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Surface modification of poly(tetrafluoroethylene) films by plasma polymerization of glycidyl methacrylate for adhesion enhancement with evaporated copper

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Abstract

Surface modification of poly(tetrafluoroethylene) (PTFE) film by H_2 plasma treatment, and by plasma polymerization and deposition of glycidyl methacrylate (GMA) in the absence and presence of H_2 plasma pre-activation of the PTFE substrates, was carried out to enhance the adhesion of the polymer with evaporated copper. The H_2 plasma treatment resulted in effective defluorination and hydrogenation of the PTFE surface, and enhanced the adhesion of evaporate Cu to the PTFE surface (the Cu/PTFE assembly) to various extents. For plasma polymerization carried out at a low RF power, a high epoxide concentration was preserved in the plasma-polymerized GMA (pp-GMA) layer on the PTFE surface (the pp-GMA-PTFE surface). However, high adhesion strength for the Cu/pp-GMA-PTFE assembly was obtained only in the presence of H_2 plasma pre-activation of the PTFE substrates prior to the plasma polymerization and deposition of GMA. In the absence of H_2 plasma pre-activation, the deposited pp-GMA layer on the PTFE surface could be readily removed by acetone extraction. The adhesion enhancement of the Cu/pp-GMA-PTFE assembly in the presence of H_2 plasma pre-activation of the PTFE substrate was attributed to the covalent bonding of the pp-GMA layer with the PTFE surface, the preservation of the epoxide functional groups in the pp-GMA layer, and the strong interaction of evaporated Cu atoms with the epoxide and carboxyl groups of the GMA chains.

Keywords: Poly(tetrafluoroethylene); Glycidyl methacrylate; Plasma polymerization

1. Introduction

Fluoropolymers in general, and poly(tetrafluoroethylene) (PTFE) in particular, are potential dielectric materials for microelectronics packaging [1–3], since they have many unique properties, such as good thermal stability, low moisture sorption, and very low dielectric constants [4–6]. Numerous studies on the metallization of PTFE have been carried out to evaluate their potential applications in electronics packaging [7–9]. However, the surface inertness of PTFE has resulted in poor adhesion of the polymer with most metallic materials. To enhance the applicability of inert fluoropolymers for microelectronics packaging, a number of methods devoted directly to the surface modification of fluoropolymers for adhesion improvement have been developed. Among them, surface modification of polymers by non-reactive gas plasma treatments and by graft copolymerization with specific functional monomers are some of the versatile means for improving the adhesion of fluoropolymer with metals [7,10–14].

For the improvement of adhesion with evaporated Cu, surface modification of PTFE films by N_2, O_2, H_2, and mixed-gas plasmas has been reported [15]. It was proposed that Cu could react with both oxygen and nitrogen to form, respectively, Cu–O and Cu–N moieties at the interfaces. The adhesion between the PTFE and evaporated Cu can also be substantially improved by surface graft copolymerization of the PTFE substrate with certain functional monomers [7,10,11]. However, the problems associated with the relatively complex process of graft copolymerization in solution, or the aging effect of the plasma-treated surface with time, have restricted these methods from extensive industrial applications [16–18]. On the other hand, the plasma polymerization and deposition technique for surface modification has many advantages. The process has a high through-put, is solvent free, and causes minimal alteration to the bulk properties, as the extent of modification is

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usually restricted to the outermost layer [19,20]. For these reasons, plasma polymerization and deposition have attracted considerable attention in recent years [21–29].

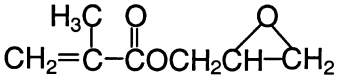
Glycidyl methacrylate (GMA) has an unsaturated carbon–carbon bond structure and an epoxide functional group. Our recent studies have shown that the adhesion strength at the metal/polymer interface can be significantly enhanced through surface modification of the polymer substrate via UV or thermally-induced graft copolymerization with GMA [7,30,31]. The epoxide functional group in the grafted GMA chain can serve as an effective adhesion promoter through chemical bonding and charge transfer interaction at the interphase. As a more practical alternative, it should be interesting to explore the direct plasma polymerization and deposition of GMA with well-preserved epoxide functional groups on various substrates of importance. It is understood that plasma with high energy can lead to monomer fragmentation, rearrangement and recombination during the deposition reaction [32].

In this study, surface modification of PTFE film via plasma polymerization of GMA, in the presence and absence of H_2 plasma pre-activation, is carried out to enhance the adhesion of PTFE surface with evaporate copper (Cu) metal. In comparison with other gas plasmas, hydrogen plasma can give rise to more extensive defluorination of the PTFE and other fluoropolymer surfaces [16]. In addition, hydrogen plasma pre-treatment can also result in the hydrogenation of the defluorinated PTFE surface. The resulting polyethylene-like surface can interact more effectively with the GMA plasma. The effects of various gas plasmas on the surface compositions of fluoropolymers have been compared and summarized [16]. The chemical composition and structure of the plasma-polymerized GMA (pp-GMA) layers are investigated by X-ray photoelectron spectroscopy (XPS) and FTIR spectroscopy, respectively. It is shown that the epoxide functional groups in the pp-GMA layer can be preserved to a large extent to serve as an adhesion promotion layer. The 180°-peel adhesion strength measurement indicates that plasma polymerization and deposition of GMA on the H_2 plasma pre-activated PTFE film is an effective means for enhancing the adhesion of PTFE with evaporated Cu.

2. Experimental

2.1. Materials

PTFE film having a thickness of about 0.1 mm and a density of 2.18 g/cm^3 was used in this study and was obtained from Goodfellow Ltd of Cambridge, UK. The PTFE film was cut into strips of 1×2 cm^2 in area. The surface of the film was cleaned by extraction with acetone for 30 min, followed by rinsing with doubly distilled water. The monomer, GMA, used for the plasma polymerization was obtained from the Aldrich Chemical Company of Milwaukee, WI, USA and was used after purification by vacuum distillation. The chemical structure of GMA is shown below:



(GMA)

H_2 with purities >99.999% were used for the plasma pre-treatment or pre-activation of the substrate surface before the plasma polymerization. Argon of the same purity was used as the carrier gas for the GMA monomer during plasma polymerization.

