REVIEW OF LITERATURE

CHAPTER 2

REVIEW OF LITERATURE

2.1 INTRODUCTION

A literature review is a survey of already existing and published articles on a given topic or area with a view to accessing their relevance to a proposed project. The use of synthetic polymers are increasing rapidly year by year and in many applications they are replacing conventional materials like metals, ceramics, wood and natural fibers such as cotton, wool etc. Polymer materials have been widely used in various fields such as optical communications and electronic sensors. The continuing interest in the technological application of polymeric film is reflected in a large number of published papers dealing with various aspects. This chapter discusses about the studies on various properties of different polymers carried out by several researchers in different parts of the world.

2.2 REVIEWS ON VARIOUS PROPERTIES OF POLYMER THIN FILMS

1. **Babita Gaihre et al., (2011)** have fabricated the bending-type microactuators less than 1 mm in length and comprising of two polypyrrole (PPy) layers separated by polyvinylidene fluoride (PVDF) membrane and was shown to operate both in air and aqueous media. The main limiting factor to increase the bending angle and to further miniaturize these actuators was the thickness of the commercially available PVDF membrane used (~110 μm). In this study, they have synthesized a porous PVDF thin film with a thickness of 32 μm using a spin coating technique, and electrochemically deposited PPy layers on both sides of this thin film to make ultra thin film polymer actuators. The electromechanical and electrochemical properties were investigated and compared with those of the thicker actuator system using the commercially available PVDF and under identical conditions. The thin film shows very promising performance compared to its thicker counterpart.

2. Fuan He et al., (2011) have investigated the ferroelectric polymers, including polyvinylidene fluoride homopolymer and poly(vinylidene fluoride-trifluoroethylene) [P(VDF–TrFE)] copolymer, extensively due to their potential application in sensors, actuators, transducers and energy harvesting. Recently, porous ferroelectric polymers have stimulated much interest because such materials have advantages of light weight, low acoustic and mechanical impedance, and high voltage sensitivity. In this work, P(VDF-TrFE) porous membranes were prepared by electrospinning and subsequent hot pressing. The morphology of the resultant electrospun membranes (nanofibers with or without beads) can be varied depending on the concentration of polymer solution used during the electrospinning process. Differential scanning calorimetry, wide-angle X-ray diffraction and Fourier-transform infrared confirmed the automatic formation of β crystallites in the P(VDF-TrFE) electrospun porous membrane. Based on piezoelectric strain coefficient measurement, dielectric constant measurement and dynamic mechanical analysis, it was found that the hot pressed P(VDF-TrFE) electrospun membrane with beads not only had a relatively high d_{33} value compared with those of other electrospun P(VDF-TrFE) membranes, but also the advantage of low dielectric constant and high flexibility.

3. Palla-Papavlu et al., (2011) have reported the deposition of thin polymer films of Polyepichlorhydrin by pulsed laser deposition. Polyepichlorhydrin polymer was deposited on flat substrate (i.e. silicon) using an NdYAG laser (266 nm, 5 ns pulse duration and 10 Hz repetition rate). The obtained thin films have been characterized by atomic force microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy and spectroscopic ellipsometry. It was found that for laser fluences up to 1.5 J/cm^2 the chemical structure of the deposited polyepichlorhydrin polymer thin layers resembles to the native polymer, whilst by increasing the laser fluence above 1.5 J/cm^2 the polyepichlorohydrin films present deviations from the bulk polymer. Morphological investigations (atomic force microscopy and scanning electron microscopy) reveal continuous polyepichlorhydrin thin films for a relatively narrow range of fluences (1–1.5 J/cm^2). The wavelength dependence of the refractive index and extinction coefficient was determined by ellipsometry studies which lead to new insights about the material. The obtained results indicate that pulsed laser deposition method is potentially useful for the fabrication of polymer thin films to be used in applications including electronics, microsensor or bioengineering industries.

4. Sandip et al., (2011) have prepared Poly (3-methyl thiophene) thin films by chemical bath deposition technique on glass substrate; the prepared thin films were characterized for structural, morphological and optical properties. The variation in the oxidant concentration has an influence on the properties of the P3MeT thin films. The increase in the oxidant concentration leads to increase in the thickness of the film. The binding energy increases due to increase in oxidation concentration. The P3MeT thin films show smooth surface morphology with increase in oxidant concentration whereas the contact angle of the thin film decreases with increase in oxidant concentration. The optical absorbance of these thin films was found to increase with decrease in the optical band gap due to increase in oxidant concentration.

