

THE CHARACTERIZATION OF POLYMER THIN FILMS GROWN BY PLASMA POLYMERIZATION

KARAKTERIZACIJA POLIMERNIH TANKIH PLASTI PRIPRAVLJENIH S PLAZMA POLIMERIZACIJO

**John T. Grant¹, H. Jiang,² K. O'Neill³, K. Eyink³, W. E. Johnson³,
E. M. Johnson³, S. Tullis³, D. W. Tomlin³, P. Fleitz³, T. J. Bunning³**

¹Research Institute, University of Dayton, Dayton, OH 45469-0168, USA

²Anteon Co., Dayton, OH 45431, USA

³Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433-7702, USA
j.grant@ieee.org

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Plasma-enhanced chemical vapor deposition (PECVD) has been used to grow homo-polymerized films, co-polymerized films, and multi-layered films on a variety of substrates. The use of polymers as linear optical materials has been growing, and organic materials offer several advantages over inorganic materials. These advantages include processability and cost. Optical polymers have refractive indices in a narrow range between 1.4 and 1.6 and for multi-layer interference films the thickness needs to be in the range of 75–100 nm. In this work, benzene and octafluorocyclobutane (OFCB) have been used as precursor materials and are reacted either downstream from the plasma or, in some cases with OFCB, in the plasma zone itself. Rates of deposition and refractive indices were measured and this information was used to design and fabricate photonic structures. The films were characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), variable-angle spectroscopic ellipsometry (VASE), and X-ray photoelectron spectroscopy (XPS/ESCA).

Key words: polymer films, plasma polymerization, chemical vapor deposition, benzene, octafluorocyclobutane, SEM, FTIR, VASE, XPS

Kemijski nanos iz pare s plazmo (PECVD) je bil uporabljen za pripravo homopolimeriziranih, kopolimeriziranih in večplastnih tankih plasti na različnih podlagah. Uporaba polimerov kot linearnih optičnih materialov raste, ker imajo organski materiali več prednosti pred anorganskimi materiali. Med prednostmi so tudi procesiranje in stroški. Optični polimeri imajo lomne količnike v ozkem pasu med 1,4 in 1,6 in za večplastno interferenco je potrebna debelina plasti med 75 nm in 100 nm. V tem delu sta kot prekursorja uporabljena benzen in oktafluorciklobutan (OFCB), ki sta bila zreagirana protitočno iz plazemske cone in v nekaterih primerih iz OFCB plazemske cone. Hitrosti nanašanja in lomni količnik so bili izmerjeni in podatek je uporabljen za načrtovanje in izdelavo fotonских struktur. Karakterizacija plasti je bila izvršena z vrstično elektronsko mikroskopijo (SEM), Fourier transformacijsko infrardečo spektroskopijo (FTIR), večkotno spektroskopsko elipsometrijo (VASE) in rentgensko fotoelektronsko spektroskopijo (XPS).

Gljučne besede: polimerne plasti, kemijski nanos iz pare, benzen, oktafluorciklobutan, SEM, FTIR, VASE, XPS

1 INTRODUCTION

The uses of thin films to produce high-efficiency broadband mirrors, anti-reflection coatings, and narrow-notch filters are common, and their performance is determined by spatial control of the refractive index profiles. The majority of these films are formed by depositing inorganic precursor materials, typically using various chemical vapor deposition (CVD) techniques. Inorganic materials have been used due to their large refractive index range and their low absorption coefficients. CVD-type processes suit these materials and also allow for the ability to make non-conventional refractive index profiles by simultaneous co-deposition of more than one component. The use of polymers as linear optical components has been growing as organic materials offer several advantages over inorganic materials. These advantages include processability, compatibility, and cost. Simple one-dimensional stacks of processed polymer films were first reported over 10 years ago ¹. With the recent advent of photonic crystal research, a

large amount of activity has been centered on using various polymer-based platforms including block copolymers ^{2,3}, polymeric hydrogels ^{4,5}, and organic/organic hybrids ^{6,7} as optical band gap materials. The successful formation of one-dimensional multi-layer interference films using organics is dictated by the refractive index contrast between the multi-layer materials, control of the optical thickness (the product of refractive index and film thickness), and the number of layers achievable. Two limitations for organics include the small refractive index range and dimensional control of periodicity. Commercially available, easily processable optical polymers have refractive indices in a narrow range of 1.4 to 1.6 ⁸, and for visible multi-layer stacks, thicknesses on the order of 75–100 nm are required.

