JOURNAL OF MATERIALS SCIENCE **40** (2005) 3535–3538 LETTERS

Influence of argon plasma pretreatment on properties of liquid crystal polymer

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Liquid crystal polymer (LCP) based on polyester or polyesteramide is a widely used polymer for Molded Interconnect Devices (MIDs) because of the high temperature resistance, chemical stability, excellent dimensional stability and assembly process compatibility [1, 2]. For MID technology it is important to get metal layers on LCP not only with constant thickness and smooth surface, but also with sufficiently high adhesion strength. However, deposition and patterning of copper with high reliability and reproducibility on dielectric substrates is still a challenging task. Since adhesion between polymers and metal layers is often poor due to chemical inertness of many polymer surfaces, surface modification of the polymer is necessary before metallization.

Plasma pretreatment is an important industrial process for modifying polymer surfaces. It avoids problems caused by wet chemical pretreatment such as residual solvent on the surface and swelling of the substrate. By plasma pretreatment almost all polymer surfaces can be modified by the excited species occurring in the plasma. Furthermore, plasma pretreatment is also an excellent method of adhesion improvement in deposition of metal layers [3–6]. For example, plasma pretreatment with mixtures of helium and 2% ammonia enhances adhesion of polypropylene (PP) to thermal evaporated aluminum [3]. The adhesion between polyphenylensulfide (PPS) and a sputtered copper layer is improved by air plasma pretreatment [6]. However, adhesion strength strongly depends on the specific type of polymer and metal used [7]. Therefore, it is necessary to investigate the influence of plasma pretreatment on the properties of LCP.

In this work, argon plasma pretreatment of LCP substrates was performed before a Cu/Cr layer was sputtered onto the surface. The behavior related to the plasma pretreatment is presented. Furthermore, adhesion strength between the Cu/Cr layer and LCP substrate is evaluated dependent on the plasma pretreatment time.

The Leybold Z400 sputter device used for metal layer deposition consists of a vacuum chamber evacuated by a turbo molecular pump. The sample holder was connected to a radio frequency power generator (13.56 MHz). The 99.99% pure Cu target was mounted on a water-cooled Cu plate.

Molded tensile bars made from commercially available LCP (Vectra E820i from Ticona GmbH, Frankfurt am Main, Germany) were used as substrates. Prior to the deposition process, the substrate was ultrasonically cleaned in an aqueous cleaning agent (Mucasol from Merz Consumer Care GmbH, Frankfurt am Main, Germany) at 50 °C for 3 min and rinsed in deionized water afterwards. After pumping the vacuum chamber to a pressure of about 3×10^{-3} Pa, argon was introduced and the pressure was maintained in the range of 0.6–0.9 Pa. The plasma pretreatment was done by application of Rf power (80–120 W). Before a copper layer with a thickness of about 1.4 μm was sputtered on the substrate, a thin chromium layer of less than 100 nm was deposited as an interlayer. The deposition rate of copper and chromium were about 10 and 3 μm/hr, respectively.

To evaluate the adhesion improvement, pull-off tests were performed in a Dage series 4000 test equipment shown in [8]. Therefore, circles with a diameter of 2.3 mm were patterned in the metal layer by laser ablation using a frequency tripled Nd:YAG laser. Afterwards metal cylinders were bonded onto the test areas by adhesive. After curing, the cylinders were pulled off with a velocity of 0.7 mm/s. The adhesion strength values were based on 25 individual measurements each.

The weight loss of LCP during plasma pretreatment was registered by a balance with sensitivity of 1×10^{-5} g. The chemical bonding state of the LCP surface was characterized by Fourier transform infrared spectroscopy (FT-IR) (Vector 22 from Bruker Optik GmbH, Ettlingen, Germany) with an attenuated total reflection (ATR) unit. The morphologies of specimens were characterized by scanning electron microscopy (TESCAN 5130 from EOS GmbH, Dortmund, Germany). The surface roughness was investigated with a mechanical profilometer (ATOS Surfascan 3CS from Atos GmbH, Pfungstadt, Germany). The roughness average value was based on three individual measurements. A mass spectrometer (HPQ2-S, from MKS instruments Deutschland GmbH, Dresden, Germany) was used to monitor the water partial pressure during the plasma pretreatment.

