Surface Modification of Polyimide Films by Argon Plasma for Copper Metallization on Microelectronic Flex Substrates

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Received 4 August 2003; accepted 21 March 2005
DOI 10.1002/app.22545
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Surface modification of polyimide films such as Kapton E(N) and Upilex S by argon plasma was investigated because of the enhanced adhesive strength with sputtered copper. Peel tests demonstrated this improvement, with a peel strength of 0.7 and 1.2 g/mm for unmodified Kapton E(N) and Upilex S, respectively, and 110.3 and 98 g/mm for argon plasma–modified Kapton E(N) and Upilex S, respectively, in certain plasma conditions. This study showed that the enhanced adhesive strength of polyimide films with sputtered copper by argon plasma was strongly affected by the surface characteristics such as surface morphology and surface energy of polyimide films. Atomic force microscopy and the sessile drop method indicated that the surface roughness and surface energy of the polyimide films were greatly increased by argon plasma, resulting in highly increased peel strength of the polyimide films with sputtered copper. It was observed in electron spectroscopy for chemical analysis (ESCA) that the increased surface energy of the polyimide films from argon plasma was a result of more of the surface being composed of O and N and of the increased number of C—O, C═O, and C—N chemical bonds. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 744–755, 2006

Key words: adhesion; surface modification; argon plasma; atomic force miscroscopy (AFM); ESCA/XPS

INTRODUCTION

Because the needs of the electronics industry increase day by day, there is a never-ending demand for ever greater quality and strength. Therefore, high-density electronic packages for portable electronics such as notebook computers, cellular phones, and personal digital assistants are needed. For various integrated circuits (ICs) used in liquid crystal display modules, a flexible design package is needed. The tape carrier package (TCP) is the main package for such ICs so far. To meet the requirements of the electronics industry for high strength, packages must continue to be of high density. The chip-on-film (COF) package uses flip chip bonding to replace tape-automated bonding for TCPs in order to provide high-density chip connections to flex substrates.[1] Polyimide is the base substrate material of flex substrates. A three-layer type of flex substrate has been used for TCP. The three layers are Cu (18 μm), adhesive (12 μm), and polyimide (75 μm). For the three-layer-flex substrate a Cu metal layer was laminated with polyimide after adhesive was applied and partially cured. However, the adhesive layer has certain disadvantages: (1) failures can occur during higher-temperature cycling, (2) problems can occur during hole drilling because of adhesive smearing, and (3) it is difficult to remove the adhesive from the copper after etching.[1] For finer patterning, a thick copper metal layer of about 18 μm can be a handicap because of underetching during the etching process. These problems can be partially avoided by using an adhesiveless flexible laminate and a thin copper film. A thin film of flexible copper (8–12 μm) with polyimide (25–38μm) is such an adhesiveless laminate. For a two-layer type of flex substrate for COF, Cu metal layers are coated onto polyimide by electrolytic plating, evaporation, or sputtering. Proper adhesion between the copper and the polyimide film has to be assured even without an adhesion promoter (an adhesive). Several studies found that surface treatment of polyimide was needed to enhance adhesive strength with copper.[2–9]

Baglin[10–11] summarized the factors that affect the adhesion of a thin film coating to a substrate: interface chemistry, interface polarization by electrostatic attraction, differential thermal expansion, interface toughness, stress in the film, and film thickness. In this work the effects of interface chemistry and interface morphology on the adhesion of sputtered copper to

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Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC-92-2216-E-035-005.

Journal of Applied Polymer Science, Vol. 99, 744–755 (2006)
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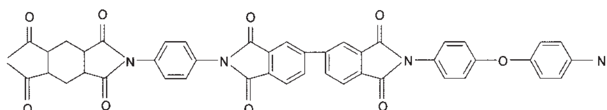

Figure 1 Chemical structure of the DuPont Kapton E(N) polyimide film.

polyimide were investigated. The interface polarization effects of electrostatic attraction did not influence the adherence of sputtered copper to polyimide film. Differential thermal expansion effects were not investigated in this study. To eliminate stress and film thickness as variables in the present study, consistent copper-sputtering procedures were used in all sample preparations.

