

Surface composition and surface energy of Teflon treated by metal plasma immersion ion implantation

Ricky K.Y. Fu ^a, Y.F. Mei ^a, G.J. Wan ^a, G.G. Siu ^a, Paul K. Chu ^{a,*},
Y.X. Huang ^b, X.B. Tian ^b, S.Q. Yang ^b, J.Y. Chen ^c

^a Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

^b State Key Laboratory of Welding Production Technology, Harbin Institute of Technology, Harbin, China

^c School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China

Received 6 July 2004; accepted for publication 5 October 2004

Available online 20 October 2004

Abstract

Plasma immersion ion implantation using a metal vacuum vapor arc (MEVVA) or cathodic arc source was used to modify the fluorine-based polymer, Teflon. Several transition metal ions such as Co, Ni, Cu were introduced into plasma and implanted into the Teflon surface. The chemical composition of the modified surface was determined by Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS). The metals were found to be distributed several nanometers from the surface and XPS results showed the formation of metallic carbides and fluorides on the surface. Contact angle measurement results demonstrate the favorable change in the wettability from being hydrophobic to hydrophilic. Our study shows that the increase of the surface energy is due to the change of the surface interaction properties after metal plasma implantation.

© 2004 Elsevier B.V. All rights reserved.

Keywords: X-ray photoelectron spectroscopy; Wetting; Polycrystalline surfaces; Surface energy; Ion implantation

1. Introduction

Polymeric materials are widely used in the industry as most polymeric materials are light in weight and possess intrinsic dielectric properties,

good electrical insulation, surface chemical inertness, and biocompatibility. However, the inert nature of the most polymer surface can impose adverse effects on some applications. For instance, the poor surface adhesion to other materials may result in the difficulty in depositing surface coatings, printings, dying, as well as poor protein absorption, platelet adhesion and cell attachment in biomedical applications. A number of

* Corresponding author. Tel.: +852 27887724; fax: +852 27887830/27889549.

E-mail address: paul.chu@cityu.edu.hk (P.K. Chu).

techniques have been applied to modify their surface chemistry. Surface modification techniques utilizing flame [1], chemical [2], grafting [3,4], corona discharge [5], low-pressure plasma [6–8], and ultraviolet exposure [9] have been proposed to improve the wetting properties of polymers. In plasma surface modification of polymers, the plasma can be composed of air, oxygen, nitrogen or inert gas to produce functional groups, chain scissions or cross linking on the surface. A recent study reports that when low-density polyethylene (LLDPE) is treated in a microwave plasma system in air ambient, C–O–C (or C–OH), C=O and O–C=O functional groups form on the surface [10]. In most plasma processes, the polymers are not subjected to a voltage bias or a very small voltage, and consequently, the modified layer is typical of thicknesses of several nanometers.

Ion implantation is a proven means to alter the surface properties of many materials including polymers. Generally, ions can be introduced into polymer surface by two ways. In conventional beam-line ion implantation, ions can be focused into a beam line, accelerated to a high energy, and implanted into the materials. The ions are mass selected but since either beam or sample rastering is employed for large specimens, the implantation time can be long for large samples and it may be difficult to accomplish uniform implantation into all surfaces if the specimen is not planar or has a complex geometry. The alternative is plasma immersion ion implantation (PIII) in which the sample is enshrouded by a plasma and when a voltage is applied to the sample, ions from the plasma are implanted into all exposed surfaces of the sample simultaneously [11–13]. The advantages of PIII are simple instrumentation, high efficiency, and small instrumentation footprint. There have been a number of studies on the enhancement of surface properties of polymers by ion implantation. Argon ion bombardment into fluorine polymers has been shown to improve the surface hydrophobicity [14] whereas the surface morphology and conductivity of some polymer films have been modified by He⁺ ion beam implantation [15]. The properties of polymeric composites have been found to be enhanced using selenium implantation [16], and several other studies have shown

that metal implantation can result in the formation of metal nano-particles and change of the magnetic properties in polymer foils [17,18].