The most important factor for high, narrow notch, reflectivity is the refractive index contrast ⁹. This contrast can be produced in different ways such as the classic ABAB stack and the rugate (sinusoidally-varying) profile ¹⁰. The advantage of the latter type structure is increased transmission (elimination of

higher-order harmonics) and better overall control of notch depth and width. Therefore, deposition techniques to produce continually varying refractive index profiles must allow for the co-deposition of both high and low refractive index compounds. Plasma enhanced chemical vapor deposition (PECVD) offers the promise of dense cross-linked films with continuously varying refractive indices, and is the deposition technique used in the work reported here. Plasma polymerization of organic compounds is well known and many studies have been reported¹¹⁻¹³. It is a dry deposition technique, suitable for automation, can be run at room temperature, and can be used for deposition on both planar and curved surfaces. Compared to conventional wet techniques, it generates very little waste and allows polymers to be formed from non-conventional precursors including aromatic heterocycles such as thiophene and furan^{14,15}. Adjusting the PECVD processing parameters also allows for fine-tuning the chemistry and the thickness of films. It also has the ability to co-deposit two precursors simultaneously to obtain a refractive index intermediate between the two starting materials.

In the work reported here, benzene and octafluorocyclobutane (OFCB) were used as precursor materials. Thin, plasma polymerized (PP) films of both compounds (PP-benzene and PP-OFCB) were characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), variable-angle spectroscopic ellipsometry (VASE), and X-ray photoelectron

spectroscopy (XPS/ESCA). The rates of deposition and the refractive indices were measured. This information was used to design and fabricate a multi-layer stack using PP-benzene as the high refractive index material and PP-OFCB as the low refractive index material. Optical spectroscopy measurements indicate good agreement with the theoretical notch as computed using the measured thickness, refractive index and absorption coefficients. Several co-polymerized films were also grown in order to tailor the refractive index of the films. From this, a six layer antireflection coating was designed and fabricated to show that PECVD can be used to fabricate complex photonic structures using non-conventional organic precursors.

2 EXPERIMENTAL PROCEDURES

Optical grade liquid benzene (Aldrich, purity > 99 %) was used as the high refractive index precursor, and compressed gaseous OFCB (TCI, purity 99 %) was used as the low refractive index precursor. Both precursor materials were used directly in this work without any further purification. **Figure 1** shows a schematic of the PECVD reactor used in this work. Argon (99.999 % pure) was used as the noble gas for generating the plasma, and flowed at 50–200 cm³ min⁻¹ (sccm) into a 10 cm diameter reactor at 0.66–1.3 mbar through a capacitively coupled radio frequency (RF, 13.56 MHz) discharge of 5 W to 30 W. The plasma density was

