Characterization of Plasma-Polymerized Allylamine Using Waveguide Mode Spectroscopy

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Amine-functionalized thin films were prepared by plasma-induced deposition of allylamine. Radio frequency (rf) plasma polymerization was carried out under both continuous wave (CW) and pulsed conditions to control the film chemistry. The chemical and physical nature of plasma-polymerized allylamine films was investigated, as well as the effect of solvent treatment on the structure of the polymeric material. The film properties were studied using Waveguide Mode Spectroscopy (WaMS), which enabled an independent determination of film thickness and refractive index. Fourier transform infrared (FTIR) spectroscopy showed that changes in duty cycle led to different film chemistries. WaMS carried out on thin films ($d < 60$ nm) showed changes in the refractive index with increasing thickness believed to suggest intermolecular reactions occurring in the bulk while the film is depositing. All films studied showed a significant loss of soluble material from the surface upon solvent extraction. After extraction however, the films were stable and could be reversibly swollen in ethanol.

Introduction

To improve the adhesion of materials onto chemically inert polymeric surfaces, the functionalization of these surfaces has been of particular interest over many years. Plasma-assisted surface modification processes have been reviewed in the literature extensively.[1,2] For many applications, amine-rich surfaces are of particular interest, because they are known to influence protein adsorption and cell adhesion, and provide sites for the covalent immobilization of graft polymers and biomolecules.[3−5]

There are basically two plasma-assisted processes used for the introduction of amino groups onto a surface. In the first process, a surface is exposed to the plasma of a nonpolymerizable gas such as pure nitrogen or ammonia,[6−9] leading to surfaces containing amino groups, amides, and imines. This surface modification changes the composition and structure of only a few molecular layers at the surface of a material, and is well-suited for thermally sensitive materials such as polymer surfaces. For many nonpolymeric substrates, however, the plasma-assisted deposition of an amino group containing organic monomer is preferred.[4,5,10] Plasma polymerization allows the deposition of adhesive, pinhole-free films on a large range of substrates in a relatively simple, solvent-free, single-step process.

Many different organic compounds can be used as a monomer. By careful selection of the process conditions, it is possible to produce thin films with a great variety in chemical structure and physical properties. The molecules of the precursor are excited in the rf discharge and undergo polymerization reactions in the gas phase and on the solid substrate. Due to the complex nature of the plasma deposition process however, the functional groups of the monomer are often lost during polymerization. Several studies have placed emphasis on improving the control over the film composition, by variations in process parameters such as substrate location, substrate temperature, peak power, monomer flow, and process pressure.[11−14] Recent studies have shown promising results by using a pulsed plasma instead of the traditional continuous wave (CW) plasma. Large progressive changes in the film chemistry with variations of the rf duty cycle (i.e., the ratio of plasma on/plasma off times) have been shown for a number of organic precursors.[15−18]

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The plasma-assisted polymerization of monomers containing amino groups, such as allylamine, propylamine, and propargylamine has previously been described.[4,5,10] These films have shown interesting properties for biomedical applications. In an effort to investigate the applicability of these films, studies have been devoted to their aging process, usually with techniques such as XPS, FTIR spectroscopy, and contact angle goniometry. In general, it has been accepted that the aging process of plasma-treated materials is a combination of a number of processes occurring, which include post-plasma reactions with oxygen from the atmosphere, as well as molecular rearrangement and functional group mobility within the surface in an attempt to minimize interfacial energy.[19,20] The effect of VUV radiation, which is emitted during the glow discharge, on surface groups and properties has also been previously described.[21,22] In combination with the process of surface aging, a poor surface stability and swelling of plasma-polymerized films when exposed to solvent environments has been noted in this laboratory and by other workers.[23,24] It was often found that when using these films in subsequent reactions involving solvents, results proved to be inconsistent and showed very poor reproducibility. This inconsistency in previous results has led to the present study, with the aim to gain a greater understanding about the nature and behavior of plasma-polymerized films by monitoring changes in their optical properties during exposure to air or a solvent environment. It has thus been possible to optimize the methods of sample preparation for subsequent wet chemical applications.

