Polymer Communication

Plasma polymerized ferrocene films

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ARTICLE INFO

ABSTRACT

This communication describes the formation of high index of refraction polymer thin films using a novel plasma polymerization deposition process. A flowing afterglow plasma reactor was modified to enable sublimation of solid samples into the gas phase for subsequent plasma polymerization. Thin films of plasma polymerized ferrocene were deposited on substrates and subsequently characterized. The refractive index as a function of processing conditions was obtained. Relatively high values of n (~ 1.73 at 589 nm) were obtained. The chemical nature of the polymer thin films was characterized using FTIR and XPS spectroscopy. This work demonstrates that plasma polymerization is an enabling technology for the fabrication of photonic thin films that utilize solid state precursors.

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1. Introduction

Polymer thin films are widely being studied for optical and electro-optical applications due to their improved performance over conventional inorganic materials which can be impractical in large area or low cost applications [1–3]. The potential of low weight, surface adaptability, variable chemical and optical performance, and excellent processability all drive interest in utilization of polymers in such applications. One drawback of polymer thin films is that they have relatively low refractive indices when compared to most inorganic and metallic compounds. There are two common approaches to increase the index of refraction of polymers including the creation of thin films with a dense internal structure (including large amounts of conjugation and crosslink density) or the incorporation of high molecular refractivity components (including inorganic moieties, metal ions, or nanoparticles). The latter is the basis behind using organometallics as precursors in the fabrication of hybrid polymer thin films [4–7].

Plasma enhanced chemical vapor deposition (PECVD) has become an increasingly popular tool for the fabrication of polymer thin films [8–10]. It is a solvent-free, easy to control, room temperature process that produces high quality polymer films of varying thicknesses. In addition to these unique features, polymers can be derived from a wealth of unconventional monomers in either a gas, liquid (evaporation), or solid (sublimation) phase. The

properties of the resulting plasma polymerized (PP-) films can be engineered to reflect the characteristics of the original monomers in addition to creating new features that do not exist in the precursor materials. Most PP-films possess highly crosslinked amorphous structures and smooth surface morphologies, leading to robust mechanical properties and strong thermal, chemical and environmental resistances. In addition, these films have very good adhesion to a variety of substrates of different shapes. All of these properties make plasma polymerized thin films ideal for optical applications, and recently there has been increased interest in utilizing these films for just that purpose. For instance, by utilizing a plasma copolymerization method, films with variable chemical compositions could be obtained which allowed for a scaling of optical properties. A variable refractive index was controlled by varying the co-monomer feed ratio [11] between the two dissimilar monomers. This method grants the ability to manipulate the film's index of refraction and has been successfully used to fabricate multi-layer antireflective (AR) coatings and $\lambda/4$ wavelength notch filters. Furthermore, PECVD can utilize many unconventional monomers to create thin films which can not be synthesized by conventional chemical methods opening up a novel way to 'tune' the optical performance (n and k).

The refractive indices of polymers are much lower than those of the typical inorganic or metal compounds currently being used in optical applications. In order to enhance the refractive index of polymer thin films, this study focuses on the plasma polymerization of thin films from a metal-containing organic precursor, ferrocene. Since ferrocene and its derivatives show a relatively high refractive index and ferrocene in its solid state at room temperature

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can easily be sublimated, a custom designed sublimation apparatus was fabricated to prepare PP-ferrocene films. The resulting chemical and optical properties of ferrocene thin films formed under different plasma reaction conditions are described here. FTIR, XPS and variable-angle spectroscopic ellipsometry (VASE) were used to characterize these novel organic films.

