PLASMA FLUORINATION FOR IMPROVING OF THE PERMEABILITY, WETTING, BIOCOMPATIBILITY AND OPTICAL ABSORPTION OF DIFFERENT POLYMERS

Fabienne Poncin-Epaillard*, Dominique Debarnot

PCI, UMR 6120 CNRS-Université du Maine, Le Mans, France

Key words: plasma, tetrafluormethane, flourine, hydrogen, substitution, polymer, epoxy

Abstract: Polymer materials are of great interest for many applications due to their easy processing, mass production and low cost compared to other materials. However, some of their surface properties are poor and must be improved for the selected application. For example, polymers such as unsaturated polyesters, (co)polyolefins are sensitive to water sorption. Reversible phenomena as water diffusion, irreversible phenomena such as chain scissions and chemical degradations can be both at the origin. CF_4 plasma-treated layer improves drastically the barrier effects. Superhydrophobic surfaces, as lotus leaves correspond to hydrophobic surfaces whose water contact angle is higher than 150°. Such surfaces present weak physical properties like optical and mechanical ones but good biocompatibility. Two new different approaches of CF_4 plasma treatment are proposed leading to stable and transparent polymeric superhydrophobic surfaces. Many integrated photonic devices for micro-electro-optical-mechanical system based on epoxy polymer present high optical losses at near-infrared (IR) wavelengths mainly assigned to absorption from vibrational overtones of the carbon-hydrogen bonds. These losses can be reduced by the substitution of hydrogen atoms from C-H bonds with heavier atoms such as fluorine obtained through a plasma fluorination.

Modifikacija polimerov s plazemsko flourinacijo za izboljšanje prepustnosti, omočljivosti, biokompatibilnosti in optičnih lastnosti

Kjučne besede: plazma, tetrafluormetan, fluor, vodik, substitucija, polimer, epoksi

Izvleček: Polimerni materiali so zanimivi za uporabo zaradi preproste obdelave in nizke cene. Nekatere njihove lastnosti pa niso najboljše, zato jih moramo pred uporabo spremeniti. Nekateri polimeri, kamor sodijo tudi nenasičeni poliestri in poliolefini, so občutljivi na absorpcijo vode. V tovrstnih materialih se pojavljajo reverzibilni procesi (na primer difuzija vode) in nereverzibilni procesi (na primer trganje polimernih verig in degradacija polimerov). Obdelava s plinsko plazmo, ki vsebuje plin CF_4, lahko drastično spremeni tovrstne procese. Po obdelavi lahko opazimo izredno povečanje hidrofobnosti materiala, saj lahko kontaktni kot vodne kapljice naraste preko 150°. Takšno stanje površine, ki ga včasih imenujemo pojav lotusovega lista, vodi k zelo dobri biokompatibilnosti materialov. V prispevku prikazujemo dva originalna pristopa k funkcionalizaciji površine polimernih materialov s CF_4 plazmo, ki vodita k stabilni funkcionalizaciji in s tem superhidrofobnosti obdelovancev. Mnoge integrirane optične naprave, ki temeljijo na uporabi epoksi polimerov, imajo visoke optične izgube v bližnjem infrardečem področju, kar razlagamo predvsem z absorpcijo na vezeh ogljika z vodikom. Tovrstne izgube lahko zmanjšamo s substitucijo vodikovih atomov s težjimi atomi, kot so fluorovi. Tovrstno substitucijo najlažje dosežemo s plazemsko flourinacijo.

1   Introduction

Many advances have been made in developing new surface treatments, such as plasma treatment, to modify physical and chemical properties of polymer surface without altering bulk properties /1-7/. One of the applications is dealing with the superhydrophobic surfaces. Natural superhydrophobic surfaces /8-9/ as observed with leaves of plants (lotus) or feathers of some birds, correspond to hydrophobic surface whose water contact angle (Q) is higher than 150° /10/. Such surfaces are sometimes called self-cleaning surfaces since a water flux will push away the particles of dirtiness /9/. Different methods to prepare such surfaces were proposed, some of them devoted to inorganic materials /11/, the other to organic materials /12-16/. The fabrication of inorganic model superhydrophobic surfaces /17-19/ allows studying the influence of the roughness on the water contact angle. Therefore, Si wafers were etched by lithography techniques to produce different topographic structures whose shape depends on the mask used. Then a hydrophobic layer of dimethyldichlorosilane, N-octyldimethylchlorosilane or heptadecafluoro-1,1,2,2-