5. Hsiang Lin et al., (2010) have generated the submicron polystyrene (PS)/poly(methyl methacrylate) (PMMA) blends by the precipitation with a compressed antisolvent (PCA) technique. The generation of PS/PMMA blends was carried out by spraying a solution containing PS and PMMA into a precipitator. The blends without coalescence were observed to only be generated when both vapor and liquid CO_2 existed in the precipitator combined with appropriate total polymer concentration in solution, molecular weights (Mw) of PS and PMMA, mass ratio of PS to PMMA, flow rates of CO_2 and polymer solution, and liquid CO_2 level in the precipitator. Two PS of Mw, 144,000 and 44,000, and two PMMA of Mw, 85,000 and 36,000, were used in this study. It was found that the blends could be easier to generate using a higher PS Mw, a lower PMMA Mw, and a higher mass ratio of PS to PMMA. Toluene with a solubility parameter smaller than that of tetrahydrofuran (THF) was found to be the more appropriate solvent for generating spherical PS/PMMA submicron blends. The SEM and TEM images show that the spherical PS/PMMA core/shell blends could be generated at a temperature of 298 K, a pressure of 6.41 MPa, a liquid CO_2 level of 1/2 of the precipitator, a CO_2 flow rate of 2000 mL/min, a solution flow rate of 5 or 10 mL/min, and a total polymer concentration of 0.72 wt% for a PS Mw of 144,000, a PMMA Mw of 36,000, and a PS/PMMA mass ratio of 9/1. Individual and spherical PS and PMMA particles or spherical PS particles partially covered by a PMMA films, however, were generated when the liquid CO_2 level was of 1/8 or lower in the precipitator. A possible mechanism for the formation of core–shell blend was proposed.

6. Marli et al., (2010) have successfully synthesized new block copolymers with narrow molecular weight distribution $(\overline{M}_n/\overline{M}_n=1.04\text{-}1.14)$ based on (2,3-epithiopropylmethacrylate) (ETMA), methylmethacrylate (MMA) and *n*-butylmethacrylate (*n*BMA) via reversible addition-fragmentation transfer (RAFT) polymerization. First, RAFT homopolymerization of ETMA and MMA was carried out using 2-(2-cyanopropyl) dithiobenzoate (CPDB) as the chain transfer agent (CTA) and 2,2-azobisisobutyronitrile (AIBN) as the initiator. PETMA–*b*-P(*n*BMA) copolymers were synthesized using PETMA homopolymers as the macro-chain transfer agent (MCTA), while PMMA–*b*-PETMA diblock copolymers were synthesized using PMMA as the MCTA. The evolution of the molecular weight and molecular weight distribution of the homo- and co-polymers were compatible with the RAFT polymerization features. Thin films from the block copolymers were prepared by spin coating a 1 wt% polymer solution from toluene, chloroform or THF. After the preparation, the films were annealed under 80% vapor pressure of chloroform for 1, 2 and 4 h and investigated with scanning electron microscopy (SEM). The most interesting results were found in the films prepared using PETMA–*b*-P(*n*BMA) copolymers . The observed images suggested the formation of hybrid lamellar structures, ascribed to the combination of its higher molecular weight and solvents viscosity.

7. Capan et al., (2009) have reported on the characterization of spin coated thin films of poly (methyl methacrylate) (PMMA) for their use in organic vapour sensing application. Thin film properties of PMMA were studied by UV–visible spectroscopy, atomic force microscopy and surface plasmon resonance (SPR) technique. Results obtained show that homogeneous thin films with thickness in the range between 6 nm and 15 nm have been successfully prepared when films were spun at speeds between 1000−5000 rpm. Using SPR technique, the sensing properties of the spun films were studied on exposures to several halo hydrocarbons. The highest PMMA film sensitivity of 0.067 normalised response per ppm was observed for chloroform vapour, for films spun at 1000 rpm sensitivity was ascribed mainly to its solubility parameter and molar volume values. Effect of film thickness on the vapour sensing properties is also discussed.

8. Lantz et al., (2009) have investigated the effects of various deposition techniques on the photoluminescence spectra of the conjugated polymer poly[2-methoxy-5--ethylhexyloxy)-1,4-(1-cyanovinylene) phenylene] (MEH-CN-PPV). Photoluminescence spectroscopy provides insight into the internal morphology of organic thin films through the identification of interchain or intrachain recombination peaks. Thin films were deposited on glass substrates by drop casting, spin casting and resonant-infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE) and were compared to the photoluminescence of the polymer in solution. The photoluminescence measurements reported in this article demonstrate that samples deposited by evaporative RIR-MAPLE have an internal morphology similar to that of MEH-CN-PPV in solution, leading to an enhancement of intrachain transitions in the conjugated polymer.