Plasma pretreatment increases the surface temperature of the processed LCP substrates. Fig. 1 presents the temperature rise of LCP bulk material dependence on argon plasma pretreatment time. The average temperature was about 110 °C after 15 min plasma

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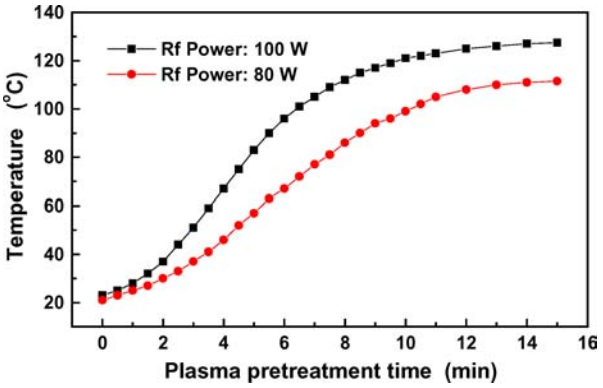

Figure 1 Substrate temperature (LCP) dependence on argon plasma pretreatment time.

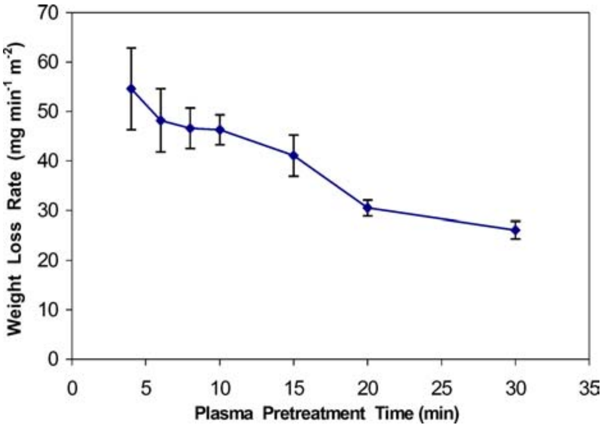

Figure 2 Weight loss rate of LCP dependence on argon plasma pretreatment time (Rf power: 80 W).

pretreatment, when an Rf power of 80 W was applied. With the higher power of 100 W, the temperature increased up to 130 °C after 15 min pretreatment time. Because of the high temperature resistance of LCP, these processing temperatures are not critical for the polymer.

Fig. 2 shows the weight loss rate of LCP substrates exposed to argon plasma environment for different times. During plasma pretreatment, no significant change of the water partial pressure in the vacuum chamber was observed by a mass spectrometer. As known generally, polymer surfaces are often covered with some ubiquitous contamination layers due to additives in the commercial polymer (e.g., lubricant, mould release, anti-blocking agent), which is harmful for adhesion. The initial weight loss rate was about 55 mg $\cdot$ min^{-1} $\cdot$m^{-2} during the plasma pretreatment due to the relatively fast contaminant removing process. Compared with possible contamination layers, it is hard to remove bulk LCP by the plasma etching process. Thus, the weight loss rate slowed down to 26 mg $\cdot$ min^{-1} $\cdot$ m^{-2} after 30 min plasma exposure.

The topographies of untreated and plasma pretreated LCP surfaces are given in Fig. 3. Before plasma exposure, the surface was smooth except where the surface is disturbed by the filler materials contained in the polymer matrix (Fig. 3a). As is known, plasma pretreatment may not only clean the polymer surface but can also etch the surface. Since amorphous polymer is etched faster than either its crystalline phase or inorganic filler materials [4], a surface micro roughness can be generated as shown in Fig. 3b. However, too long plasma pretreatment time gives enhanced scission of chemical bonds of the polymer and formation of low-molecular-weight species. In this experiment, uncovered filler materials of the polymer matrix were observed on the LCP surface after 30 min plasma pretreatment as shown in Fig. 3c.