tetrahydrodimethylchlorosilane was deposited from liquid, vapour or plasma phase /20/. The contact angle increase with the hydrophobic character of the layer depends also on the number of plots but not on their respective heights. Other superhydrophobic model surfaces are synthesized from successive alkyl ketene dimmer (AKD) and dialkyl ketone (DAK) recrystallisations /21,23/. The controlled recrystallization of such compounds allows producing surfaces with a fractal dimension varying from 2.18 to 2.29. Sol–gel techniques /24-27/ have also been developed through the copolymerization of fluoroalkylsilane with different organometallic precursors /28-29/, on aluminium /30-31/, or on titanium dioxide /32/.

Organic superhydrophobic surfaces are obtained when poly(tetrafluoroethylene) (PTFE) /33/ or polystyrene (PS) /18-19,34/ spherical microparticles are dispersed in a hy-

drophobic polymer matrix. Hozumi and coworkers /25,35/ describe the fabrication of superhydrophobic surfaces based on plasma enhanced chemical vapor deposition of organosilanes in presence of oxygen onto silicon wafer. Then in a second step, the fluoroalkylsilane replaces O_2 in the plasma phase and the deposited layer becomes hydrophobic and superhydrophobic. Pulsed plasma of 1H,1H,2H,2H-heptadecafluorodecylacrylate /13/ also leads to the deposition of a fluorinated layer whose chemical structure is close to the monomer vapour and its roughness varies from 0 to 100 ěm depending on the initial roughness of the PTFE substrate /14/. Favia et al. /15/ proposed the pulsed RF plasma deposition of tetrafluoroethylene (TFE). Superhydrophobic surfaces composed of juxtaposition of very thin ribbons whose crystallinity is close to PTFE lead to a 150°–165° contact angle. However, this surface structure depends strongly on the plasma parameters (value of the duty cycle in pulsed RF glow discharges fed with TFE). CF_4 plasma surface modification of spin coated polybutadiene onto various substrates leads also to superhydrophobic surfaces (Q = 172%) /16/. Another illustration is given with the sputtering of PTFE onto polypropylene (PP) film /36/; the roughness is due to the PTFE sputtering by Ar+ bombardment but also by the PP degradation during the sputtering. The dissolution of polypropylene in a p-xylene/methyl ethyl ketone solution followed by its deposition onto the substrate and the solvents evaporation also leads to a rough hydrophobic surface /37/.

Here, the synthesis in dry medium (plasma) is proposed leading to stable and transparent polymeric superhydrophobic polyethylene surfaces.

Barrier properties for packaging materials have been improved over the years to protect packaged foodstuffs from the oxidation and the moisture. Owing to their favourable performances as efficient barrier materials, ethylene-vinyl alcohol copolymers (EVOH) are used in many applications and therefore are widely used in packaging and protective coating. Among all the new technologies involved in improving the barrier properties of EVOH films, one in particular is often used: the creation of multilayer systems mostly through the plasma technique /38/.

The glycidyl ether of bisphenol A (epoxy-based) polymer whose common name is SU-8, widely used as negative photoresist, has also been studied for micro-electro-optical mechanical system (MEOMS) applications and optical waveguides /39-43/. However, it presents high optical losses at near-infrared (IR) wavelengths mainly assigned to absorption from vibrational overtones of the carbon-hydrogen (C-H) bonds. These losses can be reduced by the substitution of hydrogen atoms of C-H bonds with heavier atoms such as fluorine (F), deuterium (D) or chlorine (Cl) ones /11-14/ thanks to the plasma technique allowing the substitution of hydrogen atoms by fluorine ones.

The chemical and topographic modifications of the polymeric surface induced by plasma treatment were found to be strongly influenced by the type of feed gas and param-

eters employed. Studied plasma parameters are the discharge power, treatment time and nature of plasma (CF_4 or mixtures of CF_4/H_2), in order to optimize plasma treatment for different applications.