In this work, metal plasma immersion ion implantation was employed to treat a fluorine-based polymer, Teflon or polytetrafluoroethylene (PTFE). A cathodic arc vapor source was used in an immersion configuration [19,20]. Several transition metals such as Co, Ni and Cu were implanted, and the surface properties such as wettability and surface energy were evaluated. In addition, the chemical states of the implanted elements and the structure of the modified layer were examined using X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS).

2. Experimental

Specimens of Teflon with a thickness of 3 mm were employed in this investigation. The metal plasma was generated from a MEVVA source using a high voltage to trigger the metal arc and a low sustaining arc voltage between the cathode and anode. The main arc current was maintained at around 100 A and pulse arc duration time was about 250 μs with the repetition frequency of 30 Hz. In order to remove deleterious macro-particles generated from the cathode surface and control the output amount of plasma, a 90° curved duct bias to +20 V was inserted between the plasma discharge and process chamber. Electrical currents were passed through the coils wrapped around the elbow of the curved duct to produce a magnetic field to focus the plasma into the center of the duct [21,22]. The specimens were positioned 15 cm away from the exit of the duct. In order to accurately monitor the implantation dose and reduce charging on the polymer surface, the output of the plasma was controlled by lowering the electromagnetic field in the duct and varying the distance from the exit to the specimens (r) as the plasma density is proportion to $1/r^2$. The implantation voltage applied to the specimens was –20 kV.

The elemental in-depth composition was determined by Rutherford backscattering spectrometry

Table 1
Surface tension parameters of the test liquids at 20°C

Liquid	γ_{LV}	γ_{LV}^p	γ_{LV}^d
Double distilled water	72.8	51.0	21.8
Glycol	48.3	19.0	29.3
Diiodomethane	50.8	2.3	48.5
Formamide	58.2	18.7	39.5
Tritolyl phosphate	40.9	1.7	39.2
Glycerin	63.4	26.4	37.0

(RBS) using 2 MeV $^4\text{He}^{++}$ and a backscattering angle of 170° . X-ray photoelectron spectroscopy (XPS) was performed on a PHI-5600 equipped with a monochromatic Al K_α source and data acquisition and processing were conducted using the PC Access ESCA version 7.2A program. To investigate the implantation-induced surface chemical changes, the C 1s, F 1s and metal photoelectrons core level spectra were recorded. Static contact angles were performed by the sessile drop method using a JY-82 contact angle goniometer at ambient humidity and temperature. The relative surface tension components of the test liquids are listed in Table 1. Each data point shown in this paper is the average of six measurements conducted on different parts of the specimen for statistical accountability.

3. Results and discussion

To investigate the implantation dose and elementary distributions, RBS was used to acquire the spectra of the implanted specimens and the results are shown in Fig. 1. The spectra shows that the transition metals implanted in the immersion configuration are embedded in the Teflon surface to a depth of several tens nanometers. All the specimens exhibit similar distributions and implantation doses. The existence of surface oxygen on the specimens is due to the oxygen incorporation during implantation under non-UHV (ultra high vacuum) conditions and absorption of moisture after exposure to air.

The surface compositions and chemical states of both the treated and untreated specimens were examined by XPS. Fig. 2 depicts the XPS survey

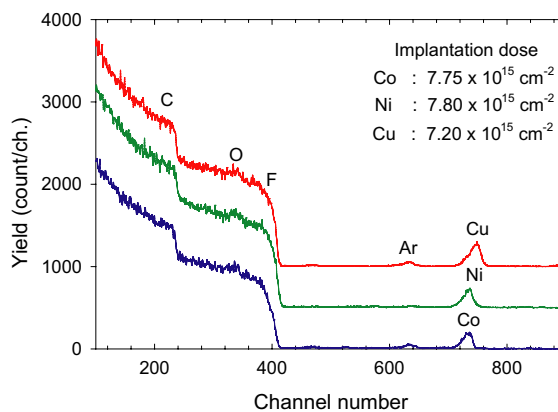


Fig. 1. RBS spectra acquired from metal implanted Teflon showing the calculated implantation dose.

scan spectra of the untreated, Co-implanted, Ni-implanted, and Cu-implanted specimens. An increase in the carbon atomic concentration and decrease in the fluorine atomic concentration are also observed. Our results thus suggest that high energy ion bombardment can result in chain scissions, carbon to fluorine bonds breakage, and escape of fluorine from the surface.