TABLE I Roughness parameters R_a and R_z of LCP substrate before and after plasma pretreatment for different times

	LCP as molded	After 8 min	After 15 min	After 30 min
R_a (μm)	0.4	0.5	0.6	0.8
R_z (μm)	3.2	4.2	4.6	5.2

The roughness of the LCP surface is presented in Table I. Two parameters R_a and R_z, which are frequently used to describe the roughness of surfaces, were used to characterize the roughness profile. R_a is the arithmetic mean roughness and R_z is the ten-point mean roughness. The surface roughness of LCP slightly increased with plasma pretreatment time. Nevertheless, plasma pretreatment results in smoother surfaces as compared to chemical pretreatment [8].

Fig. 4 gives ATR FT-IR spectra of an LCP substrate with and without argon plasma pretreatment. The C=O stretching vibration of the carboxyl and ester groups of the polymer is found near 1730 cm^{-1}. The absorption peak around 1500 cm^{-1} indicates the benzene ring of the aromatic polyester, the vibration of the C—O bond is found at about 1100 cm^{-1}. Comparing the spectra shown in Fig. 4, no new absorption peak appeared after plasma pretreatment. In order to evaluate the changes in the peak area based on the untreated samples we took the absorption peak of the benzene ring at 1500 cm^{-1} as reference. The results presented in Table II show the area of the absorption peak at 1730 cm^{-1} increases slightly and at 1100 cm^{-1}decreases slightly after plasma pretreatment of the LCP.

Fig. 5 shows the surface top view and a cross-sectional view of a Cu/Cr layer on an argon plasma pretreated LCP substrate. The surface is very smooth corresponding to the original structure as given in Fig. 3b. No cracks, voids or bubbles were observed at the metal/polymer interface (Fig. 5b).

The dependence of adhesion strength of PVD Cu/Cr layers on LCP substrates on plasma pretreatment time is given in Fig. 6. As expected, the samples without plasma pretreatment showed the lowest adhesion due to possible surface contaminants, which affect the adhesion of the metal layer on the LCP. As discussed above,

TABLE II Change in the area of each absorption peak related to the peak area at 1500 cm^{-1}

Wavenumber (cm^{-1})	Without argon plasma pretreatment	With argon plasma pretreatment
1730 (C=O)	4.90	5.33
1500 (benzene ring)	1.00	1.00
1100 (C—O)	1.23	1.05