2   Plasma fluorination of polymers

Poly(ethylene-co-vinyl alcohol) and polyethylene films have been modified by CF_4 microwave plasma. The influence of vinyl alcohol comonomer contents on the properties of these materials under CF_4 microwave plasma has been studied by means of surface energies, atomic force microscopy (AFM), secondary ion mass spectroscopy (SIMS) and calorimetric measurements (DSC). The CF_4 plasma treatment improved the hydrophobicity and the roughness of the film surfaces was hardly changed. Lower the vinyl alcohol comonomer content, higher is the increase of the water contact angle value (Table 1).

Table 1: Wettability of CF_4 plasma-treated polymers

Sample	θH_2O	γ^{Sd}	γ^{Sp}	γ^S
LLDPE [OH] = 0 mol%	92	26.3	1.2	27.5
LLDPE 50W 15 min	95	21.0	1.1	22.1
EVOH(E) [OH] = 56 mol%	76	32.8	3.8	36.6
EVOH(E) 50W 15 min	98	12.0	3.2	15.2
EVOH(F) [OH] = 68 mol%	72	30.5	7.3	37.8
EVOH(F) 50W 15 min	99	15.9	2.7	18.6
EVOH(S) [OH] = 71 mol%	52	29.3	17.2	46.6
EVOH(S) 50W 15 min	105	12.2	1.5	13.7

The decrease of surface energy of polymeric material, corresponding to an increase of the water contact angle, was associated to a chemical surface modification. XPS analyses of EVOH, polyethylene (Fig. 1) or SU8 plasma-treated surfaces give evidence of fluorinated groups attachment.

Depending on plasma parameters, the chemical surface structure varies from CHF group to the Teflon-like structure. The atomic F/C ratio can reach the value of 0.5 with pure CF_4 plasma treatment. Addition of hydrogen to the CF_4 plasma phase allows to control the fluorine atom density in the plasma phase and therefore to modify the surface fluorination rate. Addition of 10% of hydrogen leads to the lowest polar surface energy of plasma-treated SU8 surface (Fig. 2).

3   Superhydrophobic plasma-fluorinated polymers

Whatever the plasma phase composition is, the elemental composition of the CF_4 plasma-treated polyethylene is associated to the grafting of $CHF-CH_2$, CF, CF_2 and CF_3 functional groups whose proportions depend on plasma parameters. But another side effect of the plasma interaction is observed and corresponds to the surface degradation and roughness. Drastic powers, long durations or oxygen plasma pre-treatment emphasize this phenomenon. The
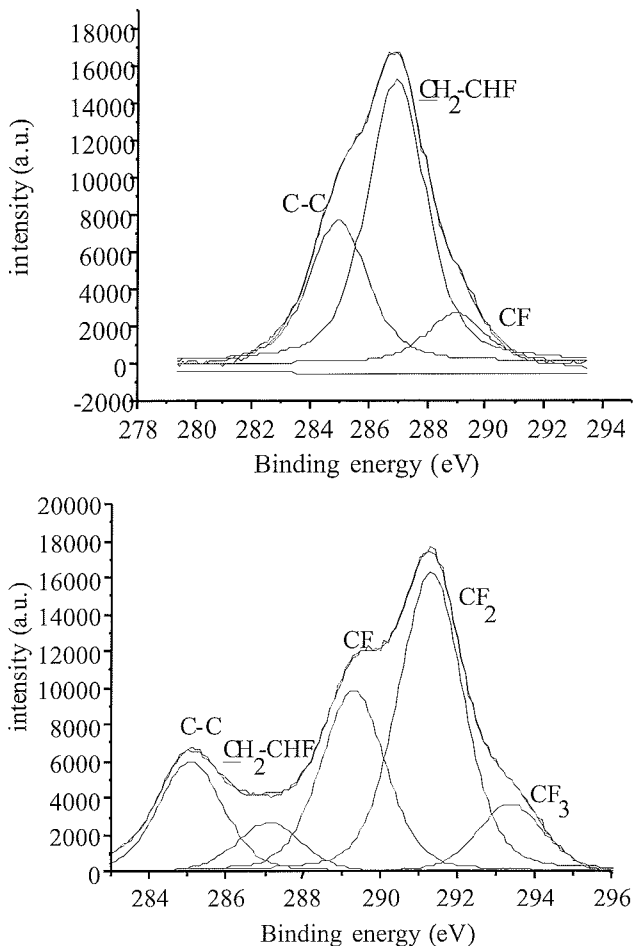
Informacije MIDEM 38(2008)4, str. 252-256

F. Poncin-Epaillard, D. Debarnot: Plasma Fluorination for Improving
of the Permeability, Wetting, Biocompatibility and Optical Absorption ...