9. Prime Dominic and Paul Shashi, (2009) have analyzed the electrical and morphological properties of polystyrene layers in the nanometre thickness range for organic and polymer based electronic applications. This article aims in providing conduction data and information on trapped charges present in the polystyrene layer, as well as investigated how polystyrene properties change under differing annealing conditions. The maximum dielectric strength was found to be 4.0 MV cm^{-1}, while fixed trapped charge and mobile trapped charge average densities were calculated to be 9.9×10^{11} cm^{-2} and 2.6×10^{12} cm^{-2} respectively. Optimum electrical characteristics were obtained at an anneal temperature of 90°C, which is just below the glass transition temperature for polystyrene.

10. Yoshimura et al., (2009) have investigated the effects of ultraviolet (UV) light irradiation on polymer dry etching processes with the use of a low-energy mass-selected ion beam injection system. Etching yields of poly(methyl methacrylate) (PMMA) by Ar or CF_3 ion beam injections were evaluated from the loss of PMMA film weight measured by a quartz crystal microbalance (QCM) during the ion beam injection process with or without simultaneous UV light irradiation. Significant enhancement of the etching yield of PMMA was observed during the simultaneous irradiation with CF_3 ion beam and UV light over the sum of its sputtering yields obtained from separate ion-beam or UV-light injection processes. By contrast, no significant change of etching yields was observed when the UV light was superposed on the Ar ion beam.

11. Emilienne et al., (2008) have used a series of homopolymer/random copolymer blends to produce heterogeneous surfaces by demixing in thin films. The chosen homopolymer is polystyrene (PS) and the random copolymer is poly(methyl methacrylate)-r-poly(methacrylic acid) (PMMA-r-PMAA), whose acidic functions could be used as reactive sites in view of further surface functionalization. The proportion of each polymer at the interface was deduced from X-ray photoelectron spectroscopy (XPS) data on one hand, and on the other hand, decomposition of the carbon peak of the blends in two components corresponding to the carbon peaks of PS and PMMA-r-PMAA. Combining the information from XPS with atomic force microscopy (AFM) images, water contact angle measurements and PS selective dissolution, it appears that the surfaces obtained from blends with a high PS content (90/10 to 70/30) display pits with a bottom made of PMMA-r-PMAA, randomly distributed in a PS matrix. On the other hand, the surfaces obtained from blends with a low PS content (30/70 to 10/90) display randomly distributed PS islands surrounded by a PMMA-r-PMAA matrix. The characteristics of the heterogeneous films are thought to be governed by the higher affinity of PMMA-r-PMAA for the solvent (dioxane), which leads to the elevation of the PS phase compared to the PMMA-r-PMAA phase, and to surface enrichment in PMMA-r-PMAA.

12. Hans-Georg Braun and Evelyn Meyer, (2008) have analyzed that the film formation of ultrathin polymers on micro heterogeneous surfaces was strongly influenced by molecular surface patterns which cause local wettability differences for liquid phases in contact with the surface. Surface coverage with polymers transferred by dip-coating from polymer solutions was controlled by surface heterogeneities prepared by soft lithography or by electron beam lithography of self-assembled monolayers. Using crystallisable polymers for ultrathin film formation (polyethyleneoxide (PEO) they investigated the competition in pattern formation resulting from the dewetting process and patterns which result from lamella crystallization of PEO in ultrathin films. For the first time it was observed that ultrathin polymer films of crystallisable polymers which were prepared in absence of any substrate surface defects form a metastable state in which they can exist over days and weeks without crystallization. Heterogeneous nucleation in these metastable films can be done by external stresses such as contact with an AFM tip. The nucleation on demand allowed them to study the diffusion controlled pattern formation that was observed during lamella crystallization and the growth process resulting in different morphological features could be studied at elevated temperatures and in lateral confined areas which were realized by the film preparation on the microheterogenized surfaces.

13. Halina Kaczmarek and Hanna Chaberska (2008) have obtained thin poly(methyl methacrylate) films by casting polymer solution onto borosilicate glass and aluminum supports from organic solvents, such as chloroform, chlorobenzene, toluene, acetone and tetrahydrofuran. Atomic Force Microscopy has been chosen as a method for investigation of the influence of solvent residue and support type on the topography and roughness of the PMMA films before and after UV-irradiation of 254 nm wavelength. It was found that, besides information on sample morphology, AFM provides valuable details on polymer–support interactions.