2. Experimental

The PECVD-sublimation system was custom built as illustrated in Fig. 1. It was designed to carry out the flowing afterglow reaction for plasma polymerization reported previously [12–14]. The plasma chamber was modified to support sublimation as a 152 mm ConFlat flange with two high current copper feedthroughs was mounted to the bottom of the 100 mm diameter glass reactor and used to support a 46 mm deep tantalum heating boat (Kurt J. Lesker Co.). A magi-drive manual motion feedthrough was also utilized to control a small shutter to regulate the release of the sublimated material. The pressure in the reaction chamber was controlled between 0.01 and 0.1 torr for the film depositions while a constant 10–100 cm^3/min flow of 99.999% pure argon (Weiler Welding, Inc.) was used as the noble gas. The ferrocene (Aldrich, 98%) was held in the dimple (1.84 cm diameter, 0.46 cm deep) of the tantalum heating boat approximately 3 cm upstream and 6 cm below the substrate. Using a Re-Vap 900 W power supply (MDC Vacuum Products Co.) coupled to the copper feedthroughs, the ferrocene was heated to approximately 123 °C to sublime.

The PP-ferrocene films were deposited directly onto potassium bromide (KBr) windows for FTIR analysis, which was performed on a Perkin Elmer Spectrum 2000 FT-IR spectrometer in the transmission mode, with a scanning range of 400–4000 cm^{-1} in 1 cm^{-1} increments. The XPS analysis was done using a Surface Science Instruments M-Probe using monochromatic Al K_α X-rays (energy 1486.6 eV) on films deposited on Si substrates. The thicknesses of the films, their index of refraction (n) and their absorption coefficient (k) were obtained using a Woollam variable-angle spectroscopic ellipsometer system and analyzed using WVASE32 software. The polarization states were acquired over the range of 400–800 nm at 2 nm intervals and at angles of incidence equal to 55°, 65° and 75°. All data were obtained for deposition times of 10 min.

3. Results and discussion

Fig. 2 shows the FTIR spectra of four PP-ferrocene films deposited at different chamber pressures and pristine ferrocene. A small
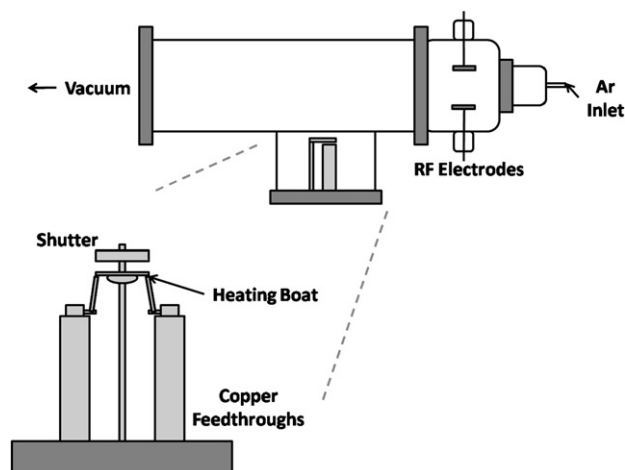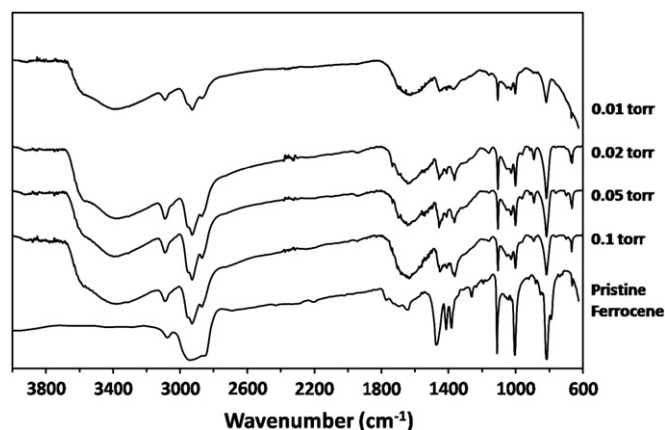

Fig. 2. FTIR spectra of PP-ferrocene at four different chamber pressures and the pristine ferrocene monomer. Spectra are normalized and offset for clarity.