Interface chemistry effects can play a key role in adhesion strength.[12–13] The atomic composition and functional groups of plasma polymers, which can be determined by electron spectroscopy for chemical analysis (ESCA), are helpful in characterizing the interfacial chemistry between sputtered copper and plasma-modified polyimide. The mechanical interlocking between sputtered copper and plasma-modified polyimide also was considered to affect the adhesive strength of sputtered copper to polyimide. Atomic force microscopy (AFM) was used to characterize the surface morphology of plasma-modified polyimide.

Menezes et al.[15] reported that a contact angle measurement technique—measuring the contact angle of a copper cluster on polyimide—could be used to estimate the interfacial energy between copper and polyimide.. However, this contact angle is not easily determined for industrial applications. However, the surface energy of polyimide film is easily measured. This provides a way to do a fast check of the surface energy, which can then be quickly related to the interfacial strength of the adhesion with copper. In this study, the surface energy of polyimide film was calculated on the basis of measurement of the contact angles of the surface tension of three different liquids on polyimide film. How the surface energy of polyimide film affects the adhesion strength of copper and whether these effects are related to the chemical composition of and chemical bonds in polyimide film also were investigated. The key roles that chemical bonds such as C—O, C═O, and C—N play in enhancing the adhesion strength of copper to polyimide film modified by argon plasma also were studied.

EXPERIMENTAL

Materials

Two polyimide films, Kapton E(N), from Du Pont (Wilmington, DE), and Upilex S, from Ube (Yamaguchi, Japan), were used in this study. The chemical structures of Kapton E(N) and Upilex S are shown in Figures 1 and 2, respectively. The particular chemical bonds of polyimide film considered in this study were the C—C/C—H, C—O, C═O, and C—N bonds. Kapton E(N) contains the chemical bonds C—C/C—H, C—O, C═O, and C—N; and Upilex S contains the chemical bonds C—C/C—H, C═O, and C—N. Upilex S does not have C—O chemical bonds. To avoid contamination of the polyimides that would affect the adhesion strength of copper to polyimide, the polyimide films were precleaned by wiping their surface 3–4 times with a Kimwipe moistened with 2-propanol.

Plasma modification

Plasma modification of the Kapton E(N) and Upilex S polyimide films was carried out in a low-temperature glow discharge plasma chamber. Argon monomer was fed into the reactor at a flow rate of 10 sccm. The other plasma settings were: 200 W of power, chamber pressure of 60 mtorr, and a duration of plasma modification of between 0.5 and 5 min. The pressure of the reactor chamber was decreased to less than 5 mtorr with a pressure leak rate of less than 0.1 mtorr/min, that is, the leak flow rate of air in the chamber was less than 1% of the monomer flow rate. As the chamber pressure stabilized, radio frequency (RF) power was applied to create argon plasma. After plasma modification, the RF power was turned off. The gases were pumped out and the system pressure returned to background pressure (around 5 mtorr). The vacuum was broken by opening a valve to admit air into the chamber. Once the chamber pressure reached atmospheric pressure (typically within 5 min), the plasma-modified Kapton E(N) and Upilex S were taken out for further treatment and testing.

Plasma-sputtered copper

After plasma modification, Kapton E(N) and Upilex S were further coated with copper by plasma sputtering at an Ar flow rate of 10 sccm, with sputtering power of 800 W, a rotary speed of 900 rpm, and a sputtering time of 8 min. Prior to the application of the copper coating to the polyimide, the copper target was pre-

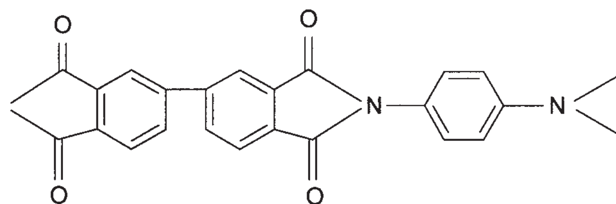

Figure 2 Chemical structure of the Ube Upilex S polyimide film.

cleaned by argon plasma sputtering for 5 min. Then the copper coating was applied to polyimide as argon plasma, which was created by argon gas fed in and RF power applied to sputter copper atoms from the copper source at the cathode and on to the polyimide at the anode. Typical thickness of the sputtered copper in this study is 8 μm.