14. Kazuya Kezuka et al., (2008) have prepared polymer thin films by RF sputtering with argon (Ar) and tetra-fluorocarbon (CF_4) gases. Four fluorocarbon polymers, poly(tetra fluoro ethylene) (PTFE), tetra fluoro ethylene-perfluoro alkylvinyl ether copolymer (PFA), fluorinated ethylene propylene copolymer (FEP), poly(vinylidene di fluoride) (PVDF) were used as the sputtering targets. Molecular structures of sputtered fluorocarbon thin films were analyzed with x-rays photoelectron spectroscopy (XPS) and Fourier transform infrared Spectroscopy (FT-IR). Wettability of these polymer thin films was estimated with contact angles of water droplets. The contact angle increased with increase of the F/C ratio (fluorine for carbon) of the thin film. PTFE target prepared by a spin coat method was also used for the sputtering target and analyzed the elemental compositions of the target after the sputtering. The F/C ratio of the polymer thin film prepared by the sputtering with CF_4 was almost the same value as that of the thin film with Ar. However, the F/C ratio of the target after the CF_4 sputtering was much higher than that after the Ar sputtering.

15. Koji Sagane et al., (2008) have studied the evaporative spray deposition using ultra dilute solution (ESDUS) technique enables layer-by-layer and pixel-by-pixel deposition of polymer semiconductors. In this study they prepared thin films of dioctylfluorene-co-bithiophene) alternating copolymer, F_8T_2, by ESDUS and by a conventional spin-coat. These films were made into fabricated field effect transistors to investigate carrier transportation properties. Since the organic films were formed by deposition of aerosol particles in ESDUS, the carrier transportation properties in ESDUS films had been expected lower than those in spin-coat films, which were formed through spread polymer solution. However, the device performance was almost identical, indicating that the polymer deposited as particles undergoes rearrangement process on the substrate.

16. Pawde and Sanmesh, (2008) have investigated the antifungal and antibacterial activities involved in the film surface. Subsequently, microbial formations were immobilized on the modified PS films. Living microorganisms such as bacteria and yeast were used. Untreated PS films show very fast rate of growth of bacteria within few hours. Films were prepared by two methods: plasma treatment under vacuum and under ongoing He–Ne laser source. The parameters such as (1) surface area by contact angle measurements, (2) quality of material before and after treatment by SEM and FTIR spectra and (3) material characterization by UV–vis spectra were studied. It was observed that plasma treatment of the PS material for different processing time improved the surface properties of PS films.

17. Ruslan Burtovyy and Igor Luzinov, (2008) have developed thin PVP films on a silicon oxide surface have been found to form a dewetting pattern when treated with basic solutions ($pH = 10$). They studied the dependence of pattern morphology on the polymer's molecular weight and thickness of the polymer layer and observed the formation of three distinctive structures. The structure formed by large drops of polymer was characteristic of a polymer with low molecular weight and the thinnest polymer layer, whereas other samples form holes or a web like pattern upon dewetting. These experiments have demonstrated for the first time the reversibility of the dewetting process in a liquid environment. The polymer layer has revealed reversible behavior toward flat film when exposed to a pH 4 buffer solution. More complex structures can be obtained by consecutive treatments with acidic (pH 4) and basic (pH 10) solutions. They used atomic force microscopy (AFM) to study both the morphology and elastic properties of polymers in media with different acidity, in order to determine the mechanism behind the dewetting process.

18. Sarantopoulou ea al., (2008), have reported that the Laser irradiation at 157 nm of polymethylmethacrylate (PMMA) thin films induces major variations of polymer film thicknesses from sorption (absorption/desorption) of methanol and ethanol analytes in the gas phase as much as 400%, in comparison to the film thickness variation of the non-irradiated areas. The structural changes of irradiated areas involve scission of polymeric chains, cross-linking and formation of new bonds. In addition, 157 nm induces surface and volume morphological changes in the nano/micro domain, with different shapes, depending on the irradiation conditions. The reversibility of the sorption processes suggests that the polymer swelling has its origin at the tendency of the system to increase its volume during sorption. The internal forces from sorption are higher than the weak dipole interactions between the polymer and the analytes and they are amplified following 157 nm irradiation. A simple qualitative model explains adequately the experimental results. The 157 nm laser treatment forms the basis to engineer a novel class of polymer sensor arrays with enhanced detection efficiency of liquid/gas analytes.

19. Toshiyuki Oya and Eiji Kusano, (2008) have deposited organic polymer thin films by sputtering using polytetrafluoroethylene (PTFE) and polyimide (PI) targets were investigated with Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), and Scanning Electron Microscopy (SEM). Films deposited from the PTFE target were poly-hydro-fluoro-carbon. The thin films showed water repellency with an H_2O contact angle of about 110° and were transparent in the visible region. C–F combination states in the films were similar to those of bulk PTFE. Films deposited from the PI target were found to contain C–N bonds and were harder than bulk PI. The color of thin films was dark brown, showing the existence of C–N bonds, such as those in imide and/or amide groups. However, the combination states characterized by FTIR and XPS analyses were considerably different from those of bulk PI. The difference in chemical composition and combination states between the films deposited from PTFE and PI is thought to result from the difference in types of particles sputtered from the targets; in the case of PTFE sputtering, less C–F bonds were broken by collision of Ar ions for sputtering, whereas in the case of PI sputtering, C–H and C–C bonds were broken by collision of Ar ions.