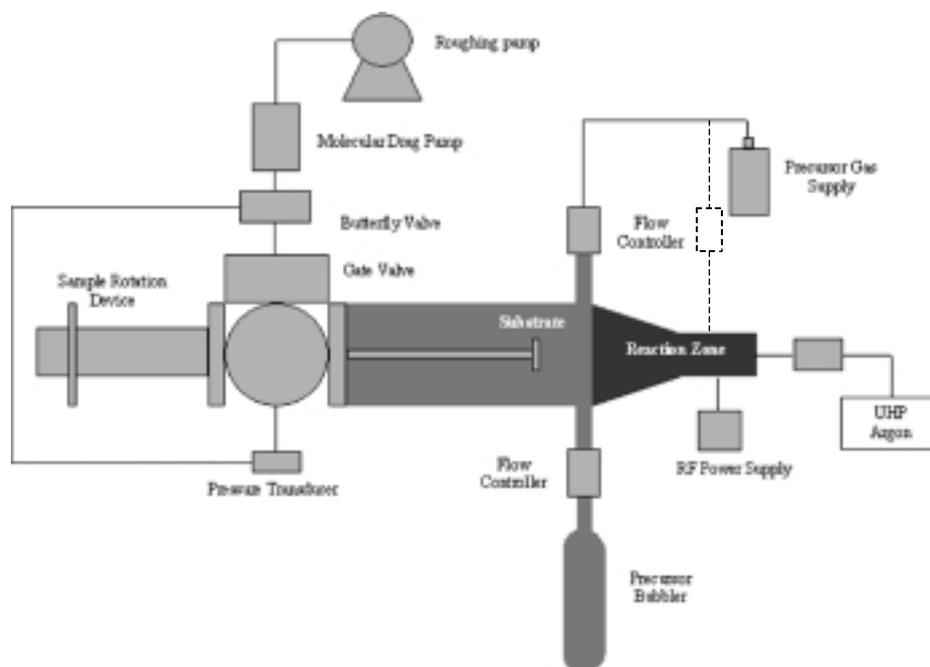


Figure 1: Schematic diagram of the plasma enhanced chemical vapor deposition system. For the homo-polymerized films, the OFCB is introduced after the reaction zone where the interaction is with metastable argon ions in the flowing afterglow region (solid line). For co-polymerized films, the OFCB is introduced directly into the plasma zone (dashed line).

Slika 1: Shema naprave za kemični nanos iz pare v plazmi. Za homopolimerizirane tanke plasti se OFCB vstavi za reakcijsko cono, kjer poteka reakcija med metastabilnimi ioni argona v območju tlenja (cela črta). Za kopolimerizirane tanke plasti se OFCB vstavi neposredno v plazmo (črtkana črta).

controlled at approximately 10^8 cm^{-3} in the afterglow region. For growing the multi-layer stack using homo-polymerized films, the precursor gas/vapor was added 7 cm downstream from the plasma generation zone. The substrate was located about 1 cm to 3 cm further downstream from the precursor inlet. Precursor flow rates of 0.5 cm^3 and 1.125 cm^3 were utilized for the benzene and OFCB films, respectively. For the co-polymerized films, benzene was added 7 cm downstream from the plasma zone at controlled rates between 0.001 cm^3 and 0.5 cm^3 , whereas the OFCB was fed into the middle of the plasma zone at a rate of 0.5 cm^3 to 5 cm^3 . Films were deposited on silica wafers, glass or IR transparent salt plates, and for some XPS studies they were deposited on Si wafers.

A Sycon STM-100 Thickness/Rate Monitor was used in preliminary measurements of film deposition rates. A Tencor P-10 surface profiler with a diamond stylus was used to perform profilometry. An average scan rate of $100 \mu\text{m s}^{-1}$ was used with a sampling rate of 200 points s^{-1} resulting in a spatial resolution of $0.5 \mu\text{m}$ per point.

Functional groups present in the plasma polymerized films were identified using FTIR. Films were deposited directly onto potassium bromide disks in the reaction chamber for subsequent analysis. FTIR analysis was performed using a Perkin Elmer Spectrum 2000 FTIR spectrometer in the transmission mode. A range of 400 cm^{-1} to 4000 cm^{-1} was scanned 128 times in 1 cm^{-1} increments and averaged.

XPS was performed using a Surface Science Instruments' M-Probe Spectrometer equipped with a monochromatic Al $K\alpha$ X-ray source (energy 1486.6 eV) for photoelectron production. The surface composition of each sample was determined from survey scans taken between 0 eV and 1000 eV binding energy. Individual elements were detected by acquiring data at appropriate energy regions using the unscanned spectrometer mode. The spectrometer energy resolution was 1.5 eV for all data; the spectrometer covered an energy range of approximately 20 eV in the unscanned mode. The analysis area on the samples was $400 \mu\text{m} \times 1000 \mu\text{m}$.

Ellipsometry was used to determine both the optical properties and the thickness of the plasma polymerized films. A Woollam variable angle spectroscopic ellipsometer system including a VB-200 ellipsometer control module and a CVI Instruments Digikröm 242 monochromator with 100 W mercury and 75 W xenon light sources was used. Data analysis was performed using Windows version 3.352 WVASE32 software. The reflected polarization states were acquired over the range of 300–900 nm at 1 nm intervals and at angles of incidence of 53° , 55° and 57° . In determining the dispersion in the refractive index for each different polymer film, the polarization data from samples containing different thickness of the polymer film on a Si(001) substrate were simultaneously analyzed.