2.2. Plasma polymerization and deposition

The apparatus for plasma polymerization was manufactured by Samco International of Kyoto, Japan. The particular model (Model BP-1) consisted mainly of two physical parts: the reactor chamber for polymerization and the gas lines for introducing monomer and/or other gases. The reactor chamber consisted of a Pyrex® bell jar, and a pair of parallel disk electrodes (70 mm in diameter) connected to a RFG-200 radio-frequency (RF) generator. The latter was operated at 13.56 MHz and was capable of delivering 0–200 W of power through an impedance matching circuit. The PTFE films were positioned on the surface of the lower (ground) electrode at least 2 cm away from the edge. The GMA monomer was heated in an electronically thermostated constant temperature bath (Model DW611B/DR61). The carrier gas, Ar in the present case, passed through the monomer reservoir and was assumed to be saturated with the monomer vapor. All the gas lines were thermally insulated and maintained at approximately the same temperature as that of the monomer bath by means of band heaters. The gas flow rate was measured by an independent mass flow meter.

Plasma polymerization was carried out according to the following steps. Initially, the system was purged with Ar and then evacuated to about 1 Pa. The non-reactive gas (H_2), or the reactive GMA monomer in Ar was allowed to flow into the reaction chamber. The gas pressure was then adjusted to a designated value. After matching the required plasma power, the glow discharge was initiated and maintained for a period for surface activation or plasma polymerization. At the end of the plasma surface activation or deposition, the system was evacuated for at least 10 min to eliminate the etched fragments or the residual un-reacted monomer, respectively, in the system.

2.3. XPS measurement

The XPS measurements were made on an AXIS HSi 2 spectrometer (Kratos Analytical Ltd, England) with a Mg Kα X-ray source (1253.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The anode voltage and current were set at 15 kV and 15 mA, respectively. The pressure in the analysis chamber was maintained at 5.0×10^{-8} Torr or lower during each measurement. The PTFE substrates were mounted on the sample stubs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron take-off angle (with respect to the sample surface) of 90°. All binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV. In peak synthesis, the line width (full width at half maximum, or FWHM) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable up to ±5%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

2.4. FTIR spectra

Samples for Fourier-transformed infrared (FTIR) spectroscopic measurements were obtained by direct plasma polymerization and deposition of GMA on the surface of a freshly pressed KBr disc for about 5 min. The spectra were recorded on a Bio-Rad FTIR, Model FTS135, spectrophotometer under ambient conditions.

2.5. Characterization of the surface morphology

The morphologies of the PTFE surfaces were studied by atomic force microscopy (AFM), using a Nanoscope IIIa AFM from the Digital Instrument Inc. In each case, an area of $10 \times 10\ \mu m^2$ was scanned using the tapping mode. The drive frequency was 330 ± 50 kHz, and the voltage was between 3.0 and 4.0 V. The drive amplitude was about 300 mV and the scan rate was 0.5–1.0 Hz. An arithmetic mean of the surface roughness (R_a) was calculated from the roughness profile determined by AFM.

2.6. 180°-peel adhesion strength measurements

A Cu layer of about 1000 Å in thickness was thermally evaporated onto the surface of the PTFE sheet in a JOEL Model LEE-4000 vacuum evaporator. The deposition was carried out at a pressure of 10^{-6} Torr or less and at a deposition rate of about 10 Å/s. The metallized sample was heat-cured in a vacuum oven at 140°C for about 2 h, and then cooled to room temperature gradually over a period of no less than 4 h. The metallized surface was then adhered to a Cu foil backing (0.1 mm in thickness) in the presence of an epoxy adhesive (Araldite® Stand, from Ciba-Geigy Chem. Co. of Switzerland). The assembly under an applied pressure of about 0.2 kg/cm^2 was then heated in an oven at 140°C for 2 h to cure the epoxy adhesive. The cured assembly was allowed to cool to room temperature gradually over a period of no less than 4 h to minimize the thermal stress at the metal/polymer interface. The assembly was then subjected to the 180°-peel adhesion test in an Instron Model 5544 materials tester. All measurements were carried out at a crosshead speed of 10 mm/min. The size of Cu/PTFE assemblies was controlled at around 5×15 mm^2. For each peel strength reported, at least three sample measurements were averaged. The variations in adhesion strength among these samples were usually within ±0.3 N/cm.

3. Results and discussion

3.1. Surface modification of PTFE films via H_2 plasma treatment

Fig. 1 shows the C 1s core-level and wide scan spectra of the pristine PTFE surface (part (a)), and the PTFE surface after the H_2 plasma treatment (part (b)) at the RF power (*W*) of 80 W, gas pressure (*P*) of 100 Pa, and gas flow rate (*F*) of 20 sccm for a period (*t*) of 20 s. The C 1s core-level spectrum of the pristine PTFE surface consists of a main component at the BE of about 291.4 eV, attributable to the $\mathit{C}F_2$ species [33], and a broad minor component which is about 8 eV lower in BE. The area of this minor component is about 12% of that of the C 1s peak component at 291.4 eV. This low BE component is attributable to the combined contribution of the X-ray satellite peaks of the CF_2 species arising from the Mg $K\alpha_{3,4}$ radiation (about 9% of the main X-ray component) and the adventitious hydrocarbon (*C*H species) present on the film surface [34]. After the H_2 plasma treatment, followed by atmospheric exposure for about 2 h, the C 1s core-level spectrum of the PTFE surface is broadened over the BE range of 282–295 eV and can be curve-fitted with seven components

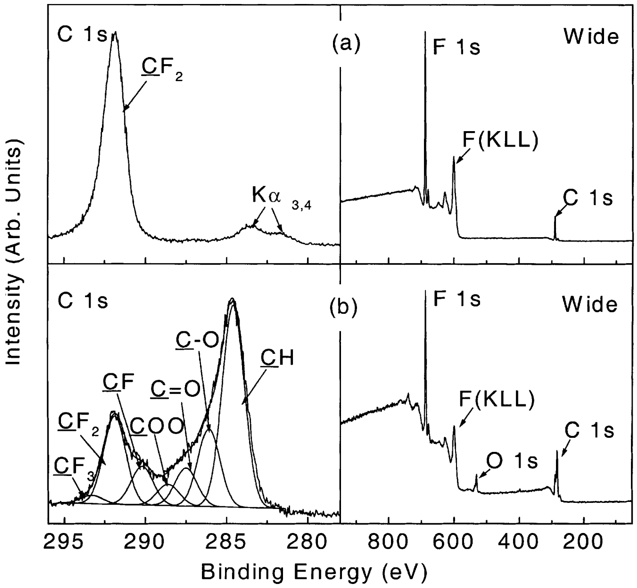


Fig. 1. C 1s core-level and wide scan spectra of: (a) the pristine PTFE surface; and (b) the PTFE surfaces treated by H_2 plasma at 80 W, 20 sccm and 100 Pa for 20 s.

