Plasma Surface Modification of Acrylic-Based Polymer Multilayer for Enhanced Ag Adhesion

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ABSTRACT

Plasma treatments were performed on an acrylic-based Polymer Multilayer (PML) coating in order to improve its adhesion with metals, such as Ag. The coating was deposited on a PET substrate in a roll-to-roll Web-coater by vacuum flash evaporation of an acrylic monomer mixture and cured by a U.V. lamp. The treatment was conducted using a microwave plasma (2.45 GHz), operated with N_2 and Ar gases and under various processing conditions. In-situ XPS measurements revealed a loss of the initial C-O and O=C-O groups upon plasma exposure. The effect was much more pronounced for N_2 than for Ar, and it increased with increasing plasma power and treatment time. A small amount of nitrogen atoms were incorporated into the surface after N_2 plasma treatment, and the incorporation increased also with the plasma power and treatment time. In-situ sputter-deposited Ag films exhibited improved adhesion to surfaces treated by N_2 than to Ar plasmas, which correlated well with the change of surface energy indicated by the water contact angle measurements. The surface of the PML coating was very smooth and appeared to be smoother after plasma exposure.

INTRODUCTION

Polymer/metal multilayer stack structures have many potential optical, packaging, semiconductor, and display applications. A primary concern in the manufacturing of such stacks is the adhesion at the polymer/metal and metal/polymer junctions. This is particularly critical for noble metals, such as Ag, because of their low chemical reactivity and for smooth substrate surfaces, such as the PML coating [1], due to the absence of physical interlocking effect. The substrate surface must be sufficiently activated to promote an interaction with the depositing metal atoms. By removing surface contaminants, incorporating new and more reactive functional groups, and crosslinking the weak subsurface layers, low-temperature plasma has proven to be very efficient for such applications. In addition, the plasma process is fully compatible with all the other vacuum technologies, allowing in-line and high-speed processing of polymer/metal multilayer structures.

The interaction of a plasma with the substrate surface results from the synergetic actions of electrons, ions, atoms, molecules, and UV quanta. Depending on the nature of gas used, the interaction of plasma species with a polymer surface can lead to etching, surface activation, and deposition of thin films. Surface activation is generally accomplished with O_2, N_2, and Ar gases, and is strongly dependent on the chemical structure of the substrate surface. For example, we observed, in a separate study using a DC Corona [1], that plasma treatment causes significant damage to acrylic-based coatings while it is less effective in activating the acrylic surface, compared to a PET surface. Therefore, for each substrate surface, the activation treatment conditions must be optimized. We report in this paper an in-situ XPS study of the effectiveness of a remote microwave plasma on the modification and activation of an acrylic-based PML coating surface.

EXPERIMENTAL

The acrylic monomer mixture, composed of mainly tripropyleneglycol diacrylate (SR 306), was deposited onto a 4 mil DuPont PET substrate using the PML technology [2] and U.V. cured.

Plasma treatments were conducted in a small vacuum chamber (Figure 1) in which a remote microwave plasma source (ASTEX, 2.45 GHz), a DC magnetron sputtering cathode (Angstrom Sciences, ONYX2-UHV™), and a sample manipulator were installed. The manipulator enabled X-Y-Z translation and 360° rotation to facilitate sample transfer to the XPS instrument. The sample (3x3 cm^2) was mounted on a sample platen and held in a sample dock. The sample was placed 20 cm away from the aperture of the plasma applicator and 10 cm from the sputtering source.

Before plasma treatment, the chamber was evacuated first to a pressure below 10^{-6} Torr. The gas or gas mixture was then introduced and allowed to stabilize. The plasma was generated and the glow observed through the windows around the chamber. The plasma treatment experiments were performed by keeping the gas flow rate (20 cm^3/STP) and pressure constant (~ 12 mtorr) while varying the applied power to the plasma source and treatment time.