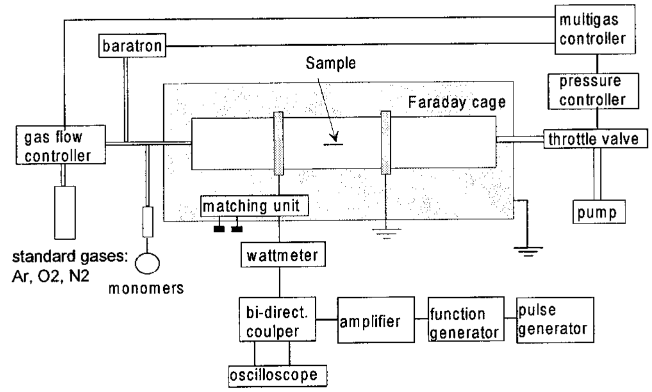

Figure 1. Schematic diagram of the plasma system.

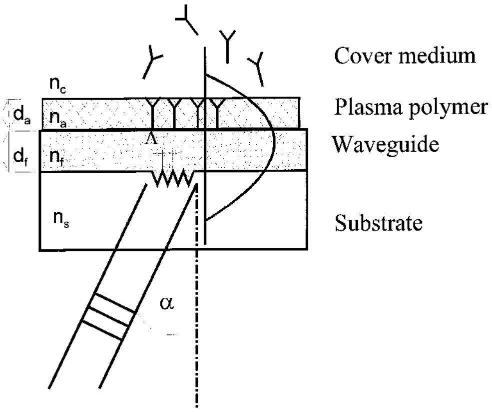

Figure 2. Waveguide modes in a planar multilayer waveguide.

Experimental Section

Plasma Polymerization. Reactions were carried out in a home-built inductively coupled cylindrical pulsed rf plasma reactor (Figure 1). The chamber consists of a 300-mm-long, 100-mm round Pyrex tube, which narrows at both ends. Gases that are fed through the system pass two glass, liquid nitrogen cooled traps for collection of excess reactant before reaching the pump (Leybold Trivac, D16BCS/PFPE). Sidearms at the narrow reactor inlet allow the introduction of gases such as oxygen, nitrogen, argon, and the monomer vapors. The flow rate of the standard gases (O_2, N_2, and Ar) is controlled by MKS gas flow meters (Type 1259C), while that of the monomer vapor is controlled by a Kobold floating ball flowmeter. A MKS Baratron (Type 122) is also connected to the inlet, to monitor the reactor pressure. A throttle valve at the other reactor end is used in conjunction with the pressure transducer to allow accurate control over the process pressure. The flow meters, the Baratron, and the throttle valve are controlled by a central multigas controller (MKS Type 647B). A Tektronix PG 501 pulse generator controls the pulsing of the rf signal, obtained from a 20 MHz function generator. The signal is amplified by an ENI 300 W amplifier and passed via a bidirectional coupler (BIRD 4266), an analogue wattmeter (BIRD 4410A), and a matching network to two concentric rings located around the exterior of the reactor. An oscilloscope connected to the bidirectional coupler was used in the tuning of the rf circuit under pulsing conditions. Reactor variables such as rf frequency (13.56 MHz), monomer flow (8 sccm), process pressure (0.2 mbar), rf power (200W), and sample position within the reactor were held constant in all experiments. Previous related work[16−18,24,25] has shown that plasma on and off times in the millisecond range provide excellent film chemistry control for a number of monomers tested. Since pulsed plasma studies include significant plasma off times, the equivalent power P_{eq} has to be taken into consideration when comparing the energy input during the pulsed experiments:

$$P_{eq} = P_{peak}[t_{on}/(t_{on} + t_{off})] \qquad (1)$$

Thus for a typical experiment at a peak power $P_{peak} = 200$ W and a duty cycle of $t_{on}/t_{off} = 10/90$ ms/ms, the equivalent power $P_{eq} = 20$ W.