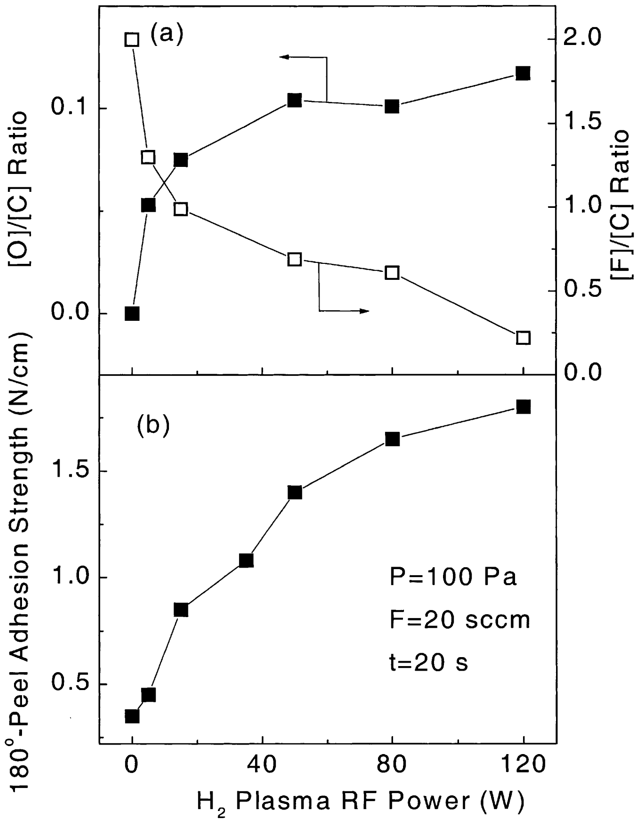


Fig. 2. Effect of the RF power of H_2 plasma treatment on: (a) the [O]/[C] and [F]/[C] ratio of the PTFE surface; and (b) the 180°-peel adhesion strength of the Cu/PTFE assembly.

(Fig. 1(b)). These peak components are assigned to the *C*–C and *C*–H species at 284.6 eV, the *C*–O species at 286.2 eV, the *C*=O species at 287.5 eV, the *C*OO species at 288.5 eV, the *C*F species at 290.1 eV, the *C*F_2 species at 291.4 eV, and the *C*F_3 species at 293.4 eV [35].

The changes in the [O]/[C] and [F]/[C] ratios of the PTFE surfaces, as determined from the corrected C 1s, O 1s, and F 1s core-level spectral peak-area ratios, as a function of the RF power of the H_2 plasma treatment are shown in Fig. 2(a). The compositions of the PTFE surfaces were measured after 2 h of atmospheric exposure. An increase in the [O]/[C] ratio and a decrease in the [F]/[C] ratio are observed upon increasing the RF power of the H_2 plasma. At the high RF power of 120 W, the [O]/[C] ratio of the H_2 plasma-treated PTFE surface has increased to 0.12, and the [F]/[C] ratio has decreased to as low as 0.3. Thus, H_2 plasma is very effective in defluorinating the PTFE surface, probably due to the formation of volatile HF compound [36,37]. Fig. 2(b) shows the dependence of the 180°-peel adhesion strength of the H_2 plasma-treated PTFE film with evaporated copper (the Cu/PTFE assembly) on the RF power of the H_2 plasma. The plasma treatments were carried out at $P = 100$ Pa, $F = 20$ sccm and $t = 20$ s, followed by 2 h of air exposure. The results indicate that simple H_2 plasma treatments at an RF power of 80 W or higher can enhance the adhesion strength of the Cu/PTFE assembly to about 1.7 N/cm, from the value of about 0.3 N/cm for the evaporated Cu on the pristine PTFE film. The formation of oxygen-containing and hydroxyl groups on the PTFE surface, arising from the interaction of the activated species with the atmosphere [38], probably accounts for the increased adhesion with evaporated copper [39]. Further adhesion enhancement is achieved through plasma polymerization and deposition of GMA on the H_2 plasma-pretreated or pre-activated PTFE surface.

3.2. Plasma polymerization of GMA on the PTFE surface: the pp-GMA-PTFE surface

It will be difficult, if not impossible, to establish the exact chemical structure of the pp-GMA (pp-GMA) layer, as the mechanism of plasma polymerization is much more complex than that of the conventional vinyl polymerization. In the present work, FTIR and XPS analyses are used to elucidate the plausible chemical structure and composition, respectively, of the deposited pp-GMA layer. Since it is of critical importance to preserve a sufficient amount of the epoxide functional groups in the pp-GMA layer, the discussion will emphasize on the dependence of the epoxide concentration in the pp-GMA layer on the glow discharge conditions.

Fig. 3 shows the respective FTIR spectra of the GMA monomer (Fig. 3(a)) and of the pp-GMA layers on KBr discs, obtained under the glow discharge conditions of 5 W, 20 sccm and 100 Pa for 5 min (Fig. 3(b)), 50 W, 20 sccm and 100 Pa for 5 min (Fig. 3(c)), and 120 W, 20 sccm and 100 Pa for 5 min (Fig. 3(d)). The absorption

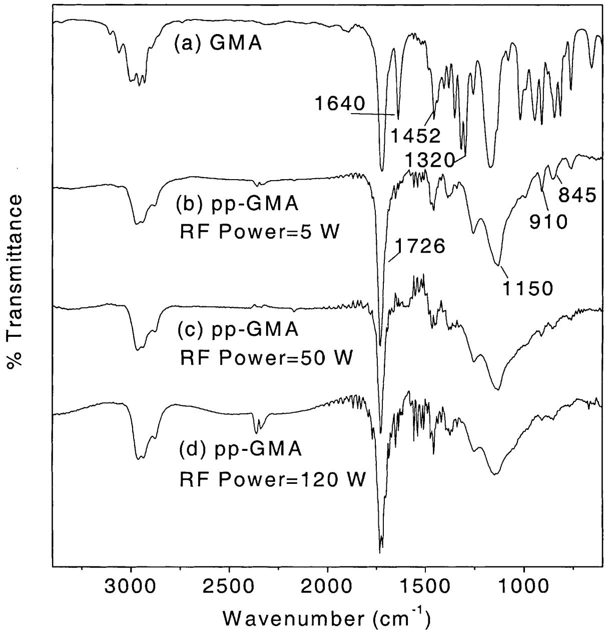


Fig. 3. FTIR spectra of (a) the GMA monomer, and the pp-GMA layers deposited on KBr discs under the glow discharge conditions of (b) 5 W, 100 Pa and 20 sccm for 5 min, (c) 50 W, 100 Pa and 20 sccm for 5 min, and (d) 120 W, 100 Pa and 20 sccm for 5 min.