After plasma treatment, the chamber was evacuated to a pressure below 10^{-6} Torr, and then the sample was transferred in-situ into the XPS chamber (Kratos Axis165) via two intercrossing transfer arms (Figure 1). The XPS analysis was per-

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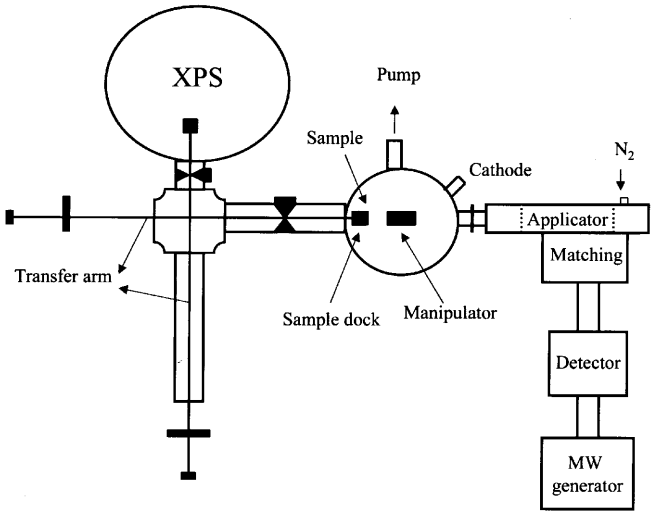

Fig.1. Description of the system for plasma treatment and Ag deposition.

formed using a monochromatic Al x-ray source (1456 eV). The filament emission current and the electron acceleration voltage were controlled to ensure that no surface damage occurred during spectral acquisition. An electron neutralizer (about 2 eV) was used to compensate the positive charges created on the surface. In addition, two C1s spectra, collected respectively at the beginning and the end of spectral acquisition sequence, were compared to ensure that the surface charging state remained unchanged. The survey spectra were obtained using a pass energy of 80 eV and the high resolution spectra, with a pass energy of 20 eV. After acquisition, the atomic concentration of each element was calculated and the surface charging corrected by placing the C-C peak to 284.8 eV and shifting all the other peaks by the same amount.

To examine the effect of plasma treatment on the adhesion of Ag to PML, 500 Å thick Ag films were sputter-deposited onto the PML surfaces. The adhesion was evaluated using a tape test, according to the standard cross-hatch procedure (ASTM D3359-93). The experiments were repeated several times for each plasma test condition.

RESULTS AND DISCUSSION

We concentrated our effort on N_2 and Ar plasma treatments of the PML surfaces based on several considerations. First, it has been demonstrated for several metal/polymer systems that a N_2 plasma is much more effective than either O_2 or Ar plasmas [3-5]. Secondly, it has been established that the etching effect caused by N_2 or Ar plasmas is substantially less, even negligible, compared to that of an O_2 plasma [6]. The ablation of materials during plasma processing not only results in a loss of polymer film thickness, it also increases the substrate surface roughness. Finally, O_2 is known as a radical quencher, and excessive presence of O_2 in a coating chamber may inhibit polymerization of the monomer mixture.

To determine the effects of the plasmas, we first collected the XPS survey spectra to examine the elements present in the PML surfaces both before and after plasma treatments. The as-prepared PML surface contained only C and O elements, which remained unchanged after Ar plasma exposure, regardless of the treatment conditions. Upon N_2 plasma exposure, a small amount of N was detected. The concentration of the incorporated N increased with both the plasma power and the treatment time, reaching about 2% at powers of 500 W for 5 minutes.

To obtain a more detailed chemical structure of each element, we plotted in Figure 2 the high-resolution C_{1s} spectra of the PML surface after treatments with Ar (2a) and N_2 (2b) plasmas. The spectra were normalized with respect to the C-C peak. The as-prepared PML surface contained three distinct chemical structures: C-C (284.8 eV), C-O (286.5 eV), and O=C-O (289.0 eV) [6]. The relative concentrations of C-O and O=C-O groups decreased upon exposure to both Ar and N_2 plasmas. The loss increased with increasing the plasma power and the treatment time (Figure 2b), and it was more pronounced in the case of N_2 than Ar. Also observed from these spectra was a gradual formation of a new component having binding energy close to 288 eV, which can be attributed to C=O.