Waveguide Mode Spectroscopy. The determination of the propagation constants of waveguide modes is an established procedure for the evaluation of the layer thickness and refractive index of a waveguide. It is based on the selective excitation of waveguide modes by means of a prism or a diffraction grating. The refractive index and the thickness of the layer can be calculated from the measured effective refractive indices of the different modes ($N_{\mathrm{eff}\ i,j}$, where i is the

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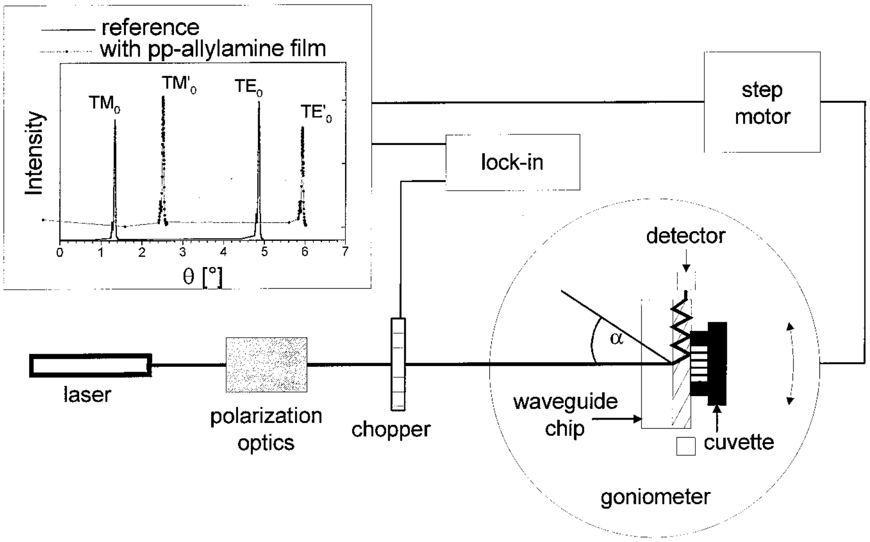

Figure 3. Schematic diagram of the WaMS setup.

polarization TE or TM, and j are the mode numbers 0, 1, etc.) using the dispersion relationship, with the assumption that the refractive index distribution within the layer is in the form of steps.[26] For this procedure the waveguide must be thicker than the wavelength of the laser used in the experiment.

Waveguide mode spectroscopy can also be used to characterize a much thinner adlayer on top of the waveguide. In this case very thin planar waveguides of high refractive index with TE0 and TM0 modes are used (Figure 2). By binding an adlayer to the surface of the waveguide the refractive index of the surrounding medium changes in the vicinity of the evanescent field of the waveguide modes. This in turn induces changes in the effective refractive indices $N_{\mathrm{eff\,TE0}}$ and $N_{\mathrm{eff\,TM0}}$ of the guided modes. The effective refractive index provides the phase velocity of the guided mode ($\nu = c/N_{\mathrm{eff}}$, where c = is the velocity of light in a vacuum) and depends on the polarization (TM0 and TE0) and the mode number. Changes in the effective refractive index, $\Delta N_{\mathrm{eff\,i,j}}$, can be measured using a grating coupler.[27] A laser beam can be coupled into the planar waveguide at an angle of incidence α if the in-coupling condition:

$$N_{\mathrm{eff\,i,j}} = n_{\mathrm{C}} \sin \alpha + I\lambda/\Lambda \qquad (2)$$

is satisfied. n_{C} is the refractive index of the covering medium (air or solvent), λ the wavelength of the laser used, I the diffraction order, and Λ the grating period. Thus, if a plasma polymer is deposited as an adlayer onto the waveguide, then its optical parameters (thickness d_{a}, and refractive index n_{a}) change the effective refractive indices $N_{\mathrm{eff\,i,j}}$ of the waveguide modes. The effective index shift $\Delta N_{\mathrm{eff\,i,j}}$ can be determined from eq 2 above by measuring the change $\Delta\alpha$. From the effective index shifts $\Delta N_{\mathrm{eff\,i,j}}$ the thickness d_{a} and refractive index n_{a} of the plasma polymer adlayer can be calculated by using the dispersion relationship for a four-layer planar waveguide.[27]

