formed at low plasma discharge power of 30 W, and the plasma polymerization of 4-phenylbenzotrile monomer took place mainly through the opening of the π bonds of $C\equiv N$ functional group. A high discharge power of 50 W brings about more severe molecular (aromatic ring) fragmentation. Moreover, the as-grown conjugated polynitrile thin films show a blue emission with a relatively high PL intensity at about 470 nm. The conjugated polynitrile thin films obtained from 4-phenylbenzotrile might be applied to light emitting diode (LED) and photodiode on device performance. The chemical structure of monomer and the desired structure of PPBPCN are shown in Scheme V.

A novel conjugated polynitrile, plasma-polymerized 1-isoquinolinecarbonitrile (PPIQCN) was also prepared by plasma polymerization [70]. The structure and surface compositions of the deposited PPIQCN thin films were investigated by Fourier transform infrared (FTIR), UV-visible absorption spectra and X-ray photoelectron spectroscopy (XPS).



Scheme V. Chemical structure of monomer 4-phenylbenzotrile and the desired structure of plasma polymerized 4-phenylbenzotrile thin films.

The results show that extensively conjugated $C=N$ double bonds were formed in PPIQCN films during the plasma polymerization of 1-isoquinolinecarbonitrile. An obvious red shift of more than 120 nm in the maximum absorption wavelength (λ_{\max}) for PPIQCN films was observed as compared with the monomer absorption spectrum. To check the possibility of PPIQCN films as optical device application, PL measurements were carried out and a maximum PL emission intensity at about 458 nm was observed (Figure 2).

Recently, another novel plasma polynitrile film, plasma-polymerized 3-quinolinecarbonitrile (PP3QCN) thin film was also reported by Zhao et al. [71]. The chemical structure of monomer and the desired structure of plasma polynitrile are shown in Scheme VI. The obtained PP3QCN thin films show a

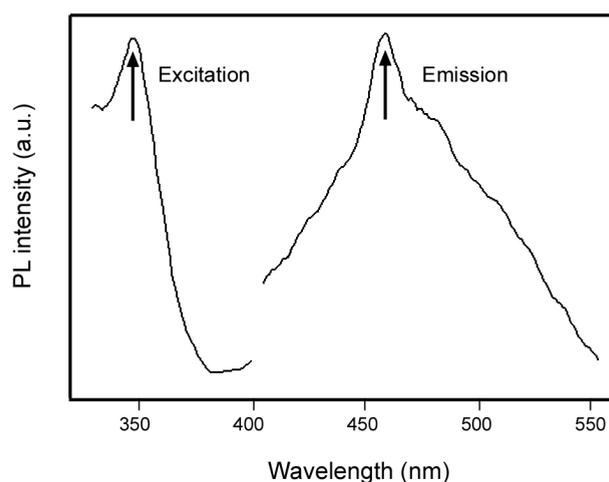
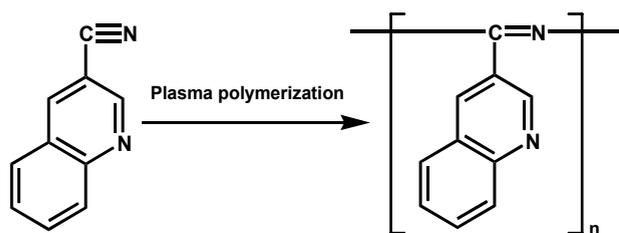


Figure 2. Photoluminescence (PL) spectrum of plasma polymerized 1-isoquinolinecarbonitrile thin film.



Scheme VI. Chemical structure of monomer and the desired structure of plasma polynitrile.

blue emission with a narrow peak at approximately 475 nm and there appeared a relatively high intensity of PL peak. The EL devices with PP3QCN as electroluminescent layer sandwiched between indium-tin oxide (ITO) and Al were fabricated. It was found that the ITO/PP3QCN/Al devices also show a blue emission and PP3QCN thin film was stable and appropriate for the electroluminescent layer. The external quantum efficiency of ITO/PP3QCN/Al devices can reach 0.0068%.

Clarson et al. [72] reported the preparation and optical property of plasma-polymerized benzene and furan films and found that photoluminescence spectra of these films show a blue emission with a broad peak at 460 nm for the plasma-polymerized benzene films and 445 nm for the plasma-polymerized furan films.

In addition, Radeva et al. [73] investigated the photoluminescence properties of plasma-polymerized hexamethyldisiloxane (HMDSO), the transparency range of the polymer layer is 55% at 400 nm and 88% at 800 nm. The PL intensity showed a slight reduction (hypochromatic shift) when the layer thickness increased from 0.4 to 0.8 mm at 365 nm.

CONCLUSION AND OUTLOOK

Glow discharge plasma polymerization represents a feasible method for preparing organic polymer films with desirable opto-electronic properties. The potential applications in devices for these plasma polymer films include sensors, transistors, organic electric circuitry, organic batteries, light emitting diode, photodiode, capacitors, NLO materials, dielectric materials on the chips, as well as optical

elements (such as optical filters, lenses and waveguides). As we peer into the future requirements for the opto-electronic polymer film materials, the challenges for plasma polymer films are definitely there. It seems that the extent of application of plasma polymer films is still in its infancy due to the fact that requirements for perfection of plasma polymer films are becoming extremely tight. It is clear that, among all the plasma polymer thin films materials mentioned above, few have been found to satisfy all the requirements for the practical application in electronic devices because of their disadvantages; for example, the expensive cost of starting materials and synthetic pathways, the mechanical toughness and thermal and chemical stability of the films, as well as the stabilities of the physical properties of the plasma films.

Thus, there is much to do to overcome some of the limitations, and new approaches for overcoming drawbacks and for improving the performance of the plasma polymer films have raised vital interest in research activities.

Based on the organic polymer films deposited by glow discharge plasma technique described in the literature so far, the future development for plasma polymer thin films with opto-electronic properties will mainly focus on the following three areas: first of all, the search for more suitable monomers and plasma polymerization methods to deposit uniform and insoluble thin conjugated polymeric (CP) layers or ordered networks with high conjugation lengths and degree of inter-chain order. This has been regarded as a possible strategy to attain better materials for light emitting diode (LED) and photodiode applications. The second most important research area for plasma opto-electronic polymer thin films is specific surface modification and functionalization in order to achieve the desired surface characteristics (e.g., environmental stability, biocompatibility, adhesion, low or high surface energy, etc.). For example, an adhesion promoter like γ -aminopropyltriethoxysilane is deposited as a self-assembled monolayer on the surface of the plasma polymer film to improve adhesion strength. Moreover, controllability and reproducibility of the surface composition of plasma deposition thin films are of utmost importance to achieve superlative performance and

should be investigated thoroughly. Thirdly, it is to improve the thermal stability of plasma polymer films. As reported, a high temperature annealing at 400~450°C is necessary to ensure void free copper deposits during copper metallization for ultralarge-scale integration (ULSI), thus, polymer dielectric materials must be able to withstand this temperature for several hours, and during this period, outgassing, shrinking, crack formation, or any other damage must be avoided completely.

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