20. Wenzhong Ma et al., (2008) have analysed the dependence of surface structure of the poly(vinylidene fluoride) (PVDF)/poly(methylmethacrylate) (PMMA) films by solution casting on properties of seven substrates by wide angle X-ray diffraction (WAXD), Fourier transform infrared (FTIR), scanning electron microscope (SEM) and differential scanning calorimetry (DSC). It revealed that the polyblend films obtained by casting onto each substrate contained exclusively β phase PVDF. Higher crystallinity of the film was obtained by casting onto ceramic, polytetrafluoroethylene (PTFE), copper (Cu), stainless steel and glass substrates than that by casting onto aluminium (Al) and polypropylene (PP) substrates, depending on the degree of close lattice matching. The surface crystalline structure of PVDF was strongly affected by the wettability of substrate. The largest size of PVDF spherulitic crystal structure with about 6 mm was developed in the casting film grown at the air/solution interface on glass substrate, while the smallest spherulite size with about 3 mm was generated by casting onto PTFE, stainless steel and PP substrates.

21. Xiaofang Wang et al., (2008) have reported that the surface structure and stability (the resistance to surface reconstruction) of end-capped poly(methyl methacrylate) films were greatly affected by the solvents used for film preparation. Films of end-capped PMMA with about four 2-perfluorooctylethyl methacrylate units cast with benzotrifluoride solution exhibited excellent stability and resistance to polar environments compared with those cast with cyclohexanone and toluene solutions. The observed difference in stability between these fluorinated surfaces is attributed to their surface microstructures formed during the film formation processes, which are closely related to the associative behavior of the end-capped PMMA in the solution. A relatively perfect close-packed and well-ordered structure of the perfluoroalkyl side chains at the surface of the $PMMA_{857}$-ec-$FMA_{3.3}$ film was formed when the film was cast with benzotrifluoride solution, in which only unimers existed. This study indicates that such a solvent effect may be used to promote the formation of a well-ordered packing structure of the fluorinated moieties at the film surface. The ordering of the packing structure to a certain extent is more important than the content of the fluorinated moieties at the surface for improving the surface stability.

22. Yadav et al., (2008) have reported the adhesion, structural and optical properties of spin coated PANI/PMMA composite thin films of different composition on glass substrate. The effect of post-deposition heating for 100 °C, 125 °C and 150 °C was also reported. The adhesion of the film was found to increase from $712 \pm 5 \times 104\ \mathrm{N/m^2}$ to $1602 \pm 3 \times 10^4\ \mathrm{N/m^2}$ and refractive index decreased from 1.852 ± 0.005 to 1.650 ± 0.004 with increase in concentration of PMMA. Due to post-deposition heating adhesion, optical band gap increased but refractive index decreased.

23. Khaydarov et al., (2007) have prepared asymmetric poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymers of molecular weight $M_n = 29{,}700\ \mathrm{g\ mol^{-1}}$ ($M_{\mathrm{PS}} = 9300\ \mathrm{g\ mol^{-1}} M_{\mathrm{PMMA}} = 20{,}100\ \mathrm{g\ mol^{-1}}$, $\mathrm{PD} = 1.15$, $\chi_{\mathrm{PS}} = 0.323$, $\chi_{\mathrm{PMMA}} = 0.677$) and $M_n = 63{,}900\ \mathrm{g\ mol^{-1}}$ ($M_{\mathrm{PS}} = 50{,}500\ \mathrm{g\ mol^{-1}}$, $M_{\mathrm{PMMA}} = 13{,}400\ \mathrm{g\ mol^{-1}}$, $\mathrm{PD} = 1.18$, $\chi_{\mathrm{PS}} = 0.790$, $\chi_{\mathrm{PMMA}} = 0.210$) via reversible addition-fragmentation chain transfer (RAFT) polymerization. Atomic force microscopy (AFM) was used to investigate the surface structure of thin films, prepared by spin-coating the diblock copolymers on a silicon substrate. We show that the nanostructure of the diblock copolymer depends on the molecular weight and volume fraction of the diblock copolymers. It was observed that a perpendicular lamellar structure for the high molar mass sample and a hexagonal-packed cylindrical patterning for the lower molar mass one. Small-angle X-ray scattering investigation of these samples without annealing did not reveal any ordered structure. Annealing of PS-*b*-PMMA samples at 160°C for 24 h led to a change in surface structure.