The experiments were carried out using a home-built spectrometer (Figure 3). A grating with periodicity Λ, incorporated into the waveguide was used to couple a HeNe laser beam (λ = 632.8 nm) from the external cover medium into the waveguide. $N_{\mathrm{eff\,i,j}}$ can be determined by scanning the angle of incidence of the incoming laser beam onto the grating, while the in-coupled power is measured by two photodetectors situated at both ends of the waveguide. The waveguide was designed for optimal sensitivity for the zeroth transversal electric, TE0, and transversal magnetic, TM0, modes.

Sample Preparation. The allylamine monomer (Aldrich, Germany) was outgassed three times before use, but was not further purified. The films were deposited either on 10 × 20 mm pieces of silicon for FTIR analysis, or on waveguide chips for the WaMS experiments. Two different kinds of waveguide chips were used. For the measurements of the plasma-polymerized allylamine films against air, a TiO_2/SiO_x film ($d_{\mathrm{F}} \approx 168$ nm, $n_{\mathrm{F}} \approx 1.82$, $\Lambda = 417$ nm) on a glass substrate was used as the waveguide. The experiments against ethanol were done with a waveguide chip consisting of a Ta_2O_5 film ($d_{\mathrm{F}} \approx 163$ nm, $n_{\mathrm{F}} \approx 2.22$, $\Lambda = 745$ nm) on glass, since this showed an increase in thickness of only 2 Å upon swelling in ethanol for 10 h. This was an order of magnitude lower than that of the TiO_2/SiO_x waveguide. The exact refractive index and thickness of the waveguide were determined before each deposition by a measurement against air. All substrates were cleaned in an argon/oxygen plasma for 10 min before deposition of the allylamine. Silicon substrates were cleaned in ethanol under ultrasound. The samples were placed on a 40 × 40 mm glass holder on top of a small glass beaker halfway between the electrodes. After each deposition process the reactor was cleaned for 1 h using an O_2 plasma at 200 W.

Results and Discussion

The pulsed plasma deposition of allylamine at different duty cycles was studied using FTIR and optical waveguide mode spectroscopy. The FTIR spectra (Figure 4) show absorption bands, indicating the presence of primary and secondary amines (3340 cm^{-1}), and a multiple absorption band due to the CH_x bond stretches (2960, 2935 and 2875 cm^{-1}). The peak at 2185 cm^{-1} indicates the presence of nitrile groups, while the broader bands around 1660 cm^{-1} can be assigned to the bending modes of primary amine groups and the stretching of imine groups. FTIR analysis of films deposited under CW conditions at a P_{peak} of 50 W and at a duty cycles of 10/40 at a P_{peak} of 250 W (P_{eq} = 50 W) showed that in going from CW to pulsed plasma polymerization, different film chemistries could be obtained as seen by the relative intensity increase of the amino band (3340 cm^{-1}) and a relative intensity decrease in the nitrile band (2185 cm^{-1}). If the duty cycle was further decreased to 10/190 (P_{eq} = 13 W), the further increase in the absorption band around 3340 cm^{-1} relative to the bands around 2960 and 1660 cm^{-1} suggests the increasing retention of the monomer structure in the plasma polymer layer. XPS elemental analysis (not shown) of