Fig. 1:   Plasma-fluorinated HDPE in different conditions.

combination of surface fluorination and roughness induc-
es the superhydrophobic character appearance (i.e. wa-
ter contact angle higher than 150°). Beside this evolution,
if the discharge power and/or duration are important, the
hysteresis of the contact angle becomes smaller. Figure 3
illustrates the domain of roughness leading to polyethyl-
ene superhydrophobic surface.

4   Applications of plasma-fluorinated polymers

These plasma-fluorinated surfaces may be used in differ-
ent domains. The first one is dealing with the biomaterials
field. The bioadhesion or the non adhesion of proteins,
cells onto the biomaterials is strongly dependent on the
nature of the interactions between these two entities.
Among them, hydrophobic-hydrophobic and electrostatic
ones are the predominant ones. However, in the case of
nonadhesion processes, biosurfaces bearing a superhy-
drophobic character may act as self-cleaning surface to-
wards the biomolecules adhesion. The self-cleaning prop-
erty implies a fast dynamic de-wetting of a water thin film
as shown in Fig. 4.

Another application is dealing with barrier properties and
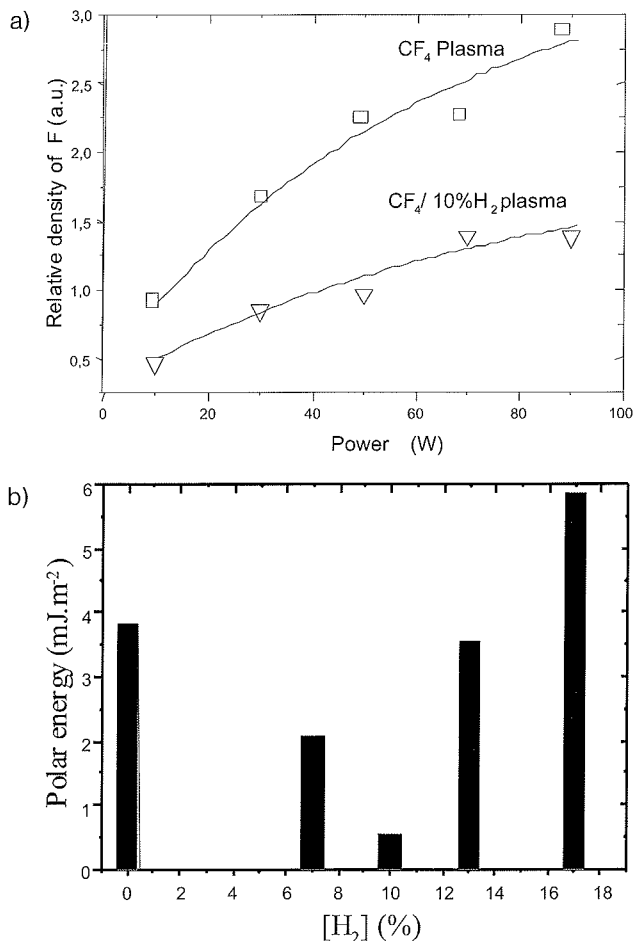permeability of plasma-treated polymers. If the water per-

Fig. 2:   Dependence of gaseous fluorinated species on
discharge power (a), of surface energy of
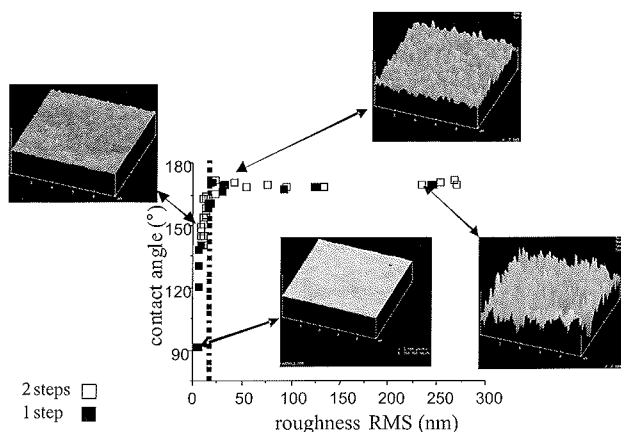plasma-treated SU8 on hydrogen proportions (b).