Peel test

An Instron 4400 tensile tester was used to determine the interfacial strength of Cu to polyimide film by 90° L-shaped peeling at a velocity of 50 mm/min. After being sputtered on polyimide film, a 3-mm copper strip was etched. Peel strength (g/mm) was recorded as the measured force (g) divided by the width of the copper strip (mm).

Surface morphology observed by AFM

Atomic force microscopy (AFM) was used to investigate the surface morphology of Kapton E(N) and Upilex S. A Digital Instruments NS4/D3100CL Multi-Mode apparatus was used to determine the surface roughness of Kapton E(N) and Upilex S. A force constant of 40 N/m, an operation voltage of 0.6–0.7 V, and a frequency of 325 kHz were applied through the silicon nitride of the tip to scan the sample surfaces. The data on Kapton E(N) and Ube-Upilex S roughness determined by AFM were analyzed using a computer. Two parameters, mean square root of roughness (Rms) and average roughness (Ra), were calculated by eqs. (1) and (2)

$$\mathrm{Rms} = \sqrt{\frac{\sum_{N=1}^{N}(Zn - \bar{Z})^2}{N-1}} \tag{1}$$

$$\mathrm{Ra(average)} = \sum_{N=1}^{N}\frac{|Zn - \bar{Z}|}{N} \tag{2}$$

where Rms is the square root of the arithmetic mean of the square of the absolute deviation from the average height of roughness and Ra is the arithmetic mean of the absolute deviation from the average height of roughness.

Surface energy

For a pure liquid on a smooth, homogeneous, rigid isotropic surface, the contact angle is related to surface energy through Young's equation

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos\theta \tag{3}$$

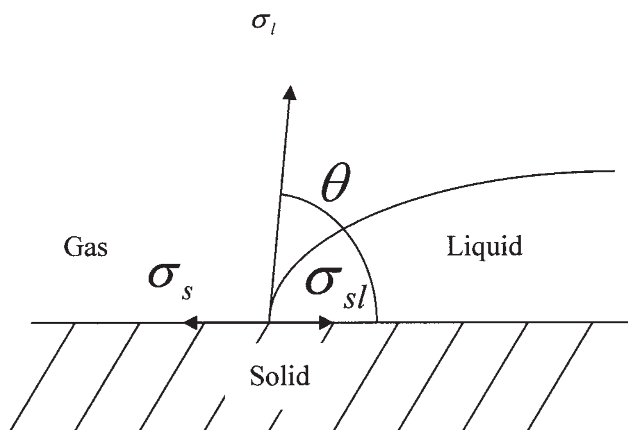

Figure 3 Contact angle, θ of liquid drop on solid.

where σ_s is the surface energy of the solid, σ_{sl} is the interfacial energy between the solid and the liquid, σ_l is the surface tension of the liquid, and θ is the contact angle (as shown in Fig. 3) as measured by the sessile drop method. σ_s, σ_l, and σ_{sl} can be written as

$$\sigma_s = \sigma_s^{\,d} + \sigma_s^{\,p} \tag{4}$$

$$\sigma_l = \sigma_l^{\,d} + \sigma_l^{\,p} \tag{5}$$

$$\sigma_{sl} = \sigma_s{}' + \sigma_l - 2 \cdot \left(\sqrt{\sigma_s^{\,d} \cdot \sigma_l^{\,d}} + \sqrt{\sigma_s^{\,p}\sigma_l^{\,p}}\right) \tag{6}$$

where σ_s^d is the dispersed surface energy of the solid, σ_s^p is the polar surface energy of the solid, σ_l^d is the disperse surface tension of the liquid, and σ_l^p is the polar surface tension of the liquid.