band at the wavenumbers of 910 and 845 cm^{-1} are assigned to the epoxide functional group [31]. Thus, the pp-GMA layers deposited under the various glow discharge conditions (Fig. 3(b)–(d)) contain the same epoxide functional groups as that of the GMA monomer (Fig. 3(a)), albeit their relative absorbance, and thus concentration, varies somewhat with the RF power. The spectra of all the pp-GMA layers lack the carbon–carbon double bond (C=C) absorption at 1640 cm^{-1}, indicating that the plasma polymerization of GMA has proceeded mainly through carbon–carbon double bonds rather than the epoxide functional groups. In Fig. 3(b)–(d), the much weaker C–H deformation at 1452 cm^{-1} and C–H wag at 1320 cm^{-1} for the CH_2 groups, as well as the less well-resolved CH_2 and CH_3 stretching vibrations in the 2800–3000 cm^{-1} region, can be attributed to the restriction to chain motion in the pp-GMA layers. The band at 1726 cm^{-1}, on the other hand, corresponds to the carbonyl groups of the GMA molecule and the carbonyl groups arise from post-oxidation of the trapped free radicals with oxygen after the pp-GMA layer has been exposed to air [20]. Too high a plasma RF power used for polymerization, on the other hand, has involved the reaction of the epoxide functional groups, leading to a reduction in epoxide concentration (compare Fig. 3(b) and (d)).

The pp-GMA-PTFE surfaces were also analyzed by XPS. Fig. 4 shows the typical C 1s core-level spectra of the pp-GMA-PTFE surfaces prepared by plasma polymerization and deposition of GMA at 5 W, 100 Pa and 20 sccm for 20 s (part (a)) and at 120 W, 100 Pa and 20 sccm for 20 s (part (b)) in the presence of H_2 plasma pre-activation of the PTFE substrates at 80 W, 20 sccm and 100 Pa for 20 s. The C 1s core-level spectra are curve-fitted with peak components with BEs at 284.6 eV for the *C*–C and *C*–H species, at 286.2 eV for the *C*–O species, at 287.5 eV for the *C*=O species, and at 288.6 eV for the O–*C*=O species [26,27,30]. Taking into account of the FTIR results and the relative proportion of the O–*C*=O and *C*–O species in the C 1s core-level spectra, it can be assumed that two thirds of the *C*–O component in GMA homopolymer is contributed by the epoxide functional groups. Thus, the effect of the plasma RF power on the epoxide and carboxyl (O–C=O) groups can be quantified. The intensities of the *C*–O and O–*C*=O components in Fig. 4(a) are significantly higher than those in Fig. 4(b). Hence, the epoxide functional groups on the pp-GMA-PTFE surface are preserved more effectively for GMA plasma polymerization carried out under the low RF power of 5 W. For the GMA homopolymer [40], the theoretical ratio for the [*C*H]:[*C*–O]:[O–*C*=O] species is 3:3:1. This ratio is closely preserved for the pp-GMA layer deposited under the low RF power. For the pp-GMA layers deposited at a low RF power of 5 W (Fig. 4(a)) and at a high RF power of 120 W (Fig. 4(b)), the [*C*H]:[*C*–O]:[O–*C*=O] ratios are about 3.3:2.9:1.0 and 11:3.5:1.0, respectively. At high RF power, the carbonyl (*C*=O) species appears on the pp-GMA-PTFE surface as shown in Fig. 4(b). The enhanced C=O species concentration probably has resulted from the scission of the *C*–O bond of the O=*C*–O group due to the increase in energy per GMA unit at the higher RF power.

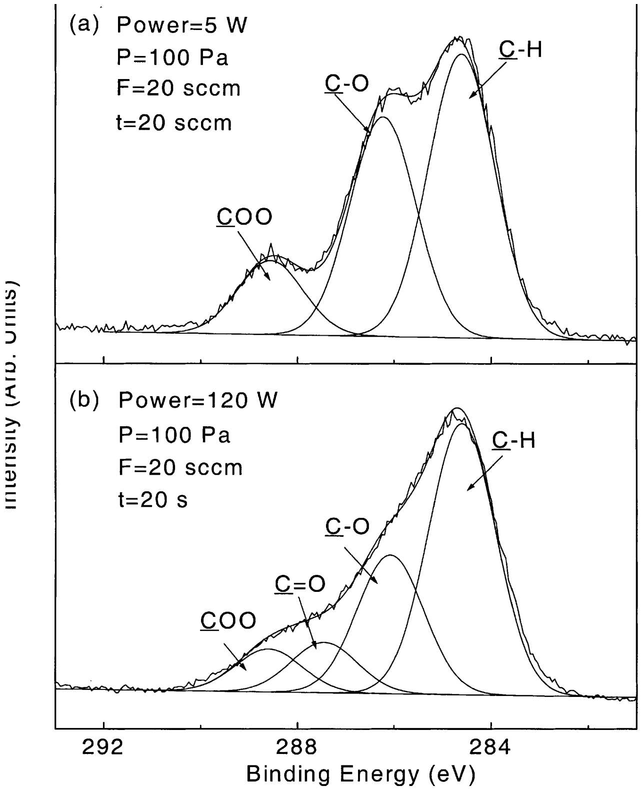


Fig. 4. C 1s core-level spectra of the pp-GMA-PTFE surface prepared under the glow discharge conditions of (a) 5 W, 100 Pa, 20 sccm for 20 s, and (b) 120 W, 100 Pa, 20 sccm for 20 s, in the presence of H_2 plasma pre-activation at 80 W, 100 Pa, 20 sccm for 20 s.