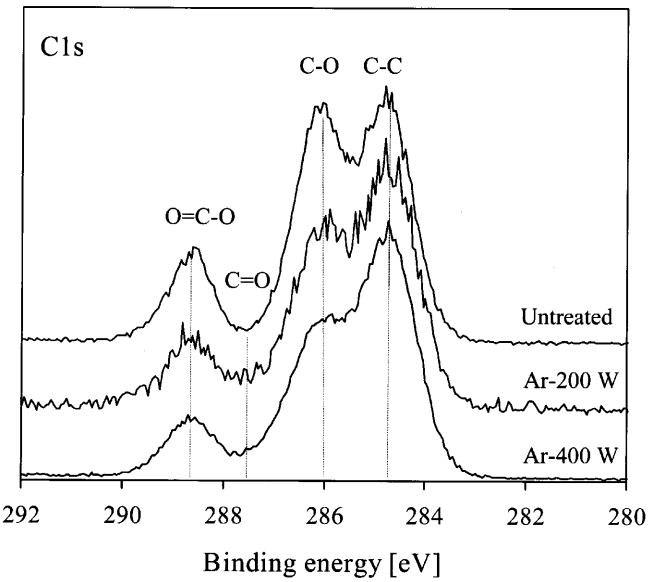

Figure 2a. C1s spectra of Ar plasma-treated PML surfaces.

The very low concentration of the nitrogen on the surface resulted in a very poor N spectra (Figure 3). The N_{1s} peak is centered at about 399.5 eV for all the samples, which most likely corresponds to an amide (NH-C=O) structure [7]. After remote plasma treatment at 500 W for 5 minutes, only 2% of atomic N was incorporated into the surface. This is significantly less than the N incorporated by an in-glow RF (13.56 MHz) plasma treatment, which resulted in an 8% uptake within 1 minute at a power of 50 W.

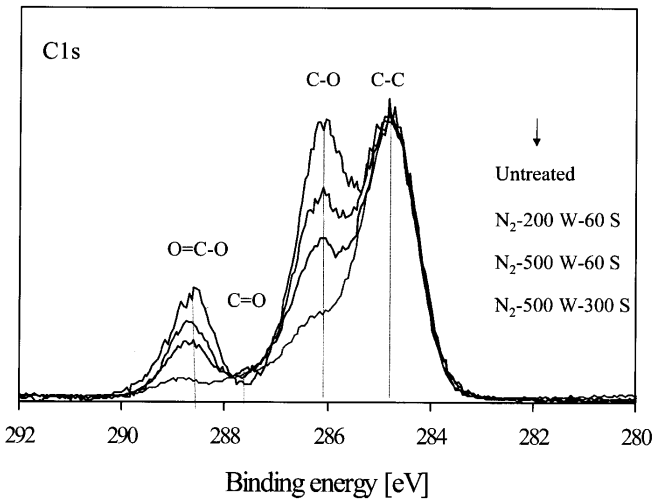

Figure 2b. C1s spectra of N_2 plasma-treated PML surfaces.

These XPS findings show that the destruction of the initial O=C-O and C-O groups is by far the major chemical effect occurring on the PML surface. The creation of new functional groups and incorporation of new atoms proceeded very slowly. A similar in-situ study performed on the PET surface showed similar effects.

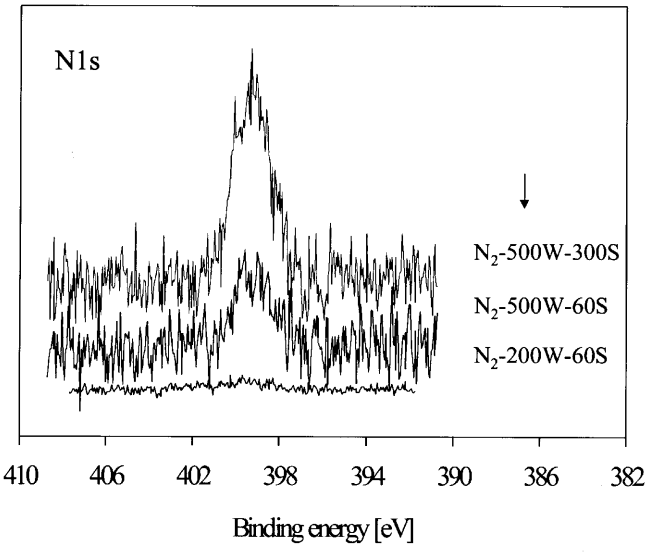

Figure 3. N_{1s} spectra of N_2 plasma-treated PML surfaces.

After XPS spectral acquisition, the sample was removed from the reactor and the water contact angle (WCA) was measured using a goniometer. The results are plotted in Figure 4. The water contact angle remained basically unchanged after Ar plasma exposure, but it decreased from 64° to 55° after exposure to the N_2 plasma. In both cases, no variation was observed with increasing the treatment power. By extending the N_2 plasma treatment time from 1 minute to 5 minutes at 500 W, the contact angle further decreased to 48°. However, even this value was significantly higher than the 33° attained by the in-glow RF plasma treatment.