A Hitachi S-900 low voltage/high resolution SEM was used to image the plasma generated polymer films. Films were deposited on silicon wafers and coated with 1–2 nm of tungsten using a VCR Group, Inc. (now South Bay Technologies) Dual Ion Beam Sputter Coater, to eliminate sample charging and to enhance edge contrast.

3 RESULTS AND DISCUSSION

3.1 Homo-polymerized films

In this part of the work, the gas phase precursors were introduced in the afterglow region, 7 cm downstream from the plasma generation zone. An XPS survey spectrum from a PP-benzene film is shown in **Figure 2a**. The oxygen content of this film is 3 atomic percent. Of particular interest is the small feature about 7 eV on the high binding energy side of the C 1s peak. This is a shake-up peak due to unsaturated carbon bonds, and is shown more clearly in **Figure 2b**. Even though this peak appears to be small, it indicates a high degree of unsaturated carbon in the PP-benzene film¹⁶. This result is consistent with the FTIR results, which showed that a

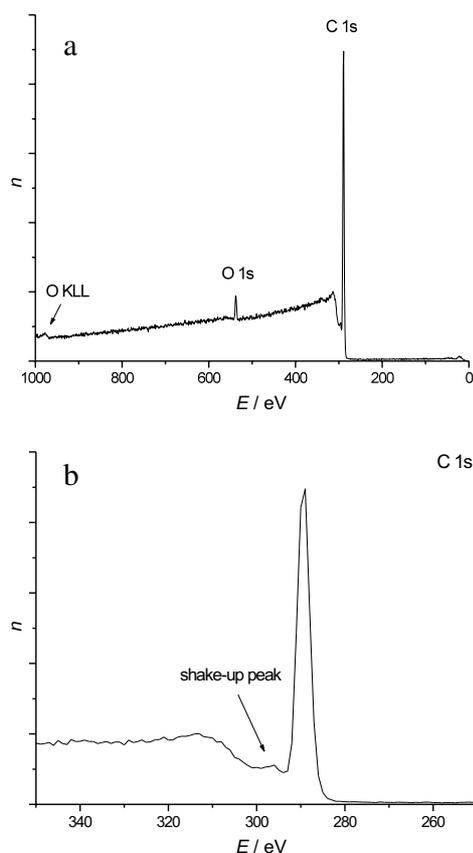


Figure 2: (a) XPS survey spectrum of a PP-benzene film; (b) C 1s spectrum from PP-benzene film showing the shake-up peak (E – Binding energy)

Slika 2: (a) XPS-spekter PP-benzenove tanke plasti; (b) C 1s spekter iz PP-OFCB plasti ima takoiimenovani shake-up vrh (E – vezavna energija)

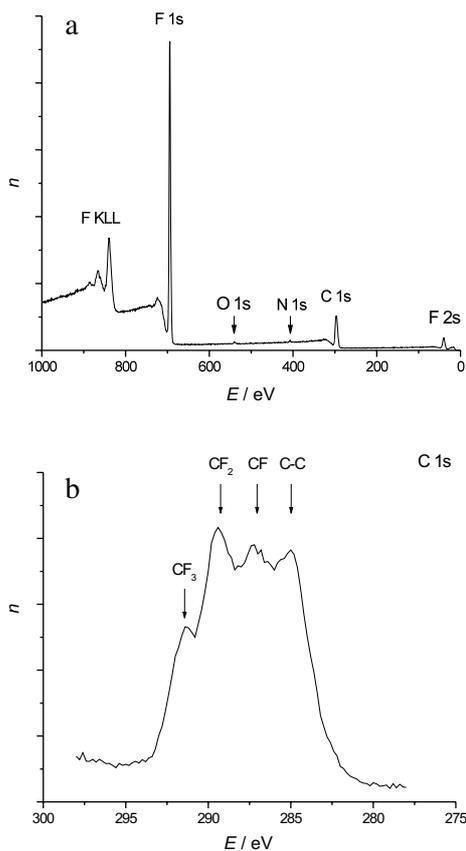


Figure 3: (a) XPS survey spectrum of a PP-OFCB film; (b) C 1s spectrum from PP-OFCB film showing the effect of fluorine chemistry

Slika 3: (a) XPS-spekter tanke plasti PP-OFCB; (b) C 1s spekter iz PP-OFCB tanke plasti, ki prikazuje vpliv fluora

small percentage of the benzene rings were broken during the PP reaction.