Fig. 5 shows the XPS-derived [*C*–O]/[*C*H] and

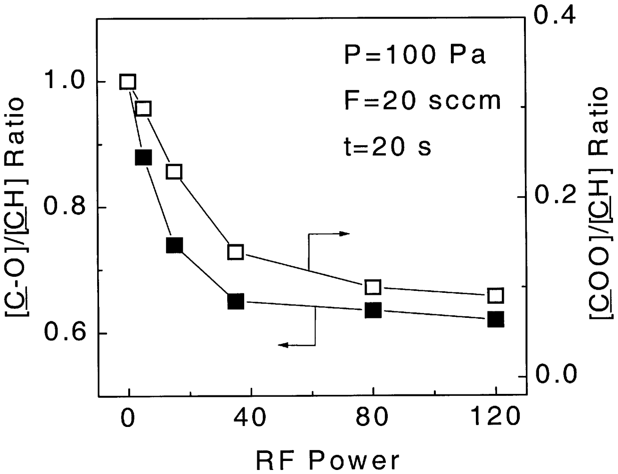


Fig. 5. XPS-derived [*C*–O]/[C] and [*C*OO]/[C] ratios of the pp-GMA-PTFE surface, as a function of the RF power of the GMA plasma, for deposition carried out at 100 Pa, 20 sccm for 20 s (H_2 plasma pre-activation at 80 W, 100 Pa, 20 sccm for 20 s).

[O–*C*=O]/[*C*H] ratios of the pp-GMA-PTFE surface as a function of the RF power. Both the [*C*–O]/[*C*H] and [O–*C*=O]/[*C*H] ratios decreases with increasing RF power, suggesting that higher RF power will lead to more severe degradation of the epoxide and carboxyl functional groups. With the increase in RF power, the [*C*–O]/[*C*H] and [O–*C*=O]/[*C*H] ratios for the pp-GMA-PTFE surfaces decrease from the respective values of about 0.90 and 0.30, which are similar to those dictated by the theoretical [*C*–H]:[*C*–O]:[O–*C*=O] ratio of 3:3:1 for the GMA homopolymer, to the respective asymptotic values of 0.60 and 0.10 at RF powers above 40 W.

The variation in composition of the GMA plasma-polymerized PTFE surface is probably attributable to the different bond scission mechanisms in the plasma polymerization process. A popular controlling parameter, the apparent input energy per unit mass flow rate, or the *W*/*FM* ratio, in which *W*, *F* and *M* are the RF power, the molar flow rate of the monomer, and the molecular weight of the monomer, respectively, has been used to explain the changes in polymer composition and structure with the plasma deposition conditions [41]. Taking into consideration the *W*/*FM* parameter, different input RF powers will give rise to different energy per GMA unit. Because of the difference in dissociation energies for chemical bonds in organic molecules, e.g. 267 kJ/mol for carbon–carbon π bond, 351 kJ/mol for C–O bond, 414 kJ/mol for C–H bond, and 347 for C–C bond [20], different RF powers will give rise to different patterns of bond scission in the GMA monomer, and hence the difference in chemical structures of the plasma-deposited films. At low RF power, bond scission occurs mainly at the carbon–carbon π bond of the GMA molecule, which has the lowest energy for bond scission. Under this condition, rearrangement of the active radicals results predominantly in a plasma-deposited polymer which has similar chain structure as that of the GMA

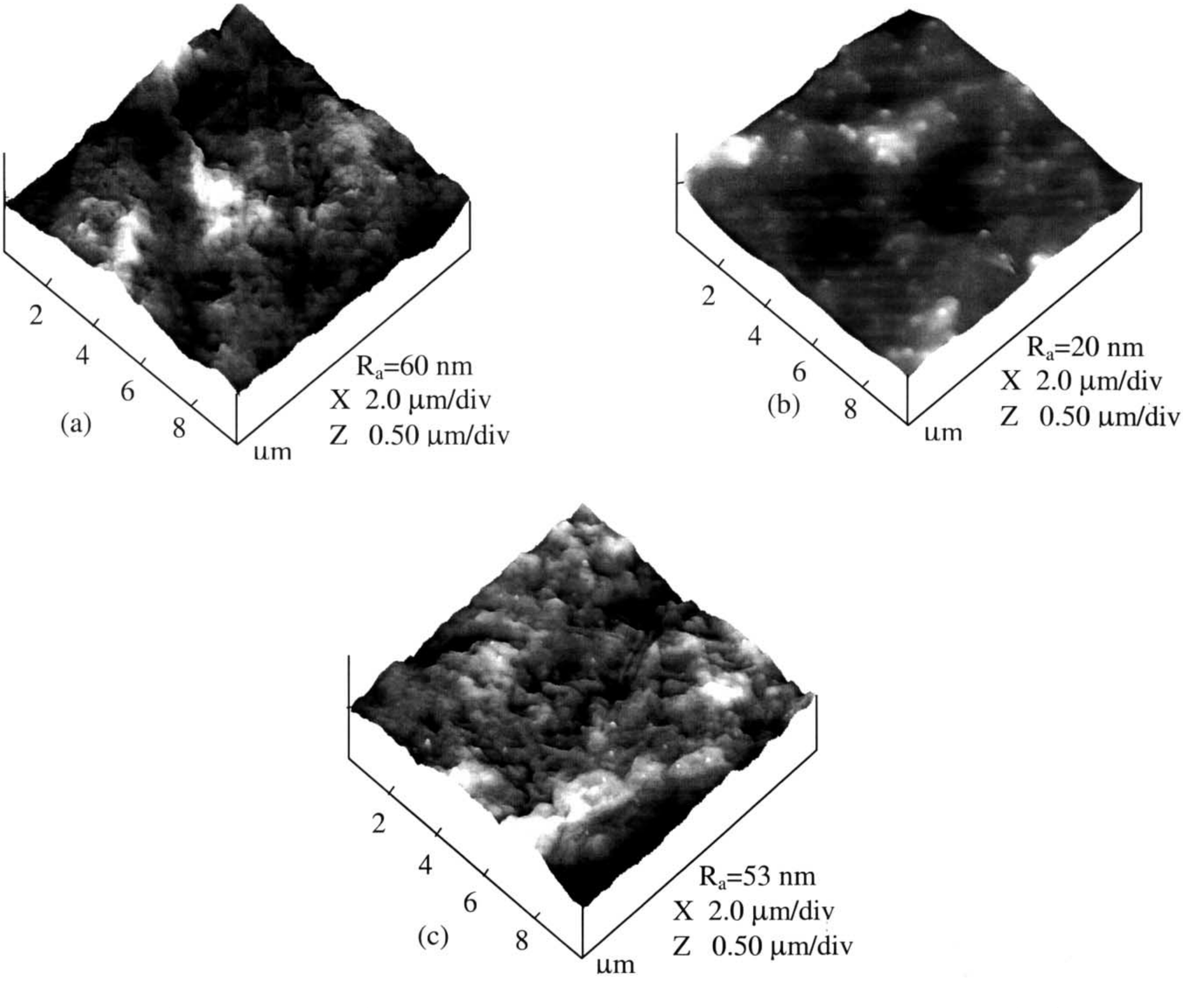


Fig. 6. AFM images of (a) the pristine PTFE surface, and the pp-GMA-PTFE surface prepared under the glow discharge conditions of (b) 5 W, 100 Pa, 20 sccm for 40 s, and (c) 120 W, 100 Pa, 20 sccm for 20 s, in the presence of H_2 plasma pre-activation at 80 W, 100 Pa, 20 sccm for 20 s.

homopolymer. With the increase in input RF power, the GMA plasma contains more active radicals, which come from the scissions of the carbon–carbon π bonds, as well as the C–O and C–C bonds. When ring-opening of the epoxide groups occurs, the cleavage of the C–O bond in O=*C*–O group is likely to occur as well.