24. Nadja Karolina et al., (2007) have investigated the effect of film thickness and different microelectrode geometries on the performance of chemical sensors made of nanostructured films of conducting polymer poly(*o*-ethoxyaniline) (POEA) and sulfonated polystyrene (PSS). Both parameters present significant influence on the sensors response. Depending upon the concentration of NaCl solutions, thicker films exhibit higher sensitivity to NaCl in comparison to thinner films according to impedance spectroscopy studies. The larger surface roughness of thicker films seems to be the main reason for such a behavior. Meanwhile, as the area of the gold electrodes was increased more sensitive sensors were obtained. At two different frequencies, namely 100 Hz and 1 kHz, the response of the sensors were found to be linear or exponentially dependent on the NaCl concentration.

25. Semaltianos, (2007) have determined the conditions for spin coating and post-processing for obtaining films whose surface morphology appears featureless or is dominated by pinholes and other surface defects by using atomic force microscopy (AFM) imaging, scratching lithography and force–distance curves spectroscopy. Featureless appear the surfaces of films spin coated at 8 krpm from a 1.25% solution on silicon substrates and post baked at 200°C for 2 min on a hot plate, while surface defects in the form of large circular pits with diameters between 10 and 20 mm and depth of ~2 nm dominate the surface morphologies of films spin coated at 7 krpm on glass substrates from a 2% solution and post baked either at 200°C for 2 min on a hot plate or at 170°C for 30 min in an oven. Surface defects in the form of pinholes appear on the surfaces of films spin coated at 8 krpm on silicon substrates from a 1.25% solution (thickness of ~8 nm) and post baked at 170°C for 60 min in an oven or left in a low vacuum chamber for a few days. The implication of the different film properties depending on the preparation parameters in lithographic techniques was also discussed in this article.

26. Tunno et al., (2007) have deposited Poly(9,9-dioctylfluorene) (PF8) thin films by matrix-assisted pulsed laser evaporation (MAPLE) using a KrF excimer laser. The influence of the laser fluence (50–500 mJ/cm2) and the nature of the solvent (chloroform, toluene, tetrahydrofuran) on the films properties have been studied. The chemical composition of the deposited films was investigated by Fourier transform infrared (FTIR) spectroscopy and compared with the one of spin coated films. To investigate the effect of the deposition parameters on the optical properties of the films, photoluminescence (PL) measurements were performed. Poor structural and optical properties were observed for films deposited starting from chloroform solutions. When using toluene as solvent, the spectra characteristics improved with increasing laser fluence, while wide PL spectra were observed. The characteristic emission bands of the PF8 polymer were nicely detected for films deposited starting from a tetrahydrofuran (THF) solution. Moreover, in this last case, the PF8 structure was preserved at high laser fluences, too.

27. Liang Cui et al., (2006) have discussed the effects of solvent nature on the surface topographies of polystyrene (PS)/poly(methyl methacrylate) (PMMA) blend films spin-coated onto the silicon wafer. Four different solvents, such as ethylbenzene, toluene, tetrahydrofuran and dichloromethane, were chosen. They are better solvents for PS than that for PMMA. When dichloromethane, tetrahydrofuran and toluene were used, PMMA-rich phase domains protruded from the background of PS. When ethylbenzene was used, PS-rich phase domains elevated on the average height of PMMA-rich phase domains. In addition, continuous pits, networks and isolated droplets consisted of PS formed on the blend film surfaces with the decrease of polymer concentrations. The mechanism of the surface morphology evolution was discussed in detail.

28. Pi-Guey Su et al., (2006) have studied the humidity-sensing properties of poly(methyl methacrylate) (PMMA) by doping with two alkali salts (KOH and K_2CO_3), whose dissociation constants were distinctly different from each other. The electrical properties of PMMA doped with different amounts of KOH or a mixture of KOH and K_2CO_3 were examined in detail as a function of relative humidity (RH), to elucidate the contribution of the salts to the sensing properties (linearity and sensitivity). The PMMA doped only with KOH had high sensitivity but low linearity. The poor linearity of the PMMA/KOH complex was improved by further doping of K_2CO_3. The PMMA doped with a mixture of KOH (0.6%, w/w) and K_2CO_3 (0.6%, w/w) was optimal in both sensitivity and linearity in the range of 30–90%RH.

29. Yanxia Li et al., (2006) have investigated the surface and interface morphologies of polystyrene (PS)/poly(methyl methacrylate) (PMMA) thin-film blends and bilayers by means of atomic force microscopy (AFM) and X-ray photoelectron spectroscopy. Spin-coating a drop of a PS solution directly onto a PMMA bottom layer from a common solvent for both polymers yielded lateral domains that exhibited a well-defined topographical structure. Two common solvents were used in this study. The structure of the films changed progressively as the concentration of the PS solution was varied. The formation of the blend morphology could be explained by the difference in the solubility of the two polymers in the solvent and the dewetting of PS-rich domains from the PMMA-rich phase. Films of the PS/PMMA blend and bilayer were annealed at temperatures above their glass-transition temperatures for up to 70h. All samples investigated with AFM were covered with PS droplets of various size distributions. Moreover, they investigated the evolution of the annealed PS/PMMA thin-film blend and bilayer and a proper explanation was given for the formation of a relatively complicated interface inside a larger PS droplet.