To clarify the bonding states, the core level spectra of C 1s and F 1s were measured and the results are displayed in Figs. 3 and 4, respectively. The principal peak at BE ≈ 292.41 eV of the untreated specimen in Fig. 3 corresponds to CF_2 and the secondary peak at BE ≈ 285.02 eV can be ascribed to C–C bonds [23]. However, the principal and secondary peaks are not detected after PIII. In all the implanted specimens, the C 1s peak shifts to a low binding energy and signifies the formation of metal carbides [23].

Apart from the dramatic chemical shift in the C 1s peak, the F 1s core level spectra also indicate significant chemical shifts as shown in Fig. 4. The F 1s peak shifts to a lower binding energy after metal ion implantation due to the formation of fluorine anion species [23]. It suggests that metal plasma implantation can cause carbon–fluorine bonds to break and facilitate the formation of metal fluorides. As illustrated in Fig. 4, the F 1s peaks can be deconvoluted into three to four components by applying Shirley background subtraction and Gaussian–Lorentzian peak fitting.

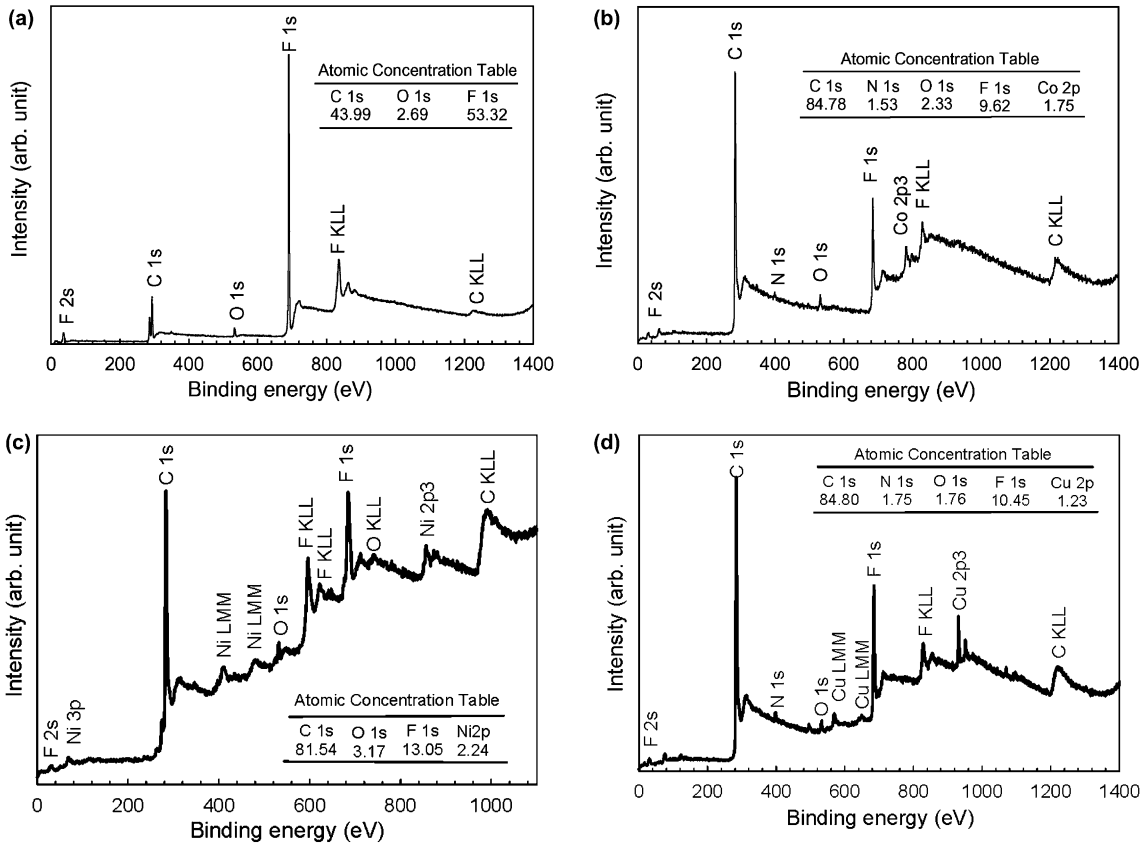


Fig. 2. XPS survey scan spectra obtained from Teflon showing the elemental concentration: (a) untreated, (b) Co-implanted, (c) Ni-implanted, (d) Cu-implanted.

The component at binding energy of BE \approx 684.22–684.62 eV can be assigned to metal difluoride. However, for the other components of BE \approx 682.25–682.53 eV and BE \approx 686.21–687.00 eV, no unequivocal assignment can be made as they can arise from different metal fluoride states. For the Ni-implanted specimen, the F 1s signal at BE \approx 688.98 eV stems from the carbon–fluorine bond and it matches the C 1s signal of BE \approx 291.25 eV in Fig. 3. In addition, the metal chemical states were determined from the XPS spectra exhibited in Fig. 5. The 2p_{3/2} peaks of the three transition metals show that there are no obvious differences between the carbide peaks and pure metal peaks. However, the broad shoulders of 2p_{3/2} peaks imply the formation of metal fluorides [23].