3.3. Surface morphology of the pp-GMA-PTFE surface

Plasma polymerization can also produce deposits in different forms, including high quality thin films, powders, and oil-like adhesives [20]. For potential industrial applications as an adhesion promoter, the pin-hole free and homogeneous pp-GMA-PTFE surfaces are preferred.

Fig. 6 shows the respective AFM images of the pristine PTFE surface (part (a)) and the pp-GMA-PTFE surfaces deposited under the glow discharge conditions of 5 W, 100 Pa, 20 sccm for 40 s (part (b)) and 120 W, 100 Pa, 20 sccm for 40 s (part (c)). The pristine PTFE surface appears to be rough (Fig. 6(a)), with an average surface roughness value, R_a, of about 60 nm. After the deposition of the pp-GMA layer at the low RF power of 5 W (Fig. 6(b)), the morphology of the surface becomes fairly smooth, with R_a value reduces to about 20 nm. When the RF power is increased to 120 W (Fig. 6(c)), the morphology of the pp-GMA-PTFE surface exhibits similar roughness as that of the pristine PTFE, with R_a value around 53 nm. Some powders were observed after polymerization. The results suggest that the pp-GMA layer deposited at the low RF power has a more uniform surface than that deposited at the high RF power.

3.4. Adhesion characteristics of the Cu/pp-GMA-PTFE assembly

Fig. 7 shows the 180°-peel adhesion strength of the assembly involving evaporated Cu on pp-GMA-PTFE (the Cu/pp-GMA-PTFE assembly), prepared in the absence (Curve a) and presence (Curve b) of the H_2 plasma pre-activation of the PTFE substrates at 80 W, 100 Pa, 20 sccm for 20 s, as a function of the RF power used for the GMA plasma polymerization. The pp-GMA polymerizations on the PTFE surfaces, on the other hand, were carried out at 100 Pa and 20 sccm for 20 s. The adhesion strength of the Cu/pp-GMA-PTFE assembly involving GMA plasma at the RF power of 5 W without any prior plasma pre-activation is less than 0.5 N/cm. The increase in the RF power for deposition only enhances the adhesion strength marginally. The poor adhesion strength can be attributed to the lack of interaction between the deposited pp-GMA layer and the inert PTFE surface. The GMA plasma under low RF power has only weak etching effect. Thus, it is difficult to activate the inert PTFE surface simultaneously. Thus, the pp-GMA layers deposited at the low RF powers are physically adsorbed on the pristine PTFE surface. Increasing the RF power may lead to more severe etching of the PTFE surface by the GMA plasma, thus

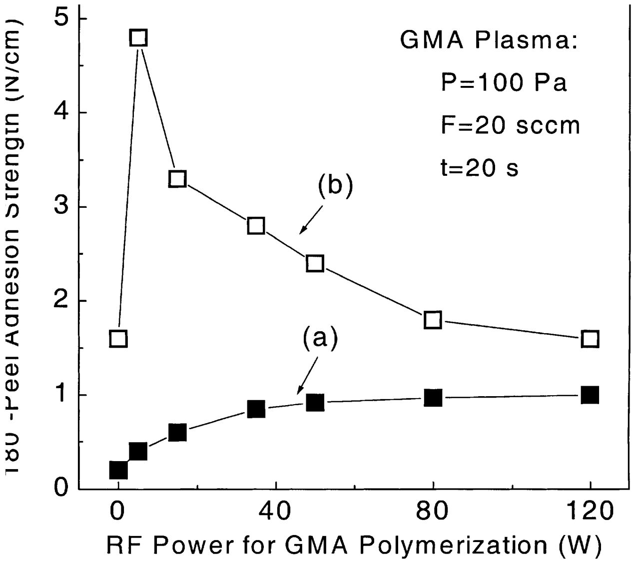


Fig. 7. The 180°-peel adhesion strength of the Cu/pp-GMA-PTFE assembly as a function of the RF power of the GMA plasma: (a) in the absence of H_2 plasma pre-activation; and (b) in the presence of H_2 plasma pre-activation at 80 W, 100 Pa, 20 sccm for 20 s.

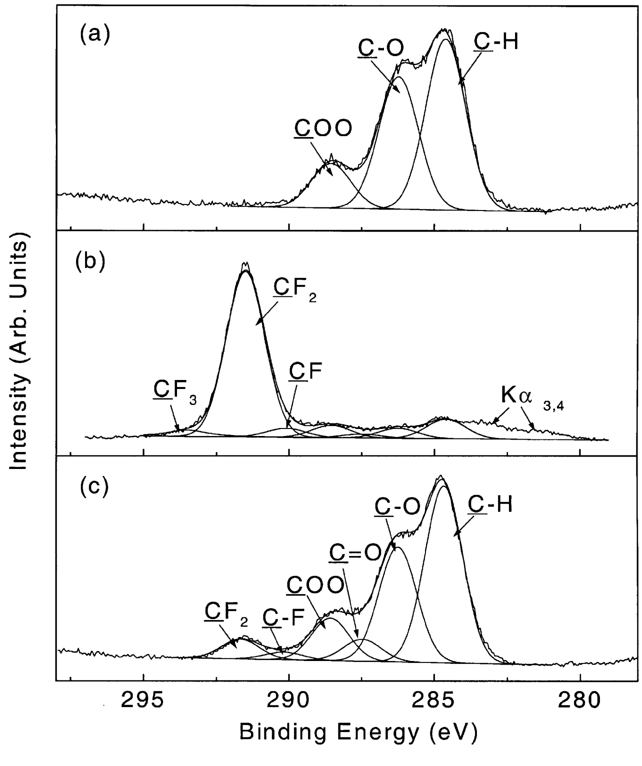


Fig. 8. The C 1s core-level spectra of the pp-GMA-PTFE surfaces prepared at the RF power of 5 W: (a) before acetone extraction, and after acetone extraction for the pp-GMA-PTFE films prepared; (b) in the absence of any plasma pre-activation; and (c) in the presence of H_2 plasma pre-activation at 80 W, 100 Pa, 20 sccm for 20 s.