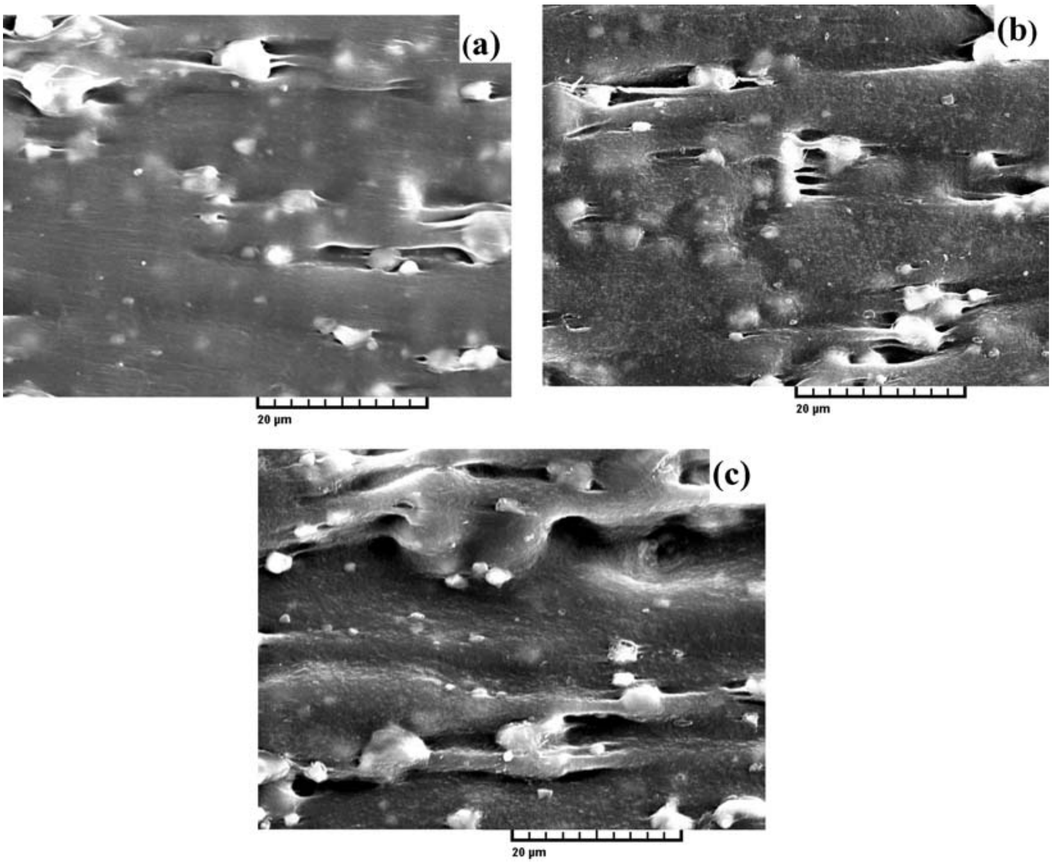

Figure 3 SEM micrographs of LCP before (a), after 8 min plasma pretreatment (b) and after 30 min plasma pretreatment (c).

plasma pretreatment can not only clean the surface but also create micro-roughness, which will improve mechanical interlocking of the sputtered layer and increase the area available for chemical interactions. Chemical bonding between oxygen containing functional groups of the polymer and the chromium interlayer is also a possible mechanism responsible for good adhesion after the plasma pretreatment. However, too excessive plasma pretreatment gives poor adhesion due to the generation of low-molecular-weight fragments by enhanced scission of chemical bonds of the polymer matrix.

Increasing the plasma pretreatment time of LCP substrate gives an enhanced adhesion of sputtered Cu/Cr layers until a maximum of adhesion is achieved. Further processing time in argon plasma gives decreasing adhesion values. Thus, the optimum plasma pretreatment can not only clean the surface and micro-roughen

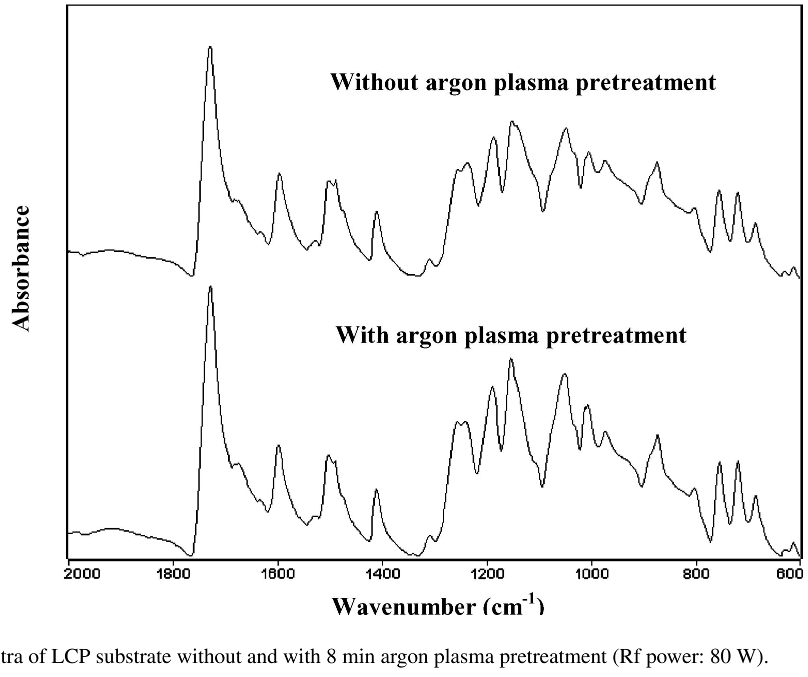

Figure 4 ATR FT-IR spectra of LCP substrate without and with 8 min argon plasma pretreatment (Rf power: 80 W).