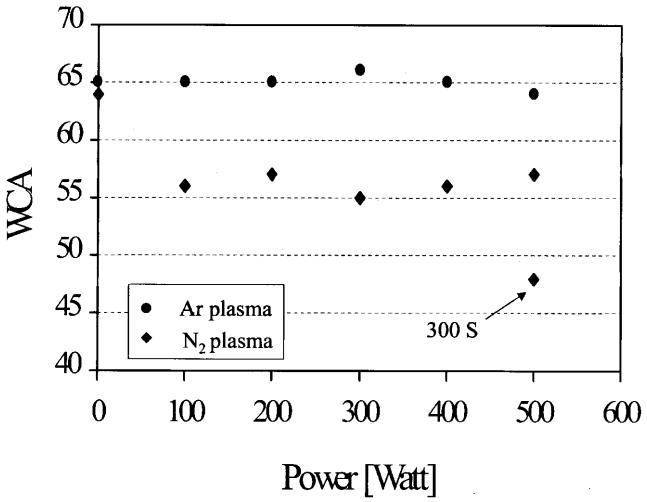

Figure 4. Effect of plasma treatment power on the contact angle of water on PML surfaces.

The adhesion of sputtered Ag to the PML surfaces after plasma treatment was evaluated according to the standard tape test procedure [ASTM D3359-93]. To make comparisons between the N_2 and Ar treatments, we increased the sputtered film thickness so that tape test results could be clearly distinguished. We found that for a 500 Å film , the Ag did not pull from the N_2 plasma-treated surfaces but sections consistently pulled on the untreated and Ar plasma-exposed surfaces. The improved adhesion of Ag to N_2- over Ar-treated surfaces is also observed for the PML samples treated in our RF plasma apparatus. Similar findings have been reported for several other polymeric systems [3-5]. These findings suggest that both the incorporated nitrogen and the improved surface energy contribute to the improved Ag/PML adhesion.

XPS analysis of the tape-pulled Ag/PML interface showed very strong Ag and weak C and O signal. Detailed analysis of the C_{1s} peak revealed that the carbon originates from contamination by adventitious hydrocarbon, but not from the PML coating. The contamination may have been introduced by the short atmospheric exposure of the peeled Ag interface. This measurement clearly indicated that the failure occurred at the Ag/PML interface.

SUMMARY

We studied the effectiveness of plasma treatment on the activation of acrylic-based Polymer Multilayer coating surface. In-situ XPS measurements indicated that plasma exposure results in the destruction of the initial C-O and O=C-O groups in the film. The effect was much more pronounced for N_2 than

for Ar plasmas, and increased with both the plasma power and treatment time. A small amount of nitrogen atoms were incorporated into the surface after nitrogen plasma treatment. In-situ sputter-deposited Ag films exhibited enhanced adhesion to surfaces treated with N_2–plasma compared to Ar-plasma, which also correlated well with the change of surface energy indicated by the water contact angle measurements.

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REFERENCES

1. J.D. Affinito*, S. Eufinger, M.E. Gross, G.L. Graff and P. M. Martin, "Comparison of Surface Treatments of PET and PML", SVC, Boston, 1997.

2. J.D. Affinito, U.S. Patent #5,260,095, "Vacuum Deposition and Curing of Liquid Monomers", (September 11, 1995).

3. L.J. Gereneser, "An X-ray Photoemission Spectroscopy Study of Chemical Interactions at Silver/Plasma Modified Polyethylene Interfaces: Correlation with Adhesion", J. Vac. Sci. Technol, A6 (5), 2897 (1988).

4. M.K. Shi, A. Selmani, L. Martinu, E. Sacher, M.R. Wertheimer and A. Yelon, "Fluoropolymer Surface Modification for Enhanced Evaporated Metal Adhesion", J. Adhesion Sci. Technol, 8, 1129 (1994).

5. L. Martinu, "Plasma Treatments and Deposition of Polymers", Italy, 1996.

6. H. Yasuda, "Plasma Polymerization", Academic Press, New York, 1985.

7. G. Beamson and D. Briggs, "High Resolution XPS of Organic Polymers", John Wiley & Sons, New York, 1995.