enhancing the adhesion strength of the Cu/pp-GMA-PTFE assembly to a certain extent. Curve b in Fig. 7 shows the adhesion strength of the Cu/pp-GMA-PTFE assembly as a function of the RF power of the GMA plasma, involving PTFE film pre-activated by H_2 plasma. The adhesion strength of the Cu/pp-GMA-PTFE assembly involving H_2 plasma pre-activated PTFE film is enhanced significantly. An adhesion strength of about 4.8 N/cm is obtained for the assembly involving pp-GMA deposited at 5 W, 100 Pa, 20 sccm for 20 s on the PTFE film pre-activated by H_2 plasma at 80 W, 100 Pa, 20 sccm for 20 s. Increasing the RF power for GMA plasma polymerization on the H_2 plasma pre-activated PTFE film, however, results in the decrease in adhesion strength of the corresponding Cu/pp-GMA-PTFE assembly. Apparently, increasing the RF power will cause the degradation of the epoxide functional groups in the GMA chains, leading to low epoxide concentration in the pp-GMA layer.

Fig. 8 shows the respective C 1s core-level spectra of the pp-GMA-PTFE surfaces prepared at the RF power of 5 W on PTFE film without any plasma pre-activation, before (part (a)) and after (part (b)) acetone extraction. The corresponding C 1s spectrum for the acetone-extracted pp-GMA-PTFE surface, prepared in the presence of H_2 plasma pre-activation of the PTFE substrate, is shown in part (c). The respective pp-GMA-PTFE films were extracted in acetone at 35°C for at least 4 h. After the acetone extraction, the C 1s core-level line shape of the pp-GMA-PTFE surface in Fig. 8(b) becomes almost identical to that of the pristine PTFE. This result suggests the removal of the pp-GMA layer during the acetone extraction and is consistent with the weak adhesion strength of the Cu/pp-GMA-PTFE assembly in the absence of plasma pre-activation of the PTFE substrate. However, in the presence of H_2 plasma pre-activation, most of the pp-GMA layer is retained on the pp-GMA-PTFE surface after the acetone extraction (Fig. 8(c)). Thus, strong interaction via covalent bonding exists between the H_2 plasma-pretreated PTFE surface and the pp-GMA layer. The presence of the covalently bonded pp-GMA layer is consistent with the enhanced adhesion strength in the corresponding Cu/pp-GMA-PTFE assembly.

Fig. 9 illustrates, schematically, the processes of H_2 plasma pre-activation of the PTFE surface and GMA plasma polymerization and deposition, as well as the interaction of the evaporated Cu with the pp-GMA layer. After the H_2 plasma pre-activation of the PTFE surface, the surface has been defluorinated and hydrogenated simultaneously. Substantial amounts of the active radicals and species are also introduced onto the PTFE surface. The reactive GMA plasma subsequently interacts with the activated PTFE surface during polymerization and deposition. Thus, the pp-GMA layer, under this condition, becomes covalently

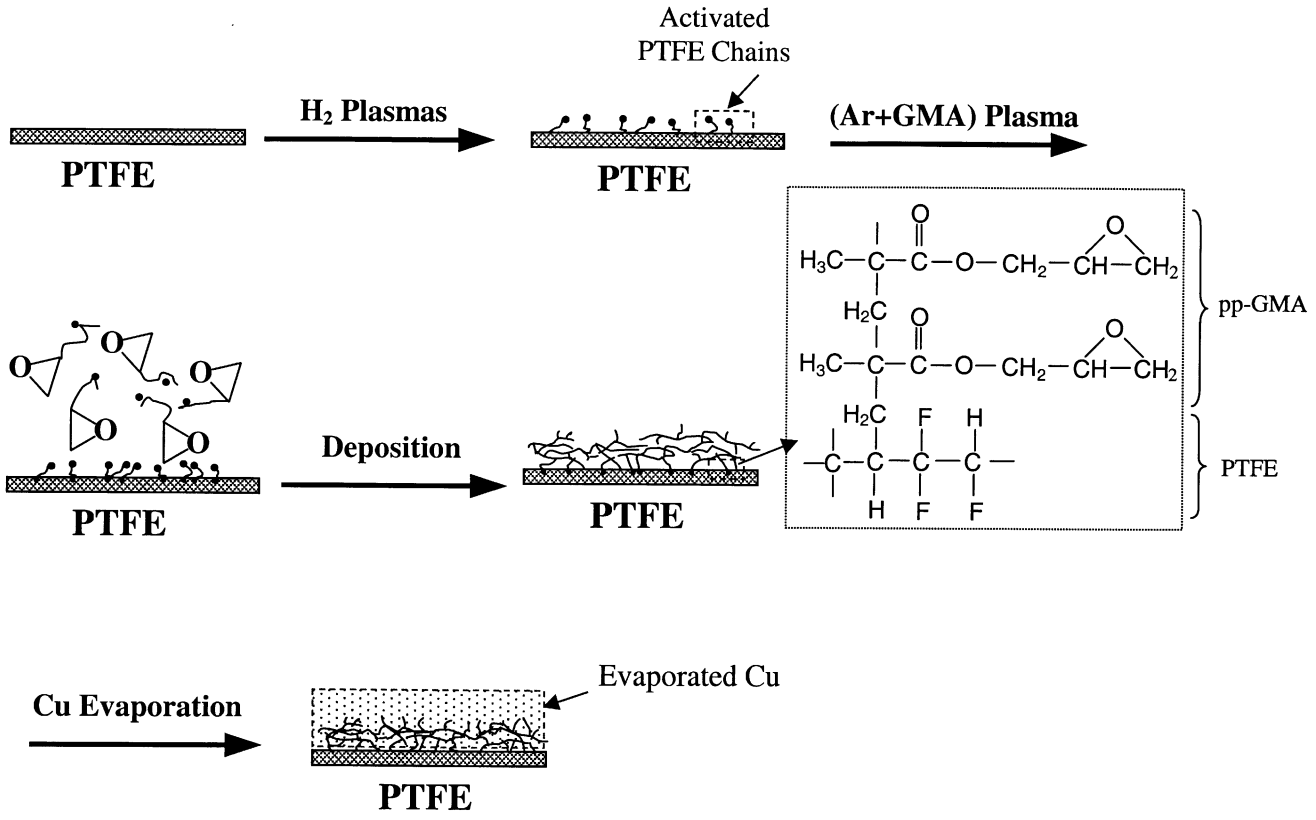


Fig. 9. Schematic diagram illustrating the processes of H_2 plasma pre-activation of the PTFE surface, the plasma polymerization and deposition of GMA, and the adhesion enhancement of the evaporated Cu on the pp-GMA-PTFE film.