From eqs. (3)–(6),

$$\cos\theta = f(\sigma_s,\sigma_s^{\,d},\sigma_l,\sigma_l^{\,d}) \tag{7}$$

The surface energy of polyimide films were calculated by measuring the contact angles of the surface tension of three liquids, deionized water, ethylene glycol, and diiodo methane, on polyimide. The dispersed surface tension and the polar surface tension were 18.7 and 53.6 mN/m, respectively, for deionized water; 29.3 and 18.2 mN/m, respectively, for ethylene glycol; and 49.5 and 1.3 mN/m, respectively, for diiodo methane.

ESCA analysis

Electron spectroscopy for chemical analysis (ESCA) has a high resolution for carbon, oxygen, and nitrogen. ESCA data were collected in both survey and high-resolution mode on a Thermo VG Scientific (Σ) probe and system equipped with a Al Kα source at 15 KV. Data were recorded at a 90° collecting angle resulting in an analysis depth of about 5 nm.

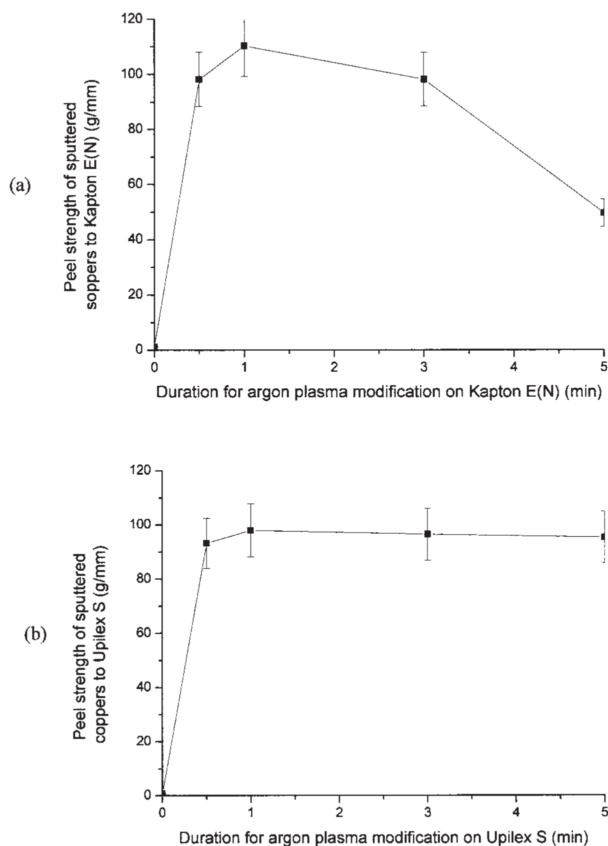

Figure 4 Peel strength of sputtered copper to (a) unmodified and argon plasma–modified Kapton E(N) and (b) unmodified and argon plasma–modified Upilex S plotted with various duration times for argon plasma modification of Kapton E(N) and Upilex S. The other plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

RESULTS AND DISCUSSION

Adhesion strength of sputtered copper to polyimide films

To enhance the adhesion of sputtered copper to polyimide films such as Kapton E(N) and Upilex S, argon gas was released into the plasma chamber in order to modify the surfaces of the polyimide films. The results for the peel strength of sputtered copper on unmodified and argon plasma–modified Kapton E(N) and Upilex S are shown in Figure 4(a,b). Figure 4(a,b) shows that the peel strength of sputtered copper on unmodified Kapton E(N) and Upilex S was 1.2 g/mm and 0.7 g/m, respectively. These values were much improved, to 49.6–110.3 and 93.2–98 g/mm, respectively, by argon plasma modification. Using optimal settings—a duration of 1 min for argon plasma modification, 200 W of power, 60 mtorr of pressure in the chamber, and an argon flow rate of 10 sccm—increased the peel strength of sputtered copper on Kapton E(N) and Upilex S to 110.3 and 98 g/mm, respectively, values 91.9 and 137.6 times higher, respectively, than the values for unmodified Kapton E(N) and Upilex S.