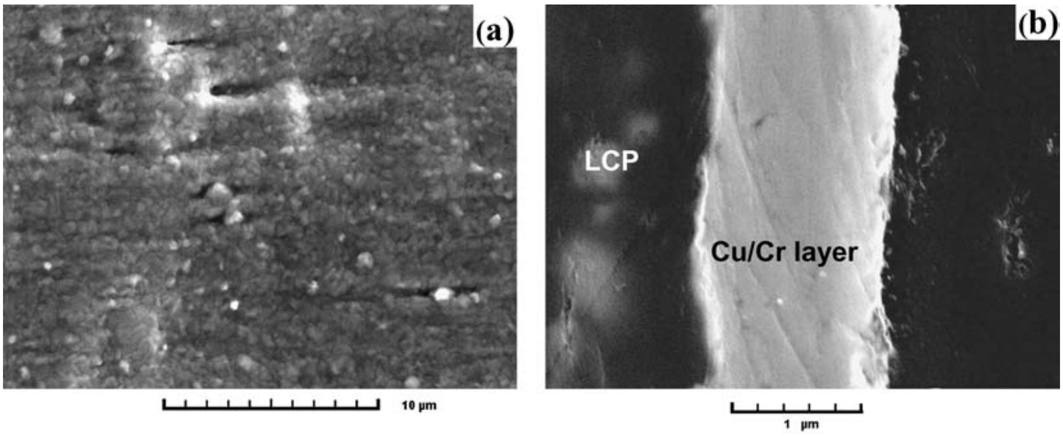

Figure 5 SEM micrographs of PVD Cu/Cr layer on LCP pretreated by argon plasma: Cu surface (a) and cross-section (b).

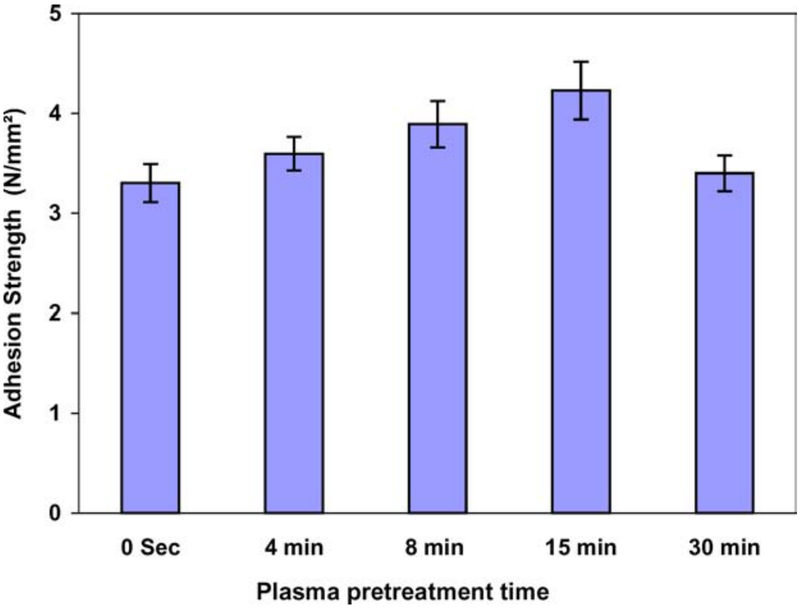

Figure 6 Adhesion strength of Cu/Cr PVD layers on LCP for different plasma pretreatment times.

the surface but also give chemical modifications, which promotes better adhesion. The temperature rise caused by argon plasma pretreatment is not critical for LCP substrates used in MID technology.

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Received 4 January
and accepted 4 January 2005