but sharp band exists at 670 cm^{-1} assigned to metal–carbon stretching of the bond connection between two rings [15]. Compared to the pristine ferrocene, this band is slightly shifted to a higher wave number, implying a change of the original ring structure upon polymerization. The sharp band at 814 cm^{-1} is attributed to C–H ring metal stretching, while the bands at 1106 cm^{-1} and 1004 cm^{-1} are attributed to the C–Fe stretching and C–H out of plane bending (ring breath), respectively [15]. For the PP-ferrocene films, the intensities of these three bands are relatively low when compared to those of the pristine ferrocene, indicating changes to the original ring structure and loss of Fe moieties in the resulting films. When compared to the spectra of polyferrocene, as reported by Phadke, the bands at 814 cm^{-1} and 1106 cm^{-1} are almost completely eliminated [16], showing that PP-ferrocene films have a greater retention of Fe moieties. A small band at 889 cm^{-1}, due to the C–H out of plane deformation in the substituted ring, is much clearer for most of the PP-ferrocene films, which also implies that there are changes to the original carbon ring structure of ferrocene. Two peaks in the region of 1350 cm^{-1} and 1450 cm^{-1} represent methyl C–H bending in CH_2 and C–H stretching, respectively. A broad plateau in the 1650 cm^{-1} range, corresponding to mixed bands of C=C in the ferrocene conjugated structure and C=O groups, is stronger for the PP-ferrocene films than the monomer. A broad shoulder, appearing in the PP-films, exists in the region of 3350–3600 cm^{-1} and is attributed to OH vibrations associated with the carbon network (at about 3400 cm^{-1}) and Fe species (at 3560 cm^{-1}, such as the formation of FeOOH). The XPS composition data, listed in Table 1 confirm the FTIR results, showing that the PP-ferrocene films contain a large amount of surface oxygen which will be explored in a later publication.

The absorption band at 2929 cm^{-1} is due to the unsaturated C–H stretching, while the band at 2870 cm^{-1} is due to CH_2 and CH stretching, both of which are much clearer for the PP-films than

Fig. 1. PECVD-sublimation chamber and heating unit design.

Table 1
Atomic concentrations from XPS data

Sample	Atomic percentage of the components (at%)		
	C 1s	Fe 2p	O 1s
0.01 torr	71	9.0	20.0
0.02 torr	71	7.5	21.5
0.05 torr	72	5.8	22.2
0.1 torr	72	4.3	22.7
Ferrocene monomer (theoretical cal.)	91	9.0	0

those of the monomer, indicating the formation of different hydrocarbon moieties in the PP-films. These results indicate that the plasma polymerized films maintain some of the original structural features of the monomer, but several new characteristics emerge as well. All these differences, including the change in the carbon ring structure and enhancement and weakening of different carbon moieties, indicate the formation of a carbon-frame cross-linked structure within the PP-ferrocene films.

In general the FTIR spectra of the four PP-ferrocene films look nearly the same, although there are a few differences depending upon the chamber pressure. As it increased (Fig. 2), the bands at 2929 and 2868 cm^{-1} became more distinct (with respect to their own spectra), indicating the formation of more aliphatic hydro-carbon moieties, which implies a more crosslinked structure. In addition, the relative intensity of the 1106 cm^{-1} band is higher for films prepared under lower chamber pressure. This suggests that decreasing the reaction chamber pressure causes an increase in the retention of the Fe-components along with the breakage of the original monomer carbon ring structure. These results correspond well with the XPS data as seen in Table 1, showing the increase of Fe component in the PP-films with decreasing chamber pressure during processing.