Inagaki et al.[2] reported that the adhesion of electroplated copper to polyimide film can be enhanced 2.3–2.4 times (44–46 g/mm) over that of unmodified polyimide (18.8 g/mm) by a combination of argon plasma treatment and silane coupling reactions with 2-cyanoethyltriethoxy silane and 3-cyanopropyltriethoxysilane on the surfaces of polyimide films (Kapton H films). Rozovskis et al.[3] reported that the adhesion of electroless coated copper to polyimide films can be enhanced by surface modification of polyimide using oxygen plasma treatment and chemical etching in alkaline solutions of permanganate. The adhesion of electroless coated copper to polyimide films showed the same increase to 60 g/mm. Ma et al.[4] found that nitrogen plasma can be used to make the adhesion of sputtered copper to polyimide films (Kapton H, HN, and Upilex R, S) by 2–3 times greater than that of unmodified polyimide film by plasma surface modification of polyimide films. The adhesion of sputtered copper to polyimide film modified by nitrogen plasma was as high as 40 g/mm. Egitto et al.[5] proposed that oxygen plasma could be used to enhance the adhesion of sputtered copper to polyimide film (Kapton H and Upilex S) by plasma surface modification of the film. The adhesion of sputtered copper to polyimide film modified by oxygen plasma was as high as 60 g/mm. Inagaki et al.[6] observed that Ar, N_2, NO, NO_2, O_2, CO, and CO_2 plasmas all can be used to improve the adhesion of evaporated copper to polyimide film (Kapton H). The adhesion of evaporated copper to polyimide film modified by Ar, N_2, NO, NO_2, O_2, CO, and CO_2 plasmas was as high as 29 g/mm. Inagaki et al.[7–9] also found that the adhesion of evaporated copper to polyimide film can be highly enhanced by plasma polymer deposition and plasma grafting of cyano compounds and vinylimidazole on the surfaces of polyimide films. The adhesion of evaporated copper to polyimide film modified by plasma polymer deposition and plasma grafting of cyano compounds and vinylimidazole was as high as 28 g/mm. The highest adhesive strength of copper to polyimide films reported by the above studies was 60 g/mm. In the present study the adhesive strength of sputtered copper to polyimide films modified by argon plasma at certain settings was 110.3 g/mm for Kapton E(N) and 98 g/mm for Upilex S. The results demonstrated that low-temperature argon plasma modification of polyimide films such as Kapton E(N) and Upilex S was an effective method of enhancing adhesive strength with sputtered copper.

Surface morphology of Kapton E(N) and Upilex S

The two-dimensional (top view) and three-dimensional AFM pictures of unmodified Kapton E(N) and