An XPS spectrum from PP-OFCB is shown in **Figure 3a**. Besides the expected peaks from C and F, peaks from N and O were also detected but they had concentrations of only about 0.7 atomic percent each. The F/C atomic ratio in the film was about 1.8, slightly less than the value of 2 for the OFCB precursor, C₄F₈. During plasma polymerization, the fluorine chemistry changed dramatically, as can be seen from the C 1s spectrum shown in **Figure 3b**. It can be seen that there are at least four peaks in this spectrum, and they correspond to (from left to right) CF₃, CF₂, CF, and CC bonds. The CF₂ and CF intensities are similar, and about double that of CF₃. The fluorine concentration required to satisfy the identification of the three carbon peaks associated with the indicated numbers of fluorine atoms agrees very closely with the measured fluorine concentration. The CC peak is somewhat broader and has an intensity of about 1.5 times that of the CF₂ or CF peaks. FTIR measurements showed that the original ring structure of the OFCB was almost entirely destroyed during plasma processing, and that several different CF_x

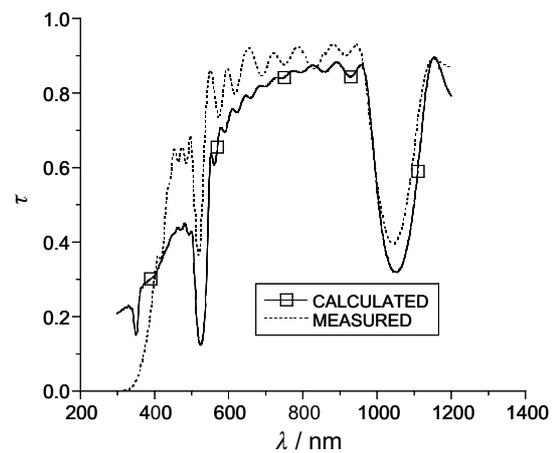


Figure 4: Comparison of the transmission τ spectrum of the multi-layer homo-polymer stack (dotted line) together with the design spectrum (solid line)

Slika 4: Primerjava izmerjenega presevnega τ spektra (TEM) večplastnega homopolimernega zloga (črtkana črta) in izračunanega spektra (cela črta)

structural groups are present in the film. The XPS results confirm that this is indeed the case.

Ellipsometry measurements showed a large difference in refractive index between the films. At 500 nm, the PP-OFCB films had a refractive index of 1.40 whereas the PP-benzene films had 1.62. This large difference was exploited to make a multi-layer interference filter.

A 10-bilayer stack was designed using these refractive indices measured from ellipsometry, and deposition rates measured from experiment, to make a notch filter at 1000 nm. The thicknesses of the individual layers were calculated from the quarter-wavelength condition and the layers were deposited onto quartz. The transmission spectrum of the multi-layer stack is shown in **Figure 4** together with the design spectrum. The

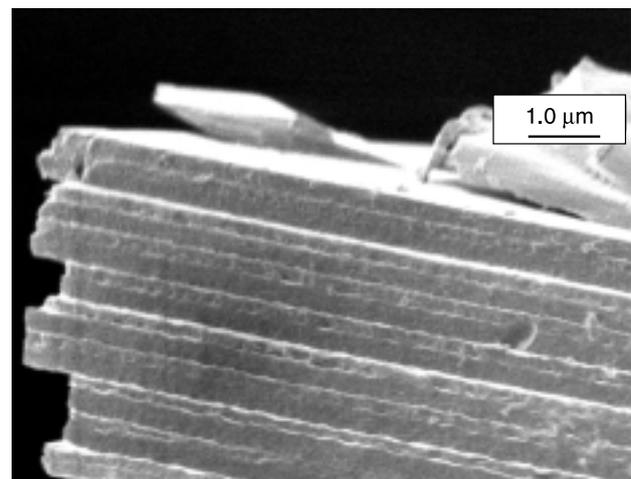


Figure 5: SEM image of the fractured cross-section of the 10-bilayer stack fabricated using PECVD