In order to determine the relative degree of crosslinking of these films, a simple solution immersion experiment was used. After deposition on the 2″ silicon wafers, the PP-ferrocene film samples were immersed into a methanol solution (an excellent solvent for ferrocene) at room temperature and the changes of the films after the immersion were observed. For the film deposited at a chamber pressure of 0.1 torr, the sample remained unchanged for the duration of the 24 h immersion experiment. The sample was then vacuum heated for 2 h at 75 °C and, after cooling, the film was weighed and it was found that there was no loss of mass, indicating a highly crosslinked film. For the film deposited at a chamber pressure of 0.05 torr, no apparent change was seen in the first 5 min of immersion. At the 2 h point, cracks began to form on the film surface, but the film as a whole remained intact. After 24 h, approximately 1/8 of the film had delaminated from the silicon wafer, and several very small pieces of film material were observed in the solution. After the same heat-vacuum treatments there was a negligible weight loss, though the delamination and damage suggest that this film is less robust and therefore less dense than the 0.1 torr deposited sample. For the film deposited at a chamber pressure of 0.02 torr, part of the film peeled off the silicon substrate and entered the methanol solution after 5 min of immersion. After 25 min most of the film had detached from the substrate and residual pieces of the film became apparent in the solution. For the film deposited at a chamber pressure of 0.01 torr, the whole film changed color, from dark blue to nearly transparent after 3 min of immersion. Since the dark blue color was caused by the light interference from the thin film, the disappearance of the color was due to swelling of the thin film by the methanol. At the same time, the film delaminated from the silicon wafer at the substrate edge. After removing the film from the solvent and vacuum heating it at 75 °C for 2 h, the dark blue color of the film returned.

These results indicate that the crosslinking density of the PP-ferrocene films increased with the applied chamber pressure. This is attributed to a longer residence time for the activated species and monomer in the reaction chamber at higher pressures, which leads to an increased breakup of the original monomer and the creation of more reactive carbon species. Concurrently, fewer Fe-moieties end up in the plasma polymerized films due to the increased residence time of the initial monomers in the flowing afterglow region. This was also confirmed by the IR results, showing that with the increase in chamber pressure, the IR absorption bands at 2929 and 2868 cm^{-1}, representing aliphatic carbon moieties, become stronger. This indicates the formation of more carbon moieties,

which are preferential to crosslinking, but leads a decrease in the retention of the original ferrocene structural characteristics.

Fig. 3 shows the refractive index (n) variation of the PP-ferro-cene films with wavelength, as determined by ellipsometry. Ellipsometry was also used to determine the film thickness and the deposition rates for all four pressures. These thicknesses were found to be 214, 231, 338 and 328 nm for the samples deposited at 0.01 torr, 0.02 torr, 0.05 torr and 0.1 torr, respectively, which gives deposition rates of 21.4, 23.1, 33.9 and 32.9 nm/min. The refractive index of these films is substantially higher than most conventional polymers and of previously studied plasma polymerized organic films [11,13]. For instance, the refractive index of the PP-ferrocene films approaches 1.75 at 486 nm, significantly higher than previously observed in PP-benzene films (1.65). Based on the Lorentz–Lorenz relation [17],

$$r\rho = (n^2 - 1)/(n^2 + 1) \tag{1}$$

where r is the specific refraction (molar refraction divided by the molar mass) of the dielectric medium, ρ is the density of the medium, and n is the refractive index, it is understandable why the plasma polymerized films have a higher index of refraction. In general, plasma polymerized films form highly crosslinked struc-tures, which increase the density of the medium and therefore raise the refractive index when compared to corresponding conventional polymers. Furthermore, due to the high molar refraction of the metal (Fe) components and the additive and constitutive features of the specific refraction (r), the incorporation of Fe-moieties into the films would also contribute significantly to the magnitude of the refractive index. This explains why the PP-ferrocene films would have even higher indices than most of the PP-hydrocarbon films and conventional polyferrocenes (these polyferrocenes include the addition of inorganic backbones, giving an average index of refraction of 1.69 at 589 nm) [18–20]. All of these results are shown in Fig. 4, a plot of the Abbé number vs. the refractive index at 589 nm that shows the regions typically occupied by common organic polymers (dotted area) and most inorganic glasses (hatched area). Polyferrocenes with inorganic backbones (trian-gles) [19,20] and several of our Fe-containing sublimated films are shown. The Abbé number (v_D) is a measure of the optical dispersion of a material, which is expressed as:

$$v_D = (n_D - 1)/(n_F - n_C) \tag{2}$$

where n_D, n_F and n_C are the refractive indices of the material at wavelengths of 589 nm, 486 nm and 656 nm, respectively. The Abbé numbers of all these PP-films fall well outside the areas established for conventional polymers.
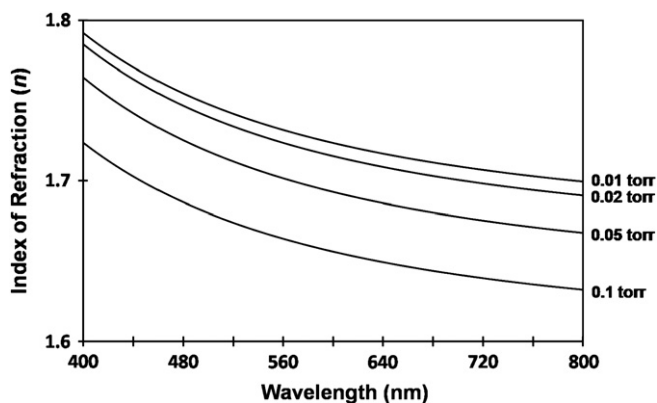

Fig. 3. Index of refraction of three PP-ferrocene films deposited at four different chamber pressures 0.01 torr, 0.02 torr, 0.05 torr and 0.1 torr.
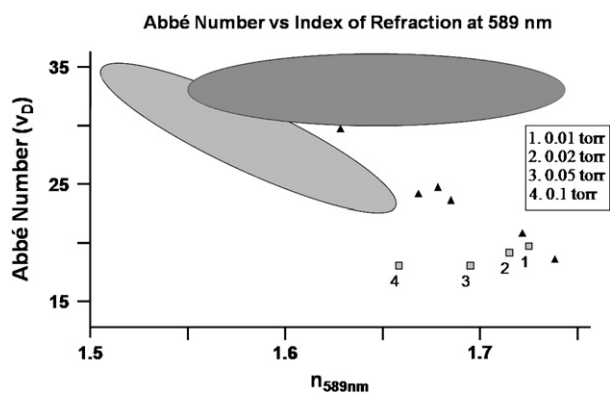
Fig. 4. Abbé number for polyferrocenes with inorganic backbones [20] (black triangles) and plasma polymerized ferrocene 1, 2, 3 and 4. The hatched and dotted regions represent inorganic glasses and conventionally polymerized materials respectively.

It is somewhat surprising to note that the PP-ferrocene films prepared at the lower chamber pressure had a higher refractive index. As described above, the XPS data prove that the films prepared under lower pressure have higher Fe concentration which is an important factor for increasing the refractive index of the PP-films. However, the structural characterization (including FTIR and the solution immersion tests) confirmed that the films prepared under lower pressure had a lower crosslinking density, which, as mentioned above, is a negative factor for increasing the refractive index of the film. This competition between retaining atomic components with higher molar refractions and the ability to form denser films is a key factor in affecting the index of refraction. This means that the contribution of the Fe-components to the films index of refraction is greater than the negative effect of the decrease in crosslinking density, indicating the importance of selecting a suitable monomer with high specific refraction for fabricating plasma polymerized photonic films.

4. Conclusions

In this study, a PECVD-sublimation technique has been developed and utilized to deposit high refractive index films from the non-volatile metal-organic precursor material, ferrocene, which opens up a wealth of new, solid state precursor materials for optical applications. The resultant PP-ferrocene films exhibit a higher refractive index, $n \sim 1.73$ (at 589 nm), than most conventional polymer materials and PP-hydrocarbon films. It has been shown that the PP-ferrocene films retain some of the characteristics of the pristine monomer including Fe-moieties in addition to novel hydrocarbon moieties. Adjusting the processing conditions during film fabrication enabled the composition and structure of the resultant films to be manipulated, including the content of their metal component and crosslinking density. The lower-pressure PP-ferrocene films retain higher Fe concentration and have a higher refractive index although their crosslinking density was lower than that of higher pressure films. This work demonstrates that plasma polymerization is an enabling technology for the fabrication of photonic thin films that utilize solid state precursors. One key benefit to PECVD is that the resultant films produced will nearly always have a greater crosslinking density than that of conventionally polymerized films, and the incorporation of metal ions with high molar refractivity is now possible through sublimation.

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