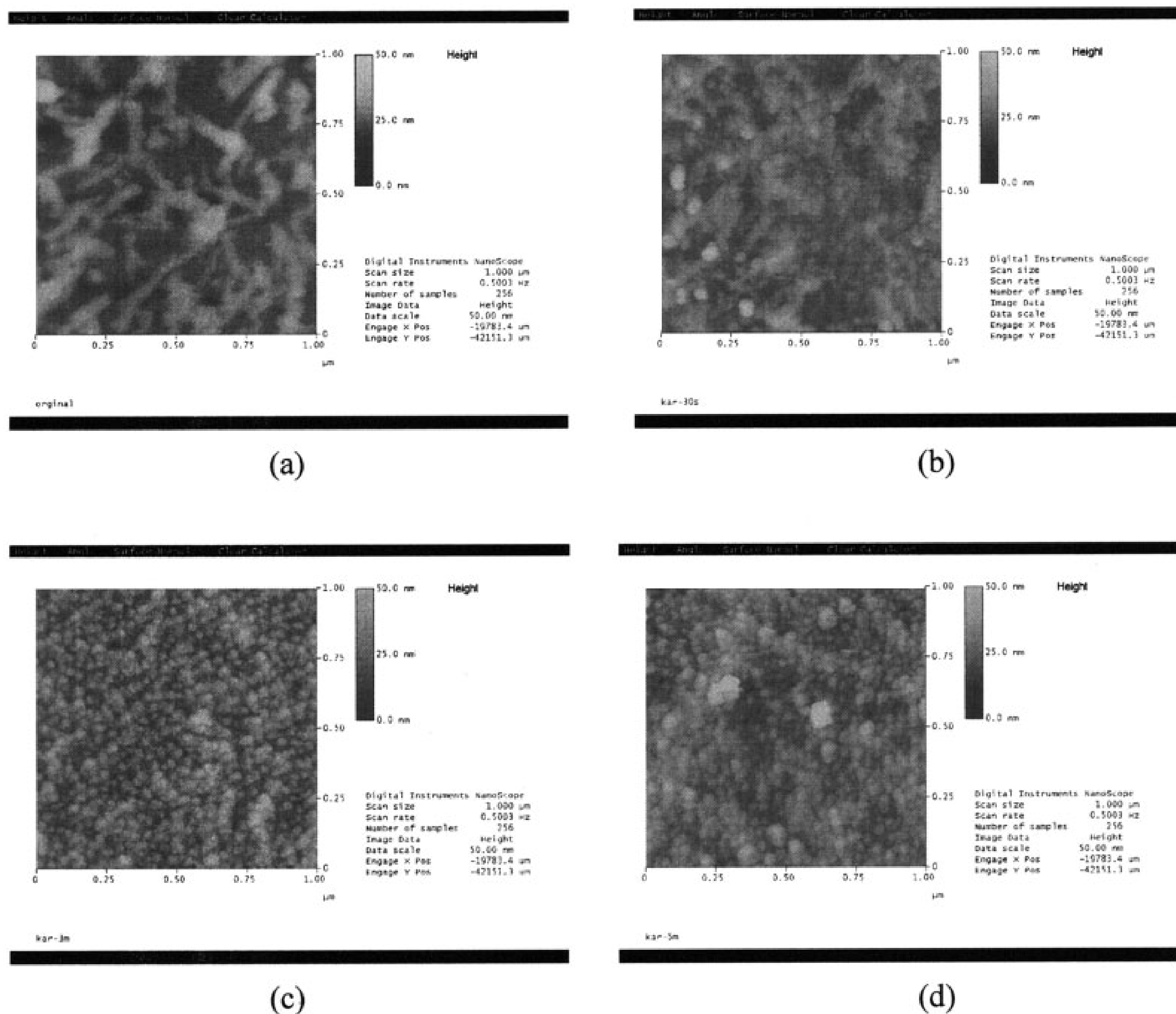

Figure 5 Two-dimensional AFM pictures of (a) unmodified Kapton E(N), (b) 0.5 min of argon plasma–modified Kapton E(N), (c) 1 min of argon plasma–modified Kapton E(N), and (d) 3 min of argon plasma–modified Kapton E(N). The other plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

argon plasma–modified Kapton E(N) for durations of 0.5, 1, 3, and 5 min are shown in Figures 5 and 6, respectively. Figure 5 indicates that argon plasma was used to modify the surfaces of Kapton E(N), referred to as crosslinking by activated species of inert gases (CASING), because much more crosslinked surfaces of Kapton E(N) were observed. Figure 6 shows that the surfaces of Kapton E(N) were roughened by applying argon plasma modification. When the optimal settings for argon plasma modification were used—duration of 1 min, 200 W of power, chamber pressure of 60 mtorr, and argon flow rate of 10 sccm—the most crosslinked and roughened surface of Kapton E(N) was established.

On the basis of the three-dimensional AFM pictures of unmodified Kapton E(N) and argon plasma–modified Kapton E(N) for durations of 0.5, 1, 3, and 5 min, the surface roughness of Kapton E(N) was calculated in order to interpret the roughened surfaces of Kapton E(N) by argon plasma modification. The surface roughness of unmodified Kapton E(N) was 2.964 nm for Rms and 3.679 nm for Ra, as shown in Figure 7. When argon plasma modification was applied to Kapton E(N) for 0.5 min, the surface roughness increased to 3.307 nm for Rms and 4.206 nm for Ra (Fig. 7). When argon plasma modification was applied to Kapton E(N) for 1 min, the surface roughness increased further to 5.748 nm for Rms and 7.131 nm for Ra (Fig. 7). When argon plasma modification was applied to Kapton E(N) for 3 min, the surface roughness decreased to 4.366 nm for Rms and 5.848 nm for Ra (Fig. 7). When argon plasma modification was applied to Kapton E(N) for 5 min, the surface roughness decreased further to 3.937 nm for Rms and 4.986 nm for