The wetting properties of the specimens were investigated using contact angle measurements. Six test liquids with known surface tension components were applied. In general, wettability is the ability of a liquid to adhere to a solid and spread over its surface to varying degrees. Normally, the classical model provided by Thomas Young suggests that

$$\gamma_{SV} = \gamma_{LV} \cos \theta + \gamma_{SL} \quad (1)$$

where θ is the contact angle, γ_{SV} is the surface tension of the solid in contact with air, γ_{LV} is the surface tension of the liquid in contact with air, and γ_{SL} is the surface tension between the solid and the liquid. The work of adhesion W_a between the solid and liquid can be expressed in terms of the Dupre equation as follows:

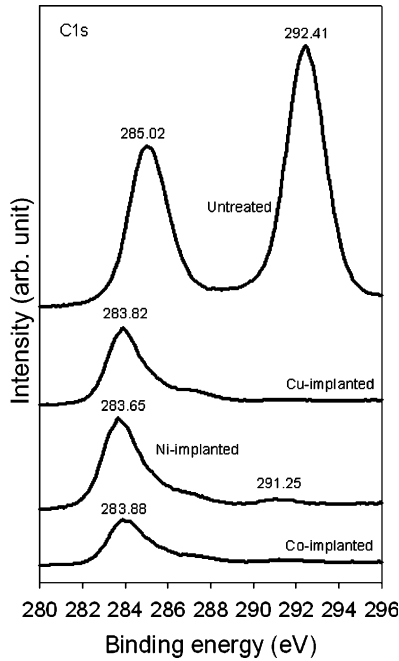


Fig. 3. C 1s core level spectra acquired from the untreated Teflon and metal implanted Teflon.

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (2)$$

A combination of the Young–Dupre equation gives

$$W_a = \gamma_{LV}(1 + \cos \theta) \quad (3)$$

The solid surface tension can be compiled into intermolecular attraction of polar interaction γ_s^p and dispersion interaction γ_s^d as

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (4)$$

Therefore, the work of adhesion can be expressed as the sum of the different intermolecular forces acted at the interface.

$$W_a = 2(\gamma_{LV}^d \gamma_s^d)^{1/2} + 2(\gamma_{LV}^p \gamma_s^p)^{1/2} \quad (5)$$

Thus, Eqs. (3) and (4) can further be simplified to

$$\gamma_{LV}(1 + \cos \theta) = 2(\gamma_{LV}^d)^{1/2}(\gamma_s^d)^{1/2} + 2(\gamma_{LV}^p)^{1/2}(\gamma_s^p)^{1/2}$$