tethered to the PTFE surface. The pp-GMA layer deposited at a low RF power still retains a high proportion of epoxide functional groups, as discussed earlier. The subsequently evaporated Cu atoms can then interact with the epoxide functional groups to form the Cu–O–C complex [42]. Thus, the substantially enhanced adhesion strength of the Cu/pp-GMA-PTFE assemble, prepared in the presence of H_2 plasma pre-activation of the PTFE substrate, can be attributed to the synergestic effect of coupling the reaction of epoxide functional groups in the pp-GMA chains with the evaporated Cu atoms, interactive mixing of Cu atoms into the pp-GMA layer, and the fact that the pp-GMA layer is covalently tethered on the H_2 plasma pre-activated PTFE surface.

In the absence of H_2 plasma pretreatment of the PTFE surface, the GMA plasma at a low RF power is not sufficiently energetic to induce a significant amount of active radicals and species on the PTFE surface. Under this circumstance, the extent of covalent bonding between the pp-GMA layer and the PTFE substrate is rather limited. As a result, poor adhesion is observed in the corresponding Cu/pp-GMA-PTFE assembly. With increasing RF power of the GMA plasma, the interaction between the pp-GMA layer is enhanced. Nevertheless, the increase in RF power will result in a concomitant decrease in the amount of the epoxide species in the pp-GMA layer. Thus, for pp-GMA-PTFE surfaces prepared in the absence of H_2 plasma pretreatment, the increase in adhesion strength with Cu soon levels off with the further increase in RF power of the GMA plasma.

3.5. Failure mode of the Cu/pp-GMA-PTFE assembly

The failure mode of the Cu/pp-GMA-PTFE assembly in the presence of H_2 plasma pre-activation was briefly investigated. Fig. 10(a) and (b) show the respective wide scan spectra of the delaminated PTFE and Cu surfaces from two Cu/pp-GMA-PTFE assemblies having 180°-peel adhesion strengths of about 0.5 and 4.8 N/cm, respectively. For these two assemblies, the pp-GMA depositions were carried at the glow discharge conditions of 5 W, 100 Pa, 20 sccm for 20 s on the PTFE surface in the absence (part (a)) and presence (part (b)) of the H_2 plasma pre-activation at 80 W, 100 Pa, 20 sccm for 20 s. The XPS wide scan spectrum of the delaminated PTFE surface in Fig. 10(a) is grossly similar to that of the pristine PTFE surface while the XPS wide scan spectrum of the delaminated Cu surface contains the C 1s, O 1s and F 1s signals, as well as strong Cu core-level and background signals. Therefore, for the Cu/pp-GMA-PTFE assembly prepared in the absence of H_2 plasma pre-activation and having a low adhesion strength of only about 0.5 N/cm, the pp-GMA layer has delaminated almost completely from the PTFE surface. In contrast, the XPS wide scan spectra for the delaminated PTFE and Cu surfaces in Fig. 10(b) are grossly similar to that of the pristine PTFE surface. The fact that the wide scan spectrum of the delaminated Cu surface resembles that of the pristine PTFE surface, and with the complete absence of any Cu signal, readily suggests that the Cu/pp-GMA-PTFE assembly, having an adhesion strength of about 4.8 N/cm, has delaminated by cohesive failure inside the PTFE substrate.

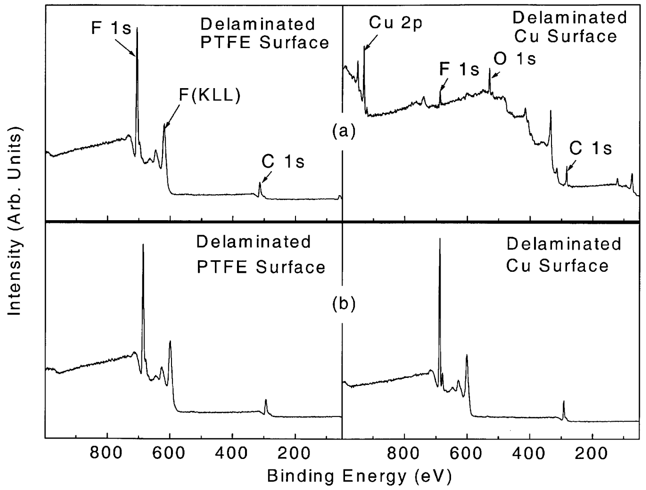


Fig. 10. The XPS wide scan spectra of the delaminated PTFE and Cu surfaces of the Cu/pp-GMA-PTFE assemblies: (a) having a 180°-peel adhesion strength of about 0.5 N/cm and prepared in the absence of H_2 plasma pre-activation; and (b) having a 180°-peel adhesion strength of about 5 N/cm and prepared in the presence of H_2 plasma pre-activation.

4. Conclusions

H_2 plasma-pretreated PTFE films were subjected to further surface modification via plasma polymerization and deposition of GMA. The H_2 plasma caused defluorination of the PTFE surface. The epoxide functional groups in the GMA plasma-polymerized PTFE (pp-GMA-PTFE) surface were preserved more effectively at the low RF power (e.g. 5 W) than at the high RF power (e.g. 120 W) used for plasma deposition. GMA plasma polymerization at low RF power and in the presence of H_2 plasma pre-activation of the PTFE substrate was shown to be an effective method for enhancing the interfacial adhesion of the PTFE with the evaporated Cu. An optimum 180°-peel adhesion strength close to 5 N/cm was obtained for the Cu/pp-GMA-PTFE assembly. This adhesion strength represents a three-fold increase over that involving PTFE surface treated by H_2 plasma alone, or more than eight-fold increase over that involving PTFE surface modified by GMA plasma polymerization in the absence of any plasma pre-activation. The Cu/pp-GMA-PTFE assembly, having an adhesion strength of about 5 N/cm, delaminated by clean cohesive failure inside the PTFE film.

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