Fig. 3:   Dependence of the contact angle versus
roughness of plasma-fluorinated polyethylene.

meability coefficient is almost constant after the plasma
fluorination of linear low density polyethylene, this coeffi-
cient is strongly altered by the surface fluorination of EVOH,
especially when the vinyl alcohol content is increasing (Ta-
ble 2). This barrier effect is also noticed with plasma fluor-
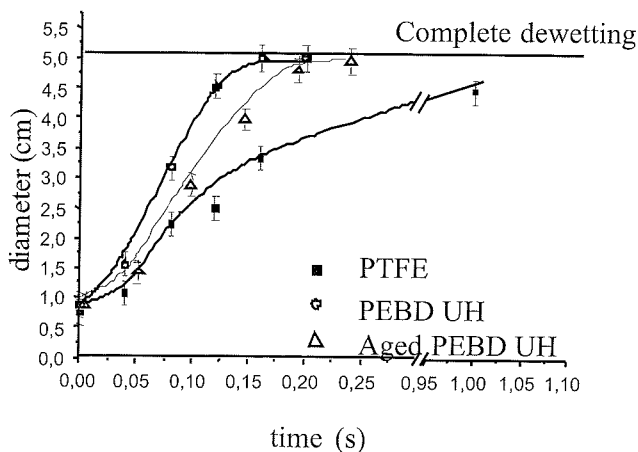ination of polyamide 12.

Fig. 4:   Dynamic de-wetting of thin water layer onto
            polymer surfaces.

Table 2: Water permeability of plasma-fluorinated polymers.

Sample	[OH] (mol %)	Thickness (µm)	P (Barr)	γ^S
LLDPE [OH] = 0 mol%	0	55	68	27.5
LLDPE 50W 15 min	0	55	64	22.1
EVOH(E) [OH] = 56 mol%	56	15	241	36.6
EVOH(E) 50W 15 min	56	14	86	15.2
EVOH(F) [OH] = 68 mol%	68	15	222	37.8
EVOH(F) 50W 15 min	68	15	1865	18.6
EVOH(S) [OH] = 71 mol%	76	14	31350	46.6
EVOH(S) 50W 15 min	76	101	17754	13.7

Fluorination, obtained with the CF4 plasma treatment allows reducing water permeability of the films. The higher hydrophilicity of the base materials, the more water barrier effect of CF4 plasma treatment is obtained compared to the non-treated materials. However, the very significant enhancement of the water barrier properties of EVOH(S) after plasma treatment was explained not only by the introduction of fluorine groups but an increase of the crystallinity too, so that the diffusivity and solubility of water through the CF4 plasma treated film were more reduced. The effect of surface modification on water permeability decreased the water uptake at the film surface at the feed side so that the plasticization effect of the hydrophilic films by the sorbed water molecules was decreased during the water vapour permeation.

The last illustration will be given with the decrease of optical losses thanks to the plasma fluorination. The measured propagation loss values of untreated and plasma-treated SU8 single-mode planar waveguides for both transverse electric (TE) and transverse magnetic (TM) polarizations at 632.8, 1304 and 1540 nm are shown in Fig. 5.
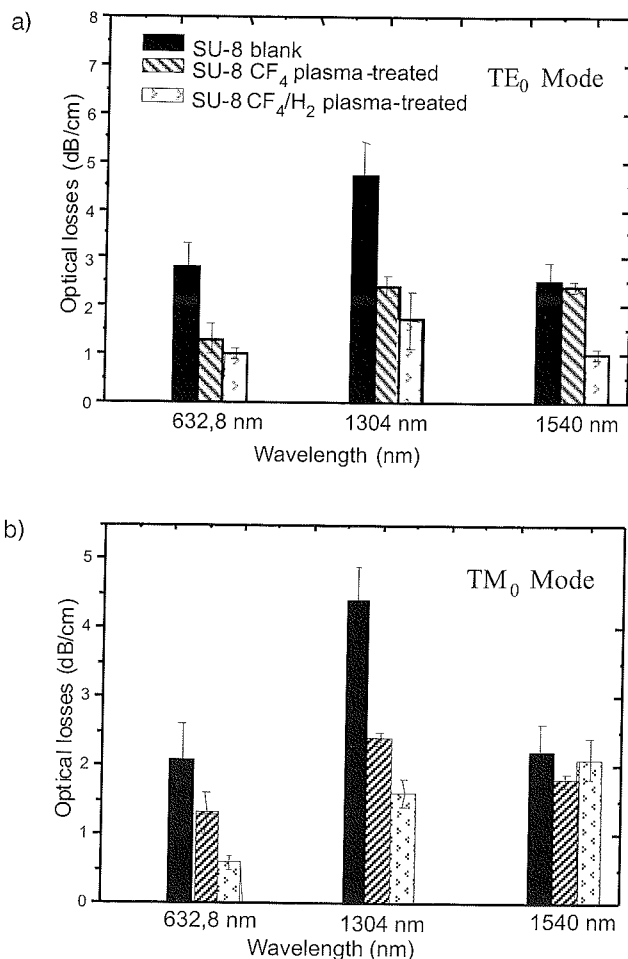
a)