(b) (b)

(c) (d)

Figure 6 Three-dimensional AFM pictures of (a) unmodified Kapton E(N), (b) 0.5 min of argon plasma–modified Kapton E(N), (c) 1 min of argon plasma–modified Kapton E(N), and (d) 3 min of argon plasma–modified Kapton E(N). The other plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

Ra (Fig. 7). This shows that the surface roughness of Kapton E(N) increased with increases in duration of argon plasma modification from 0 (unmodified) to 1 min and decreased with increases in the duration of argon plasma modification from 1 to 5 min.

Figures 8 and 9 show the two- and three-dimensional AFM pictures of unmodified Upilex S and of Upilex S modified by argon plasma for durations of 0.5, 1, 3, and 5 min. Figure 8 indicates that argon plasma also was used to modify the surfaces of Upilex S by CASING, as surfaces of Upilex S that were much more crosslinked also were observed. Figure 9 shows the surfaces of Upilex S were roughened by argon plasma modification. When the optimal settings of argon plasma modification were used—duration of 1 min, power of 200 W, chamber pressure of 60 mtorr, and argon flow rate of 10 sccm—the most crosslinked and roughened surface of Upilex S was approached.

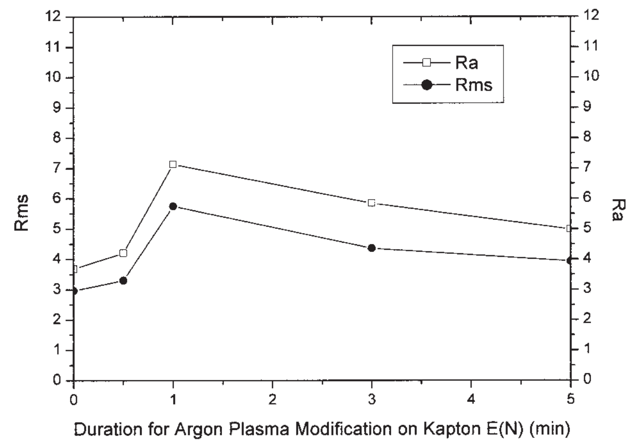

Figure 7 Surface roughness such as Rms and Ra of unmodified and argon plasma–modified Kapton E(N) plotted with various duration times for argon plasma modification of Kapton E(N). The other plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

