

# Inhomogeneous growth of plasma polymer films

Behnam Akhavan<sup>1</sup>, Bernhard Menges<sup>2</sup>, Renate Förch<sup>3,a</sup>

<sup>1</sup>School of Physics, A28, University of Sydney, Sydney 2006, NSW, Australia

<sup>2</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz 55128, Germany

<sup>3</sup>Fraunhofer ICT-IMM, Carl-Zeiss-Str. 18-20, Mainz 55129, Germany

**Abstract:** Plasma polymerization is traditionally recognized as a homogenous film-forming technique. However, are plasma polymerized films really homogenous across the film thickness? Studying the properties of the interfacial, near-the-substrate (NTS) region in plasma polymer films represents considerable experimental challenges due to the inaccessibility of the buried layers. A novel non-destructive approach has been used to evaluate the homogeneity of plasma polymerized acrylic acid (PPAc) in a single measurement. Our results challenge the traditional view that considers plasma polymers as homogenous and continuous structures.

**Keywords:** surface plasmon resonance, film thickness, near surface, bulk.

## 1. Introduction

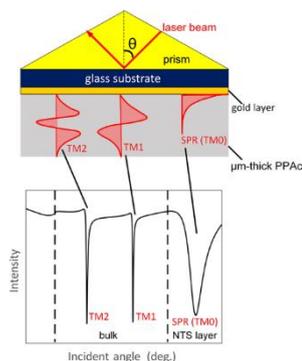
A widely held belief about plasma polymerization, which is often cited as a desirable feature, is its ability to produce uniform coatings.<sup>1,2,3,4</sup> Although the lateral uniformity of PP films is easily assessable, almost no information is available regarding the concealed underlying layers. Studying the properties of the inaccessible ‘near-the-substrate’ (NTS) layer represents particular challenges but is of extreme importance for the understanding of growth mechanisms and the improvement of film adhesion. Surface plasmon resonance (SPR)/optical waveguide (OWG) spectroscopy make it possible to measure variations of refractive index throughout the depth of the films. We were able to show that the NTS layer of PPAc exhibits a significantly lower refractive index than the bulk of the film, which suggests a lower cross-linking density and a higher concentration of internal voids.<sup>5</sup>

## 2. Experimental section

Acrylic acid was used as a model precursor monomer since PPAc has been extensively applied for both theoretical studies and practical applications during the past few decades.

*Figure 1 Schematic illustration of the sample configuration and excitation of SPR ( $TM_0$ ) and OWG modes ( $TM_1$  and  $TM_2$ ) as observed in the angular reflectivity curve.*

In a Kretschmann configuration, a metallic surface (generally Au or Ag) in contact with a dielectric material is required to excite the surface plasmon.<sup>6</sup> Gold-coated LaSFN9 glass slides with a refractive index ( $n$ ) of 1.845 at  $\lambda = 632.8$  nm, were used as substrates. The SPR/OWG angular spectra were simulated using Fresnel equations and an algorithm based on a matrix formalism implemented in Winspall software (V. 3.2). Fresnel theory explains the overall transmission and reflection of a general multilayer assembly.<sup>7,8</sup> A multilayer model composed of a prism, chromium film, gold layer,



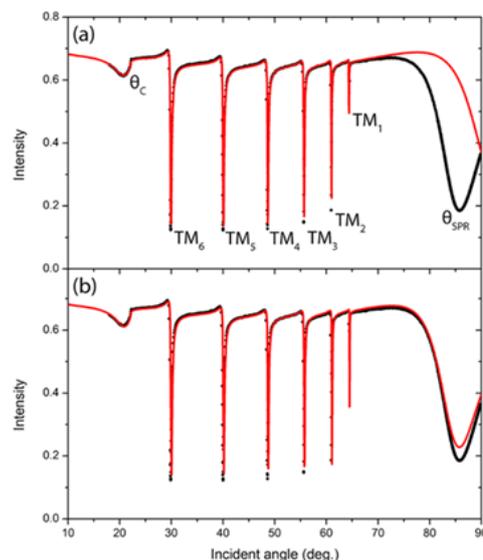
PPAc film, and air as the medium was applied, while the fitting parameters in calculations were the complex refractive index and thickness of each layer.

The low-pressure plasma polymerization system<sup>9</sup> consisted a Pyrex flow tube (130 cm,  $\varnothing$  10 cm) equipped with a 13.56 MHz RF power generator, a matching network and appropriate gas flow control system. Acrylic acid was plasma polymerised as films ranging in thickness from 600nm to 2  $\mu$ m using an input RF power of 10 W (selected experiments 5-50W) and a monomer flow rate of  $\sim$  2 sccm.

## 3. Results

Optical waveguides are excited once a minimum thickness of a film is reached. In our case this was experimentally found to be  $d > 600$ nm. The excitation of OWG modes within these relatively thick layers allowed independent evaluation of physical thickness ( $d$ ) and refractive index ( $n$ ) of PPAc films. A typical SPR/OWG reflectivity spectra of PPAc film deposited for 40 minutes ( $d = 1790.4 \pm 95.1$  nm) is shown in Figure 1.