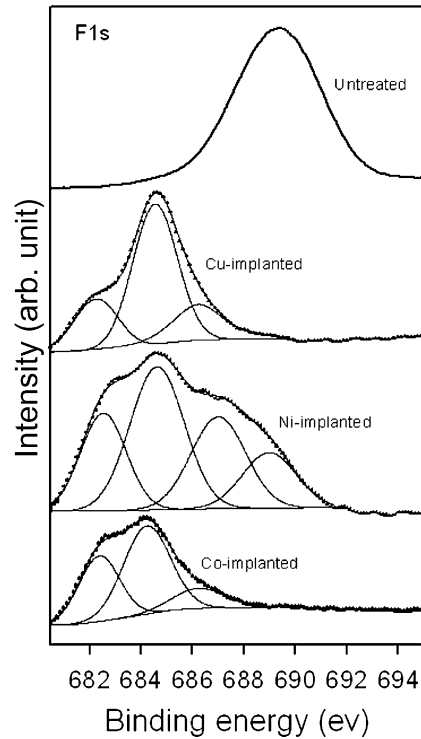


Fig. 4. F 1s core level spectra measured from the untreated Teflon and metal implanted Teflon.

Finally,

$$\frac{\gamma_{LV}(1 + \cos \theta)}{2(\gamma_{LV}^d)^{1/2}} = (\gamma_s^d)^{1/2} + (\gamma_s^p)^{1/2} \left(\frac{\gamma_{LV}^p}{\gamma_{LV}^d} \right)^{1/2} \quad (6)$$

Fig. 6 shows an obvious decrease in the contact angle measured on all the treated specimens. The Co-implanted specimen exhibits the lowest contact angle. The decrease of the contact angle and improvement of wetting property can be attributed to the change of physical and chemical properties of the surface after ion bombardment. The surface energy of solid is determined by the intermolecular attraction of polar interaction and dispersion interaction as described in Eq. (4). Any changes in these two interaction components can result in alteration of the surface energy. Fig. 7 shows the increase of both the polar and dispersion interactions after metal ion implantation. The XPS chemical states shifts shown in the C 1s and F 1s core

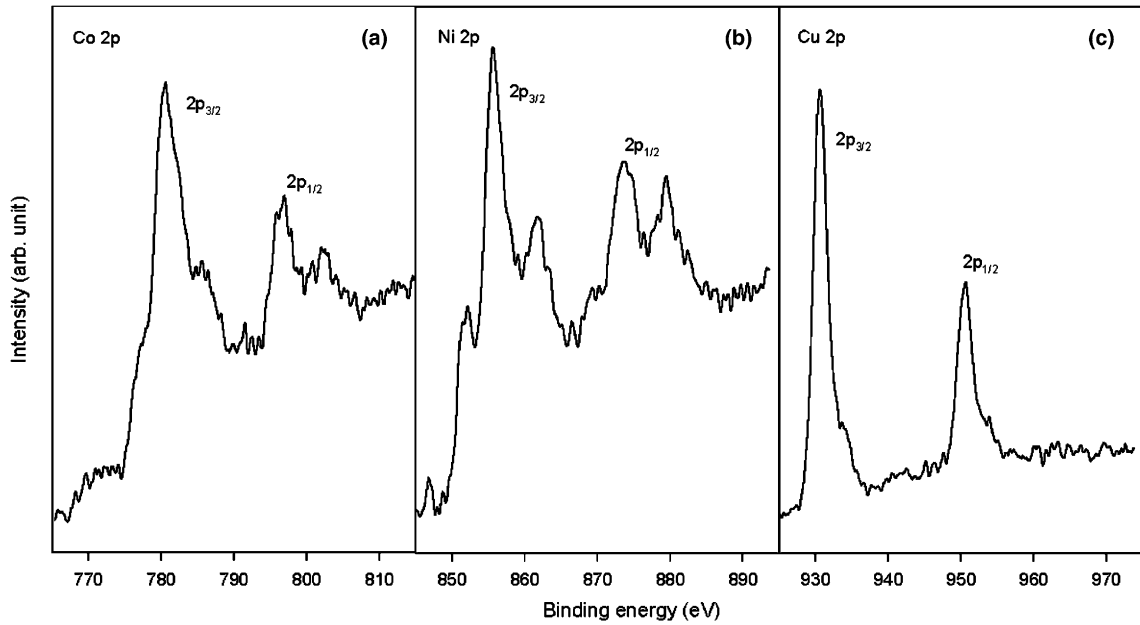


Fig. 5. XPS spectra taken from the metal implanted Teflon: (a) Co 2p spectrum, (b) Ni 2p spectrum, and (c) Cu 2p spectrum.