Slika 5: SEM-slika prereza zloga iz 10 dvoplastnih delov, izdelanih po PECVD-postopku

positions of the peaks and the magnitude of the notch are in good agreement, which is remarkable given the serial nature of the deposition process. This indicates good control over the deposition conditions and also that PECVD of organic precursors can be utilized to deposit optical films with good thickness control. SEM studies of the cross-section of the 10-bilayer stack (fractured in liquid nitrogen) show that the individual layers are dense and have good adhesion. This is illustrated in **Figure 5**.

3.2 Co-polymerized films

In the initial work on plasma co-polymerization of benzene and OFCB, the same inlet location, 7 cm downstream from the plasma zone, was used for both precursors. Even though the flow rates were varied from 0.5 cm³ to 5 cm³ and the plasma parameters (power and argon flow rate) were adjusted, the co-polymerized films always had a high refractive index that was close to the homo-polymerized benzene film. XPS measurements showed that the fluorine content in the films was always low, the atomic fraction being less than 5 % even when the OFCB flow rate was at its maximum (5 cm³) and the benzene at its minimum (0.5 cm³). The FTIR spectra were also very similar to that from the homo-polymerized benzene film, and only traces of vibrations associated with CF_x groups were observed.

Based on this initial work, it appears that in the afterglow reaction area, the lower dissociation energy barrier and higher reactivity by opening the π bond of the C=C bond in benzene (about 2.74 eV) as compared to the C-C bond (3.61 eV) and the C-F bond (5.35 eV), preferentially facilitate the formation and interaction of benzene excited species. Further, the deposition rate of plasma homo-polymerized benzene films was much higher than plasma homo-polymerized OFCB films for the same deposition conditions. Based on these considerations, two important changes were made, the first being the movement of the OFCB monomer inlet position to the plasma zone to facilitate OFCB monomer initiation. By introducing the OFCB precursor in the middle of the plasma zone, the formation of a large quantity of CF_x reactive species is ensured due to the much longer residence time in the plasma region. The second change was the replacement of the benzene mass flow controller with a manually adjusted, high-accuracy metering valve in order to further decrease the benzene flow rate.

These two modifications allowed films with specific refractive indices to be grown. Several co-polymerized films, as well as the two homo-polymerized films, were grown to calibrate the plasma polymerization as a function of precursor flow rates, and these are shown in **Table 1**. Note that the benzene flow rate is now small, and for the co-polymerized films was between 0.004 and 0.18 cm³. The OFCB flow rate was much higher and was between 0.5 cm³ and 3 cm³. The concentration of fluorine in the films was determined by XPS and it was

Table 1: The flow rates for benzene and OFCB used in making several co-polymerized films for calibration, together with the benzene to OFCB flow rate ratios and the fluorine to carbon atomic ratios in the films (measured by XPS).

Tabela 1: Hitrost toka benzena in OFCB, uporabljena za pripravo več kopolimeriziranih tankih plasti za kalibracijo, razmerje hitrosti pretokov benzena in OFCB in razmerje atomskih deležev fluor/ogljik v tankih plasteh (določeno z XPS)

Sample	Benzene Flow Rate (cm ³)	OFCB Flow Rate (cm ³)	Benzene/OFCB Flow Rate	Fluorine/Carbon Atomic Ratio
PP-OFCB	0	3	0	1.62
Co-polymer film 1	0.004	3	0.0013	1.36
Co-polymer film 2	0.010	3	0.0033	1.25
Co-polymer film 3	0.012	3	0.0040	0.96
Co-polymer film 4	0.013	3	0.0043	0.81
Co-polymer film 5	0.040	3	0.0133	0.62
Co-polymer film 6	0.079	3	0.0263	0.60
Co-polymer film 7	0.18	3	0.0593	0.47
Co-polymer film 8	0.18	1	0.178	0.46
Co-polymer film 9	0.18	0.5	0.356	0.23
PP-benzene	0.18	0	-	0

found that the refractive index (at 700 nm) had a nearly linear dependence on the fluorine to carbon atomic ratio. This relationship is shown in **Figure 6a**, and it can be seen that the refractive index (at 700 nm) decreases from over 1.6 to below 1.4 as the fluorine content increases.