*Figure 2. SPR/OWG reflectivity spectra of PPAc film obtained using p-polarized light (black dots) and fit of the (a) one-layer and (b) two-layer models (continuous red lines).*



<sup>a</sup> Now at: Eura AG, Max Eyth Str 2, 73479 Ellwangen, Germany

The sharp peaks shown in the SPR/OWS spectra in Figures 1 and 2 related to OWG modes (TM1 – TM6) are excited in the film at incident angles higher than the critical angle of total internal reflection ( $\theta_c = 22.3^\circ$ ), where the evanescent field at the gold/PPAc interface exponentially decays into the PPAc layer.<sup>6</sup> The broader peak is attributed to the excitation of SPR at the gold/PPAc interface and is detected at  $\theta_{SPR} = 85.8^\circ$ . Quantitative evaluation of the spectra was carried out by comparing the experimental data (black dots) with the theoretical reflectivity curve (solid red lines) calculated based on the Fresnel theory, while the refractive index (n) and optical thickness (d) of PPAc film were varied to achieve the best fit.

As observed in Figure 2a, the best theoretical fit obtained for a homogenous one-layer model can only cover the OWG modes (TM1 – TM5), whilst the SPR mode could not be recovered. According to this one-layer model ( $d = 1819.7 \pm 8.8$ ,  $n = 1.528 \pm 0.002$ ), the SPR peak is recorded at a lower angle than expected for a homogeneous PPAc film. In order to recover the SPR peak, a model with at least two layers has to be implemented (Figure 2b). This model consists of: (i) the bulk of the film with a refractive index of  $1.530 \pm 0.002$ , and (ii) a near-the-substrate (NTS) layer with a lower refractive index ( $1.498 \pm 0.004$ ) and an estimated thickness of approximately 200 nm. A thickness of 200 nm was applied for the NTS layer in calculations, since it denotes the depth of an organic film where the surface plasmon evanescent field completely decays.<sup>10,11</sup> It should, however, be noted that the actual thickness of the NTS layer might be much thinner than this value.

The refractive index of PPAc films as a function of RF input power can also be used to elucidate the way thick plasma polymer films grow. PPAc films were deposited at input powers of 5-50W at constant deposition time  $t=10$  minutes. From Table 1 it is observed that the refractive indices for both bulk and NTS layers increase with increasing input power. This data supports the assumption of an increase of cross-linking degree at greater power densities resulting from a higher degree of AC fragmentation and recombination.<sup>12,13</sup>

Table 1 Refractive index of PPAc films as a function of RRF input power for bulk and NTS Layers.

refractive index (n)	RF input power			
	5	10	25	50
NTS layer	1.507 $\pm$ 0.003	1.500 $\pm$ 0.002	1.523 $\pm$ 0.001	1.539 $\pm$ 0.004
Bulk layer	1.507 $\pm$ 0.003	1.533 $\pm$ 0.001	1.545 $\pm$ 0.002	1.555 $\pm$ 0.003

#### 4. Conclusions

The combination of surface plasmon resonance and optical waveguide spectroscopy provided a simultaneous evaluation of near-the-substrate layer and bulk of micrometre-thick plasma polymerized acrylic acid (PPAc) films. It could be shown that PPAc films grow inhomogeneously due to the presence of an interphase layer near the substrate, accommodating a higher content of internal voids compared to the bulk of the film. Higher

concentration of internal voids produced a low-density structure with a greater apparent thickness and a lower refractive index. A similar inhomogeneous structure was also observed for micrometre-thick plasma polymerized 1,7-octadiene films.<sup>5</sup> These findings provide new insights into the growth mechanism of plasma polymer films and are of great interest from both fundamental and practical points of view. Identifying other possible mechanisms behind such an inhomogeneous manner of growth and studying the behaviour of other plasma polymer systems deserve further research.

#### 5. References

- [1] K. Vasilev, A. Michelmore, H.J. Griesser, R.D. Short, *Chem. Commun.*, **57**, 3600 (2009)
- [2] N.A. Bullett, J.D. Whittle, R.D. Short, C.W.I. Douglas, *J. Mater. Chem.*, **13**, 1546 (2003)
- [3] T.J. Swait, C. Soutis, F.R. Jones, *Compos. Sci. Technol.*, **68**, 2302 (2008)
- [4] C. Amorosi, T. Fouquet, V. Toniazzo, D. Ruch, L. Averous, V. Ball, M. Michel, *React. Funct. Polym.*, **72**, 341 (2012).
- [5] B. Akhavan, B. Menges, R. Förch, *Langmuir*, **32**, 4792 (2016)
- [6] W. Knoll, *Annu. Rev. Phys. Chem.*, **49**, 569 (1998)
- [7] S. Scarano, M. Mascini, A.P.F. Turner, M. Minunni, *Biosens. Bioelectron.*, **25**, 957 (2010).
- [8] C.E. Reed, J. Giergiel, J.C. Hemminger, S. Ushioda, *Phys. Rev. B*, **36**, 4990 (1987)
- [9] S. Kuhn, J. Kroth, U. Ritz, A. Hofmann, C. Brendel, L.P. Muller, R. Förch, P.M. Rommens, *J. Mater. Sci.- Mater. Med.*, **25**, 2549 (2014)
- [10] L.Q. Chu, Q. Zhang, R. Förch, *Plasma Process. Polym.*, **12**, 941 (2015)
- [11] E.T. Hoppe, I. Hopp, M. Port, B. Menges, C. Papadakis, *Colloid Polym Sci*, **290**, 1731 (2012)
- [12] H.J. Griesser, K.S. Siow, L. Britscher, S. Kumar, *Plasma Process. Polym.*, **3**, 392 (2006)
- [13] S. Vallon, B. Drevillon, F. Poncin-Epaillard, *Appl. Surf. Sci.* **108**, 177 (1997)