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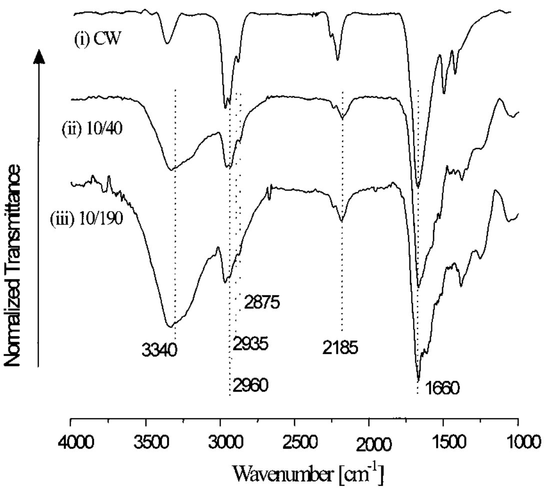

Figure 4. Typical FTIR spectra of (i) CW, (ii) pulsed plasma deposited allylamine at 250 W and high (10/40), or (iii) low-duty cycle (10/190)

samples deposited at CW conditions showed N/C ratios typically < 0.25, while at low-duty cycle XPS typically showed N/C ratios ≥ 0.3.

The differences observed between CW and the pulsed plasma-deposited allylamine films suggest very different reaction mechanisms to take place during the two processes. During a CW plasma deposition, the competing deposition and etching reactions of the excited species in the plasma led to a different polymer structure than a pulsed plasma treatment. It appears, that the plasma off periods in the pulsed experiments play a very important part in the deposition process, allowing polymerization reactions to take place which could not normally occur under CW condition. During the plasma on period highly energetic ions, radicals and electrons are created, of which some will undergo polymerization reactions, while others will in turn cause dissociation and bond breaking. During the plasma off phase most of these energetic species are lost and it is believed that only some of the longer lived radicals will continue polymerization reactions, leading to a unique polymer structure.

Film properties were studied using waveguide mode spectroscopy on thin plasma-polymerized allylamine films deposited at duty cycles of 10/90 and 10/190. For both duty cycles the film thickness increased linearly with the deposition time (Figures 5 and 6). At deposition times shorter than 5 min the films obtained for these duty cycles showed an increase in refractive index (Δn) with increasing film thickness. For the higher duty cycle, deposition the maximum Δn observed was 0.08, while for the lower duty cycle Δn was observed to be 0.15. With longer deposition times, and thus increasing thickness, Δn remained approximately constant with both sets of films eventually reaching the same absolute value of refractive index. The films deposited at low-duty cycle (10/190), therefore, initially showed a lower absolute refractive index than the films deposited at higher duty cycle, these diverging to the same value at a thickness approximately >60 nm. At thicknesses greater than 60 nm, it was observed, that the duty cycle no longer appeared to have such an effect on the absolute refractive index, such that variations in refractive index between films deposited at different duty cycles were seen to remain within the experimental error of the data (Figure 7).

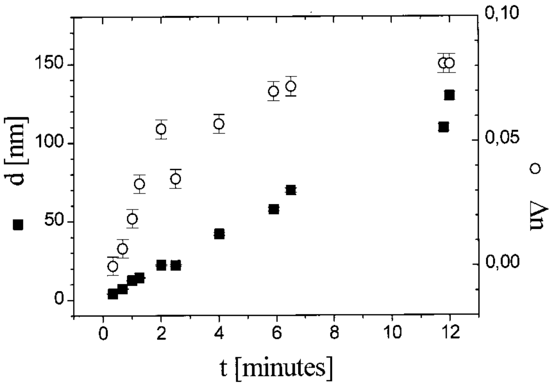

Figure 5. Thickness and refractive index of pulsed plasma-polymerized allylamine after varying deposition times, at a duty cycle of 10/90 and a peak power of 200 W.