b)

Fig. 5:   Optical losses of plasma-fluorinated SU8
            waveguide

5   Conclusions

Plasma fluorination of polymers leads to a chemical surface modification through the grafting of fluorinated groups. The appearance of new pendant groups induce a hydrophobic and sometimes a superhydrophobic character leading to specific properties requested in biomaterial, permeation or photonic fields.

References

/1/   F. Poncin-Epaillard, J. C. Brosse, and T. Falher, Macromolecules, vol. 30, pp.4415, 1997.

/2/   J. Fresnais, J. P. Chapel, and F. Poncin-Epaillard, Surf. Coat. Techn., vol. 200, pp. 5296, 2006.

/3/   S. Marais, M. Metayer, M. Labbe, J. M. Valleton, S. Alexandre, J. M. Saiter, F. Poncin-Epaillard, Surf. Coat. Techn., vol. 122, pp. 247, 1999.

/4/   N. Médard, J.-C. Soutif, F. Poncin-Epaillard, Surf. Coat. Techn., vol. 160, pp.197, 2002.

/5/   A. Vesel, I. Junkar, U. Cvelbar, J. Kovac, M. Mozetic, Surf. Int. Anal., vol. 40, no.11, pp. 1444, 2008.

/6/   A. Vesel, M. Mozetic, A. Zalar, Surf. Int. Anal., vol. 40, no.3-4, pp. 661, 2008.

Informacije MIDEM 38(2008)4, str. 252-256

F. Poncin-Epaillard, D. Debarnot: Plasma Fluorination for Improving
of the Permeability, Wetting, Biocompatibility and Optical Absorption ...

/7/   A. Vesel, M. Mozetic, A. Zalar, Vacuum, vol. 82, no. 2, pp. 248, 2008.

/8/   C. Neinhuis, and W. Barthlott, An. Bot., vol. 79, pp. 667, 1997.

/9/   E. Nun, M. Oles, and B. Schleich, Macromolecular symposium, vol. 187, pp. 677, 2002.

/10/   K. Tadanaga, J. Morinaga, A. Matsuda, and T. Minami, Chem. Mater., vol. 12, pp. 590, 2000.

/11/   T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, and Y. Ueda, Langmuir, vol. 15, pp. 4321, 1999.

/12/   F. Poncin-Epaillard, I. Rouger, J. P. Gilles, and J. P. Grandchamp, J. Macromol. Sci., vol. 31, pp. 1087, 1994.

/13/   S. R.Coulson, I. S. Woodward, J. P. S. Badyal, and S. A. Brewer, C. Willis, Chem. Mater., vol. 12, pp. 2031, 2000.

/14/   S. R. Coulson, I. S. Woodward, J. P. S. Badyal, S. A. Brewer, C. Willis, J. Phys. Chem., vol. 104, pp. 8836, 2000.

/15/   P. Favia, G. Cicala, A. Milella, F. Palumbo, P. Rossini, R. D'Agostino, Surf. Coat. Tech, vol. 169-70, pp. 609, 2003.

/16/   I. S. Woodward, W. C. E. Schofield, V. Roucoules, J. P. S. Badyal, Langmuir, vol. 19, no.8, pp. 3432, 2002.

/17/   R. E. Jonson, Jr. and R. H. Dettre, Adv. Chem. Ser., vol. 43, pp.112, 1964.

/18/   D. Öner and T. J. McCarthy, Langmuir, vol. 16, pp. 7777, 2000.