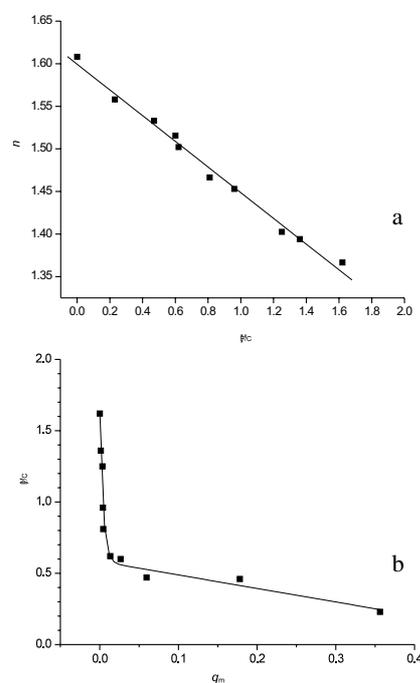


Figure 6: (a) The refractive index n at 700 nm as a function of the fluorine to carbon atomic ratio $\gamma_{F/C}$ in the deposited films; (b) The fluorine to carbon atomic ratio in the deposited films as a function of the benzene to OFCB flow rate ratio q_m

Slika 6: (a) Uklonski indeks n pri 700 nm v odvisnosti od razmerja fluor/ogljik $\gamma_{F/C}$ v nanosenih tankih plasteh; (b) atomsko razmerje fluor/ogljik v nanosenih tankih plasteh v odvisnosti od razmerja hitrosti tokov q_m benzena in OFCB

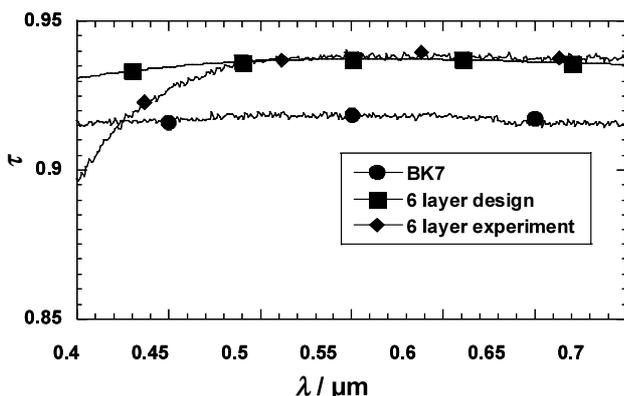


Figure 7: Transmission τ for a single-sided 6-layer co-polymer antireflection coating on BK7 glass \blacklozenge , compared to the coating design \blacksquare , and the uncoated glass \bullet .

Slika 7: Presevnost τ enostranske 6-plastne kopolimerne antirefleksne plasti na steklu BK7 \blacklozenge primerjave z načrtovano prevleko, \blacksquare primerjava z naneseo stekleno podlago in \bullet stekleno podlago

The fluorine to carbon atomic ratio in the films is shown as a function of the benzene to OFCB flow-rate ratio in **Figure 6b**. Therefore, films with a particular refractive index in this range can be grown by adjusting the flow-rate ratio.

To demonstrate this design flexibility, 6-layer anti-reflection coatings were designed for BK7 and F2 glass substrates. In these designs, the refractive index of the first layer is the same as the substrate (1.515 for BK7 and 1.614 for F2) and the other layers have gradually decreasing refractive indices, terminating with a coating of PP-OFCB. Such coatings have improved performance over single layer antireflection coatings using magnesium fluoride. An example of the improved transmission for BK7 glass is shown in **Figure 7**. The uncoated glass has a transmission of 93 % between 400 nm and 700 nm, and this increased to 97 % between 500 nm and 700 nm. A comparison between the designed performance and the experimental result is also shown in **Figure 7**. Note

that this agreement is excellent above 500 nm, but the transmission drops below 500 nm due to the small absorption coefficients of the films.

4 CONCLUSION

This work shows that plasma polymerization using PECVD is an easy method to fabricate multi-layered homo-polymerized and co-polymerized films of known optical thicknesses for photonic applications.

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