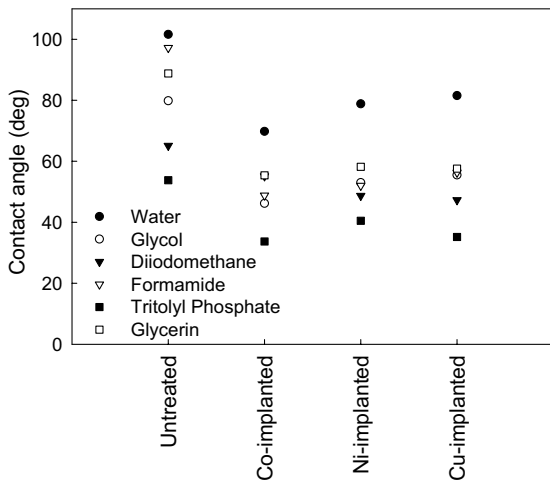


Fig. 6. Contact angles of six test liquids measured on the untreated Teflon and metal implanted Teflon.

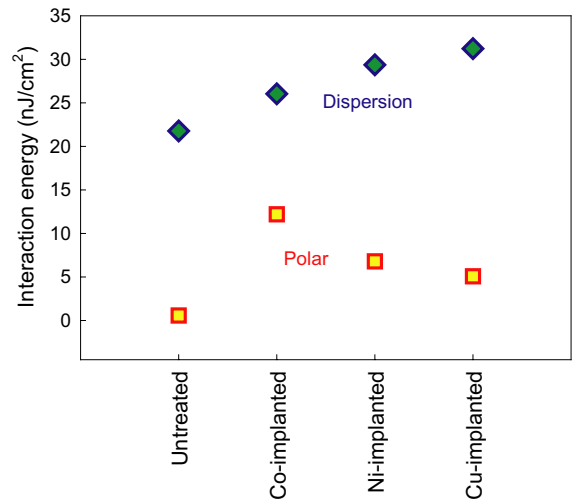


Fig. 7. Polar and dispersive interactions on the untreated Teflon and metal implanted Teflon.

level spectra reveal the formation of metal carbides and metal fluorides on the surface. The structure of these metal carbides and fluorides are totally different from that of high molecular weight polymer chains thereby changing the dispersion com-

ponent. Moreover, the electron cloud distribution of the ionic bonds of the carbides and fluorides results in a higher polar effect than that of covalent bonds in C–C and C–F. Combining these two effects as in Fig. 7 and based on Eq. (4), it is not

Table 2
Surface energy of the untreated Teflon and metal implanted Teflon

Specimen	Surface energy (nJ/cm ²)
Untreated	22.33
Co-implanted	38.22
Ni-implanted	36.15
Cu-implanted	36.29

difficult to understand the enhancement of the surface energy of the implanted specimens as shown in Table 2.

4. Conclusion

Three transition metals, Co, Ni and Cu, have been successfully implanted into the fluorine-based polymer, Teflon in an immersion configuration. The XPS chemical shifts of the C 1s and F 1s core level spectra reveal the formation of metal carbides and fluorides in the modified layer. As the physical structures and chemical states of metal carbides and fluoride are totally different from that of high-molecular polymer chains of Teflon, significant improvement in the wetting properties, polar and dispersion interactions as well as surface energy can be attained. Our work suggests that metal plasma immersion ion implantation is a viable and relatively straightforward technique to enhance the surface properties of polymers.