/19/   W. Chen, A. Y. Fadeev, M. C. Hsieh, D. Öner, J. Youngblood and T. J. McCarthy, Langmuir, vol. 15, pp. 3395, 1999.

/20/   S. Tsuruta, K. Morimoto, T. Hirotsu and H. Suzuki, J. Appl. Phys Part 1, Jpn, vol. 45, pp. 8502, 2006.

/21/   T. Onda, S. Shibuichi, N. Satoh and K. Tsujii, Langmuir, vol. 12, pp. 2125, 1996.

/22/   S. Shibuichi, T. Onda, N. Satoh and K. Tsujii, J. Phys. Chem., vol. 100, pp.19512, 1996.

/23/   F. Iacona, G. Casella, F. La Via, S. Lombardo, V. Raineri and G. Spoto, Microelectronic Eng., vol. 50, pp. 67, 2000.

/24/   A. Hozumi and O. Takai, Thin Solid Films, vol. 334, pp. 54, 1998.

/25/   T. Nakagawa and M. Soga, J. Non-crystalline Solids, vol. 260, pp.167, 1999.

/26/   Y. Li, W. P. Cai, B. Q. Cao, G. T. Duan, F. Q. Sun, C. C. Li and L. C. Jia, Nanotechnology, vol. 17, pp. 238, 2006.

/27/   B. S. Hong, J. H. Han, S. T. Kim, Y. J. Cho, M. S. Park, T. Dolukh-anyan and C. Sung, Thin Solid Films, vol. 351, pp. 274, 1999.

/28/   T. Yoneda and T. Morimoto, Thin Solid Films, vol. 351, pp. 279, 1999.

/29/   K. Tadanaga, N. Katata and T. Minami, J. Am. Ceramic Soc., vol. 80, pp. 1040, 1997.

/30/   K. Tadanaga, N. Katata and T. Minami, J. Am. Ceramic Soc., vol. 80, pp. 3213, 1997.

/31/   X. T. Zhang, M. Jin, Z. Liu, S. Nishimoto, H. Saito, T. Murakami and A. Fujishima, Langmuir, vol. 22, pp. 9477, 2006.

/32/   G. Yamauchi, J. D. Miller, H. Saito, K. Takai, T. Ueda, H. Taka-zawa, H. Yamamoto and S. Nishi, Colloids Surfaces, vol. 116, pp. 125, 1996.

/33/   A. Nakajima, K. Hashimoto and T. Watanabe, Monatsh. Chem.,vol. 132, pp. 31, 2001.

/34/   A. Hozumi, H. Sekoguchi, N. Sugimoto and O. Takai, Trans. Inst. Metal Finishing, vol. 76, pp. 51, 1998.

/35/   J. Youngblood and T. J. McCarthy, Macromolecules, vol. 32, pp. 6800, 1999.

/36/   H. Y. Erbil, A. L. Demirel, Y. Avci and O. Mert, Science, vol. 299, pp. 1377, 2003.

/37/   R. D'Agostino, Plasma Deposition, Treatment and Etching of Polymers, Academic Press, Boston, 1990.

/38/   N. Pelletier, B. Bęche, E. Gaviot, L. Camberlein, N. Grossard, F. Polet, J. Zyss, IEEE Sensors J., vol. 6, no. 3, pp. 565, 2006.

/39/   B. Bęche, N. Pelletier, E. Gaviot, J. Zyss, Opt. Commun., vol. 230, no. 1-3, pp. 91, 2004.

/40/   J. S. Kim, J. W. Kang, J. Kim, J. Jpn. J. Appl. Phys., vol. 42, pp. 1277, 2003.

/41/   B. Bęche, J. F. Jouin, N. Grossard, E. Gaviot, E. Toussaere, J. Zyss, Sens. Act. A, vol. 114, no. 1, pp. 59, 2004.

/42/   N. Pelletier, B. Bęche, N. Tahani, J. Zyss, L. Camberlein, E. Gaviot, Sens. Act. A, vol. 135, pp. 179, 2007.

*Fabienne Poncin-Epaillard, Dominique Debarnot
PCI, UMR 6120 CNRS-Université du Maine, avenue O
Messiaen 72085 Le Mans France
Email: Fabienne.poncin-epaillard@univ-lemans.fr