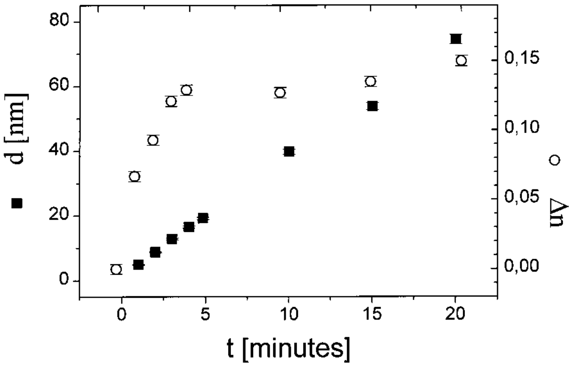

Figure 6. Thickness and refractive index of pulsed plasma-polymerized allylamine after varying deposition times, at a duty cycle of 10/190 and a peak power of 200 W.

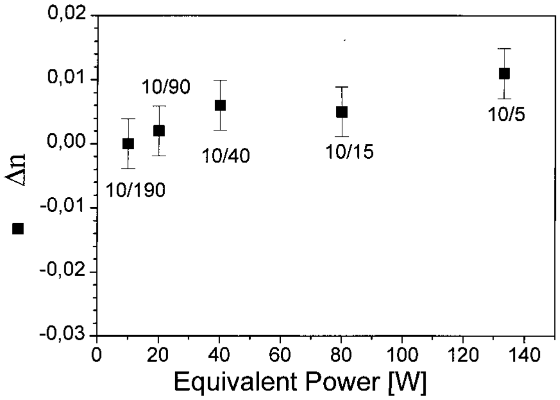

Figure 7. Refractive index as a function of P_{eq} for pulsed plasma-polymerized allylamine films of similar thickness (d > 70 nm), deposited at 200 W at different duty cycles.

The refractive indices measured may give indications toward the degree of polymerization within the film during the early stages of the deposition mechanism. Low refractive indices could be taken to indicate a lower density, less intermolecular bonding, and a low degree of polymerization within the polymer film. The change in refractive index observed with increasing deposition time and film thickness could thus be taken to suggest structural changes occurring within the polymer film as the film grows. It could thus be envisaged that as material is depositing at the solid/gas interface, the underlying "bulk" material continues to endure consid-

Table 1. Film Thicknesses of Plasma-Polymerized Allylamine Deposited at 250 W for 5 Min at Different Duty Cycles before and after Cold Extraction in Ethanol

		d [nm]		
duty cycle	P_{eq} [W]	before extraction	after extraction	% decrease
10/240	10	20	3	85
10/120	19	42	20	52
10/40	50	145	111	23
CW	50	186	85	54

erable structural changes, independent of the plasma-initiated polymerization. This structural change is probably due to intermolecular reactions, possibly initated by the VUV during the plasma on-times or due to cross-linking and molecular rearrangement within the network during the plasma off times. As the molecules rearrange within the "bulk", a more densely packed polymer network results which is assumed to be reflected in the higher refractive indices measured. At higher duty cycle, the plasma on time and the P_{eq} per cycle is greater than during the low-duty cycle deposition, which results in an apparently higher initial refractive index at short deposition times. Such a model could imply that the uppermost layers of a plasma polymer near the solid/gas interface have a lower degree of polymerization and probably show a lower refractive index. This could not be measured and confirmed in this work, but will be the subject of another study. Below this interface layer the underlying "bulk" material continues to polymerize to form a more closely packed network with a higher refractive index. As the overall film thickness increases, the influence of the refractive index of the "bulk" material eventually dominates the total refractive index measured during waveguide mode spectroscopy, leading to negligible index changes observed with greater thickness.