Acknowledgments

The authors acknowledge Prof. S.P. Wong and Dr. W.Y. Cheung for RBS measurements. The work was jointly supported by Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grant (CERG) No. CityU 1137/03E, City University of Hong Kong Strategic Research Grant No. 7001642 and National Natural Science Foundation of China under Grant Nos. 10345003 and 50373007.

References

- [1] M. Strobel, N. Sullivan, M.C. Branch, J. Park, M. Ulsh, R.S. Kapaun, B. Leys, *J. Adhes. Sci. Technol.* 14 (2000) 1243.
- [2] E.Y. Kim, J.S. Kong, S.K. An, H.D. Kim, *J. Adhes. Sci. Technol.* 14 (2000) 1119.
- [3] F.Z. Sidouni, N. Nurdin, P. Chabreck, D. Lohmann, J. Vogt, N. Xanthopoulos, H.J. Mathieu, P. Francois, P. Vaudaux, *P. Descouts, Surf. Sci.* 491 (2001) 355.
- [4] C. Mao, C. Zhang, Y. Qiu, A. Zhu, J. Shen, S. Lin, *Appl. Surf. Sci.* 228 (2004) 26.
- [5] M.J. Bader, J.J. O'Brien, K.L. Riddle, US Patent 5,725,962, 1998.
- [6] J.M. Grace, L.J. Gerenser, *J. Dispersion Sci. Technol.* 24 (2003) 305.
- [7] E.M. Mount, J.R. Wagner, US Patent 5,981,079, 1999.
- [8] Q. Toanle, J.J. Pireaux, R. Caudano, P. Leclere, R. Lazzaroni, *J. Adhes. Sci. Technol.* 12 (1998) 999.
- [9] K. Gotoh, Y. Nakata, M. Tagawa, M. Tagawa, *Colloid Surf. A* 224 (2003) 163.
- [10] R. Foerch, G. Kill, M.J. Walzak, *J. Adhes. Sci. Technol.* 7 (1993) 1077.
- [11] P.K. Chu, S. Qin, C. Chan, N.W. Cheung, L.A. Larson, *Mater. Sci. Eng. R* R17 (1996) 207.
- [12] X.B. Tian, R.K.Y. Fu, P.K. Chu, A. Anders, C.Z. Gong, S.Q. Yang, *Rev. Sci. Instrum.* 74 (2003) 5137.
- [13] R.K.Y. Fu, X.B. Tian, P.K. Chu, *Rev. Sci. Instrum.* 74 (2003) 3697.
- [14] Y. Inoue, Y. Yoshimura, Y. Ikeda, A. Kohno, *Colloid Surf. B* 19 (2000) 257.
- [15] M.R. Murthy, E.V. Rao, *Bull. Mater. Sci.* 25 (2002) 403.
- [16] K. Krezhov, K. Velitchkova, S. Balabanov, *Vacuum* 69 (2003) 113.
- [17] Y. Wu, T. Zhang, H. Zhang, X. Zhang, Z. Deng, *Surf. Coat. Technol.* 131 (2000) 520.
- [18] B.Z. Rameev, F. Yildiz, B. Aktas, C. Okey, R.I. Khaibullin, E.P. Zheglov, J.C. Pivin, L.R. Tagirov, *Microelectron. Eng.* 69 (2003) 330.
- [19] R.K.Y. Fu, K.L. Fu, X.B. Tian, P.K. Chu, *J. Vac. Sci. Technol. A* 22 (2004) 356.
- [20] P.K. Chu, J.Y. Chen, L.P. Wang, N. Huang, *Mater. Sci. Eng. R* 36 (2002) 143.
- [21] T. Zhang, P.K. Chu, R.K.Y. Fu, I.G. Brown, *J. Phys. D: Appl. Phys.* 35 (2002) 3176.
- [22] T. Zhang, B.Y. Tang, Z.M. Zeng, Q.C. Chen, X.B. Tian, T.K. Kwok, P.K. Chu, O.R. Monteiro, I.G. Brown, *Surf. Coat. Technol.* 128 (2000) 231.
- [23] J.F. Moulder, W.F. Stickler, P.E. Sobol, K.D. Bomben, in: J. Chatain (Ed.), *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, MN, 1992.