30. Yimsiri and Mackley , (2006) have reported the experimental observations on spin and dip coating of light-emitting polymer (LEP) solutions where both the process conditions as well as the solution properties are factors influencing thickness and uniformity of thin LEP films. In terms of spin coating, which is a typical process for the manufacture of polymer light-emitting diodes (PLEDs), a number of process variables including spin speed were systematically explored. A matching series of dip-coating experiments was also carried out with the retraction speed as a primary variable. Modifications of existing models for both spin and dip coating were developed to include solvent evaporation and the effect of solution viscosity change during evaporation. Both models were found to give reasonable agreement with the major observed trends for final film thickness as a function of process conditions tested in this article.

31. Bae et al., (2005) have synthesized Polymer-like thin films on glass, silicon, and copper substrates at a room temperature to 100 °C by the plasma-enhanced chemical vapor deposition method using cyclohexane (C_6H_{12}) as a precursor for analysis of these substrates electrochemical and optical characteristics. Cyclohexane was utilized as an organic precursor and hydrogen and Ar (argon) were used as a bubbler and carrier gases, respectively. In order to compare the difference between the corrosion-resistant and the optical properties of the plasma-polymerized organic thin films, conditions of various radio frequencies (rf) using 13.56 MHz power in the range of 20–50 W and deposition temperature were used. The optical and electrical properties of the as-grown plasma polymerized thin films were analyzed by Fourier transform infrared spectrophotometer, ultraviolet-visible spectroscopy, current–voltage, and capacitance-voltage curves. The corrosion-protective abilities of cyclohexane were also examined by ac impedance measurements in a 3.5 wt.% NaCl solution. They found that the corrosion-protection efficiency (P_k), which is one of the important factors for corrosion protection in the interlayer dielectrics of microelectronic-device application, was increased with increasing rf power. The highest P_k value of plasma-polymerized cyclohexane film was (85.26% at 50 W), atomic-force-microscope, and scanning electron microscopy showed that the polymer films with smooth surfaces and sharp interfaces could be grown under various deposition conditions.

32. Seong et al., (2005) have employed thin film blends of diblock copolymers with functional homopolymers as a simple strategy to incorporate organic functional materials into nanodomains of diblock copolymers without serious synthesis. A blend pair of polystyrene–poly(methyl methacrylate) (PS–PMMA) diblock copolymers and poly(vinylidene fluoride) (PVDF) was selected as a model demonstration because PVDF is a well-known ferroelectric polymer and completely miscible with amorphous PMMA. Thin films of symmetric PS–PMMA copolymers provided the nanometer-sized PMMA lamellae, macroscopically parallel to the substrate, in which PVDF chains were dissolved. Thus, amorphous PVDF chains were effectively confined in the PMMA lamellae of thin film blends. The location of PVDF chains in the PMMA lamellae was investigated by the dependence of the lamellar period on the volume fraction of PVDF, from which they found that PVDF chains were localized in the middle of the PMMA lamellae. After the crystallization of PVDF, however, some of PVDF migrated to the surface of the film and formed small crystallites.

33. Kim et al., (2004) have deposited Polymer-like thin films on glass and silicon substrates at temperatures in the range 300–673 K, by a plasma enhanced chemical vapor deposition (PECVD) method using thiophene (C_4H_4S) as a precursor. A power with radio frequency (13.56 MHz) was applied for the ignition of the plasma, and hydrogen and Ar(argon) were used as the bubbler and the carrier gases, respectively. In order to compare physical properties of the as-grown thin films, an effect of the plasma power and deposition temperature on the dielectric constant and thermal stability were mainly studied. XRD and FT-IR studies revealed that the as-grown films at 373 K have highly oriented amorphous polymer structure. XPS revealed that the polymerized thin films have the same stoichiometric ratio (8:1) between C and S, indicating that dimer-like thin films were mainly grown under our experimental condition. From the electrical properties measurements such as I–V and C–V characteristics, they found that the relative dielectric constants increased from 2.96 to 4.0 when the RF power was increased up to 200 W. Moreover, the leakage current density was increased with increasing RF power and deposition temperature. The maximum deposition rate obtained was 110 nm/min for the polymerized thin film deposited at 300 K and 100 W. The activation energy for polymer-like thin film deposition calculated from the Arrhenius plot was −6.9 kJ/mol, signifying that a diffusion control process was the rate-determining mechanism.