Many applications of plasma-polymerized films involve solvent-based chemical reactions and quite often, changes in the film thickness are taken as a control over the attachment of biomolecules or the subsequent grafting of polymers to the plasma-polymerized film. It was observed in numerous wet chemical, post-plasma treatments that the measured film thicknesses after the treatment were inconsistent and led to misinterpretations. We have previously reported on the necessity of a stabilizing posttreatment of plasma-polymerized allylamine films before further use, such as an extraction in ethanol.[24] For the duty cycles studied in this work it was found that with decreasing duty cycle the films showed an increasing amount of soluble, not covalently bonded material on the surface, which could be removed by cold extraction in ethanol (Table 1). After each extraction and before analysis the films were dried in a vacuum at 40 °C for 2 h. It was thus found that the films deposited at a low-duty cycle of 10/240 showed a thickness decrease of up to 85%, while films deposited at the higher duty cycle of 10/40 showed a typical loss of 23%. Thus, while low-duty cycle depositions produce films which largely resemble the monomer structure, these films also suffer from a low degree of polymerization with a large amount of soluble and unbound shorchain material on the surface. For comparison, films deposited at CW conditions also showed considerable loss of material, part of which is probably due to the simultaneous etching reactions occurring at the surface. XPS and FTIR analysis of the films before and after extraction showed no measurable changes in either the chemical composition or the chemical structure.

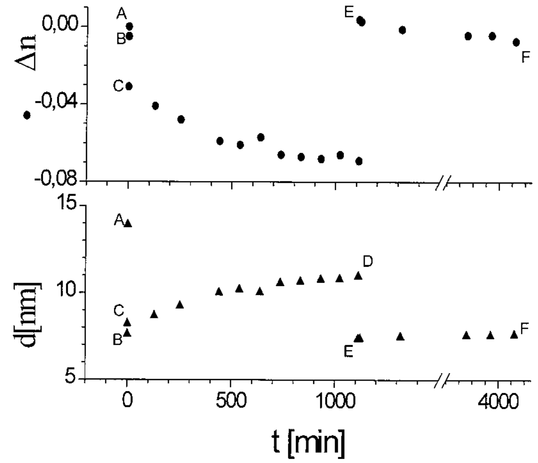

Figure 8. (a) Refractive index and (b) thickness of pulsed plasma-polymerized allylamine (200 W, 10/190, 5 min) immediately after deposition (A), after 24 h cold extraction in ethanol and drying in a vacuum for 12 h (B), after exposure to ethanol (C), after swelling for 19 h (D), after drying in a vacuum for 12 h (E), and after 55 h in air (F).

Although 24-h extraction in ethanol caused a significant loss of material, FTIR and XPS analysis of the remaining material showed no significant changes in the chemical structure or composition of the films. The fact that the films could be stabilized by this posttreatment made it possible to study the swelling behavior of the plasma-polymerized allylamine films in ethanol, by following the refractive index and the film thickness using Waveguide Mode Spectroscopy (Figure 8). Thus for a film deposited at a duty cycle of 10/190 and 200 W, extraction caused an almost negligible change in refractive index (Δn), but a considerable change in thickness (Δd) (Figure 8, points A and B). When this film was then submersed and left in ethanol for a period of 19 h, a decrease in refractive index of 0.04, accompanied by an increase in thickness of ~50% was observed (Figure 8, points C and D). During swelling, the solvent molecules penetrate into the plasma polymer network such that the refractive index measured now represents a combination of the ethanol and the plasma polymer. After subsequent drying in a vacuum overnight, the ethanol could be completely removed from the polymer network and the thickness and refractive index were seen to return to their value before solvent treatment (point B). Monitoring the films against air for another 50 h resulted in small changes in either refractive index, but only negligible variations in thickness.

By allowing the simultaneous determination of refractive index and thickness against different cover media, waveguide mode spectroscopy has enabled new insights into the structure, aging, and swelling behaviors of these films. The data have provided vital information required for the application of these films. The results of this work suggest the bulk of the material, which has been subjected to the glow discharge for a longer period of time than the material just below the surface, appears to have a higher degree of cross-linking and therefore a higher refractive index. Further, the results have shown that plasma-polymerized allylamine films are partly soluble in ethanol and that treatment with a suitable solvent can lead to a loss of material. Films produced under low energetic conditions (low-duty cycles) have shown to result in films with a higher $-NH_2$ content, but are also less stable upon subsequent solvent treatment. Despite the loss of material however, enough insoluble material always remains, with interesting properties that can be utilized successfully for grafting and derivatization reactions, which will be the subject of future publication.

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