34. Xue Li et al., (2004) have investigated the surface morphology evolution of three thin polystyrene (PS)/polymethyl methacrylate (PMMA) blend films (<70 nm) on SiO_x substrates upon annealing by atomic force microscopy (AFM) and some interesting phenomena were observed. All the spin-coated PS/PMMA blend films were not in thermodynamic equilibrium. For the 67.1 nm and the 27.2 nm PS/PMMA blend films, owing to the low mobility of the PMMA-rich phase layer at substrate surfaces and interfacial stabilization caused by long-range vander Waals forces of the substrates, the long-lived metastable surface morphologies (the foam-like and the bicontinuous morphologies) were first observed. For the two-dimensional ultrathin PS/PMMA blend film (16.3 nm), the discrete domains of the PS-rich phases upon the PMMA-rich phase layer formed and the secondary phase separation occurred after a longer annealing time.

35. Christopher et al., (2003) have produced the films of atactic poly(methyl methacrylate) (PMMA) by spin-coating from toluene solutions, and their properties were compared to similar PMMA films produced by spin-coating from chloroform. Two-angle ellipsometry at $\lambda = 6328$ A° was used to probe the film thicknesses, refractive indices, and their overall quality and uniformity. Ellipsometry was also used with microspot optics at one angle to determine the film thickness uniformity. The films from toluene were approximately 4-fold thinner, but more uniform and of higher quality, than the films from chloroform, evidently because of the lower volatility and slower evaporation, of toluene. Films with thicknesses $d_1 = 0.003$ to 1 μm were produced for initial PMMA concentrations c=0.1–10 wt. %, and spinning speeds of 1000–3000 rpm. The thicknesses fit the equation d_1 (μm) $= 0.92\ c^{1.56}\ \omega^{-0.51}$. The ω dependence agrees with predictions of simple theoretical models. The results may find use in production of high-quality polymer films for resists or other applications.

36. Smarsly et al., (2003) have attempted to incorporate methacrylate-based polymers into ordered lamellar organic/inorganic nanocomposite films composed of alternating SiO_2/polymer layers. The films were prepared by dip-coating from a solution containing the monomers and silica precursors, thus leading to composite lamellar mesostructured materials through evaporation-induced self-assembly (EISA). A polymerizable coupling agent was added to covalently link the polymers to the silica matrix. The final polymer/SiO_2 hybrid material was obtained by a separate free-radical polymerization step, initiated by UV exposure or thermal treatment. Using trimethoxy(7-octen-1-yl)silane as a coupling agent, a procedure was established that preserved the mesostructure and maintained the swelling properties of the polymers, while acrylate-based coupling agents lead to a significant distortion of the film mesostructure. Structure and composition of the films were studied by X-ray diffraction, NMR and IR.

37. Pujari et al., (2002) have fabricated thin films of perylene in polystyrene matrix by spin coating technique. The concentration of polystyrene was kept constant to 1 wt% while that of perylene dopant varied in the range 1×10^{-5}- 1×10^{-1} wt%. The thickness of the films depends upon the concentration of perylene and varies from 45.48 to 582.16 nm. The structural aspects of the films were studied by recording the X-ray diffractogram of the films. The results of X-ray diffraction analysis reveal the crystalline nature of the film. The optical properties were studied by recording absorption, excitation and fluorescence spectra. The band gap energy of perylene in polymer films was calculated from absorption curves. The fluorescence spectra of the films show monomeric as well as dimeric emission bands. The films with lower concentration of perylene show monomeric emission similar to that of dilute solution, while the films with higher concentration of perylene exhibit structure-less broad emission. These emission bands appeared at 509 and 525 nm are attributed as arising from dimmer, formed in the ground-state by parallel orientational alignment of neighbouring molecules. The additional bands observed in the blue region of the absorption and excitation spectra of the films containing higher concentration of perylene confirm the formation of ground-state dimer.

38. Ton-That et al., (2001) have examined the films of polystyrene (PS) and poly(methyl methacrylate) (PMMA) blends of two different thicknesses by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Blends with different compositions were spin-cast onto a mica substrate with chloroform as the mutual solvent. XPS measurements revealed surface enrichment of PMMA in all compositions. The thicker (66 nm) films exhibit a higher degree of PMMA surface enrichment than the thinner (17 nm) films. AFM imaging allows distinctions to be drawn between blends with differing compositions. The blend films with less than 50% PMMA bulk concentration generally exhibit pitted surfaces; the pit size varies with film thickness and bulk composition. When the PMMA bulk concentration is greater than 50%, the film surface changes to show island-like phase-separated structure.

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