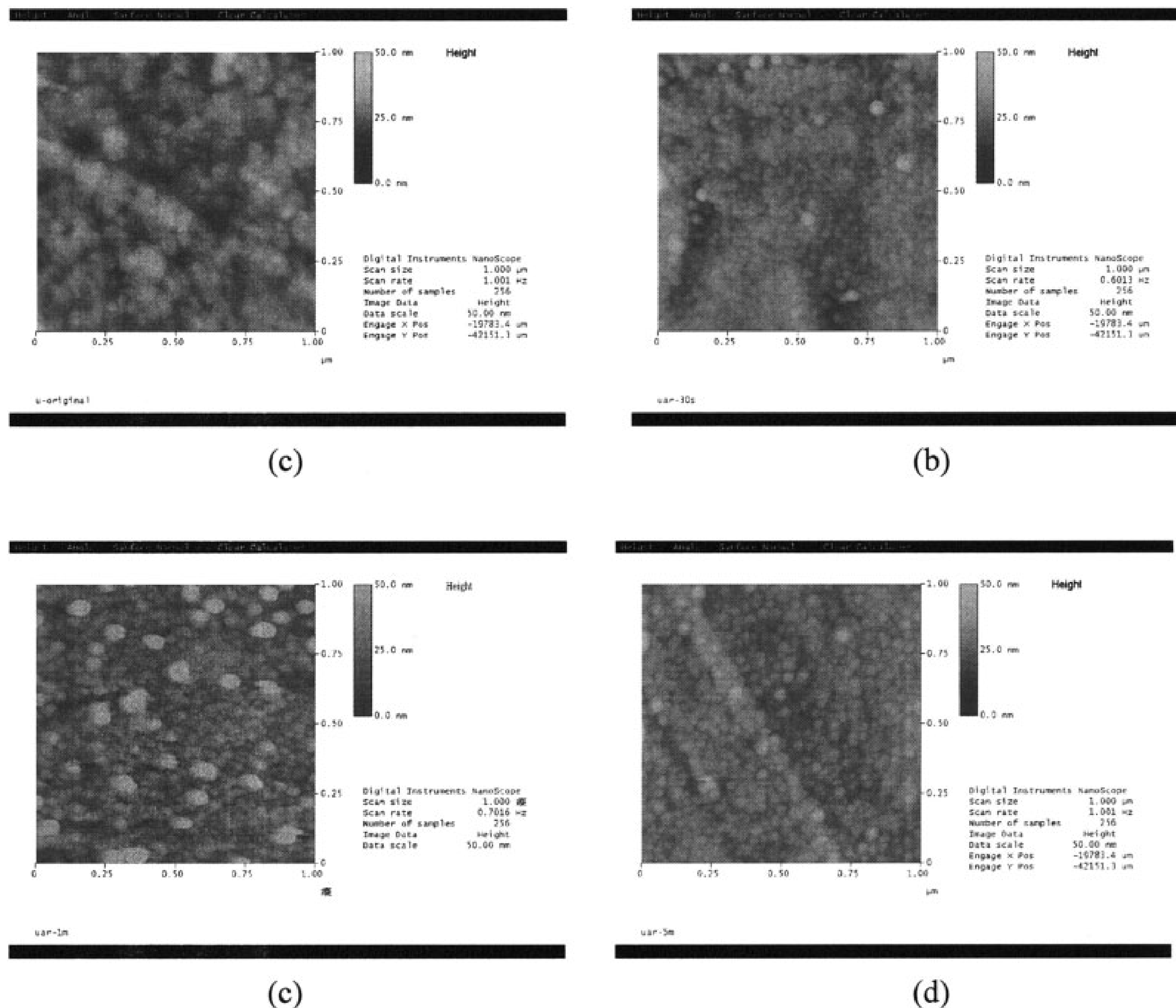

Figure 8 Two-dimensional AFM pictures of (a) unmodified Upilex S, (b) 0.5 min of argon plasma–modified Upilex S, (c) 1 min of argon plasma–modified Upilex S, and (d) 3 min of argon plasma–modified Upilex S. The other plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

On the basis of three-dimensional AFM pictures of unmodified Upilex S and of Upilex S modified by argon plasma for durations of 0.5, 1, 3, and 5 min, the surface roughness of Upilex S also was calculated in order to interpret the roughened surfaces of Upilex S by argon plasma modification. The surface roughness of unmodified Upilex S was 2.453 nm for Rms and 3.318 nm for Ra, as shown in Figure 10. When argon plasma modification was applied to Upilex S for 0.5 min, surface roughness increased to 3.21 nm for Rms and to 4.176 nm for Ra (Fig. 10). When argon plasma modification was applied to Upilex S for 1 min, the surface roughness increased further to 7.412 nm for Rms and 10.663 nm for Ra (Fig. 10). When argon plasma modification was applied to Upilex S for 3 and 5 min, surface roughness increased to 2.953 and 2.835 nm for Rms and 3.781 and 4.986 nm for Ra, respectively (Fig. 10).

According to the results shown in Figures 4, 7, and 10, the enhanced peel strength of sputtered copper on Kapton E(N) and Upilex S by argon plasma modification was strongly affected by the surface roughness of Kapton E(N) and Upilex S. The rougher surfaces of Kapton E(N) and Upilex S that had been modified by argon plasma showed higher peel strength with sputtered copper.

Surface energy of Kapton E(N) and Upilex S

Figure 11(a,b) shows the surface energy of unmodified and argon plasma–modified Kapton E(N) and Upilex S plotted with various durations of argon plasma modification. Figure 11(a) indicates that the total surface energy of unmodified Kapton E(N) was 51.58 mN/m, which increased to 70 mN/mm after 0.5 min

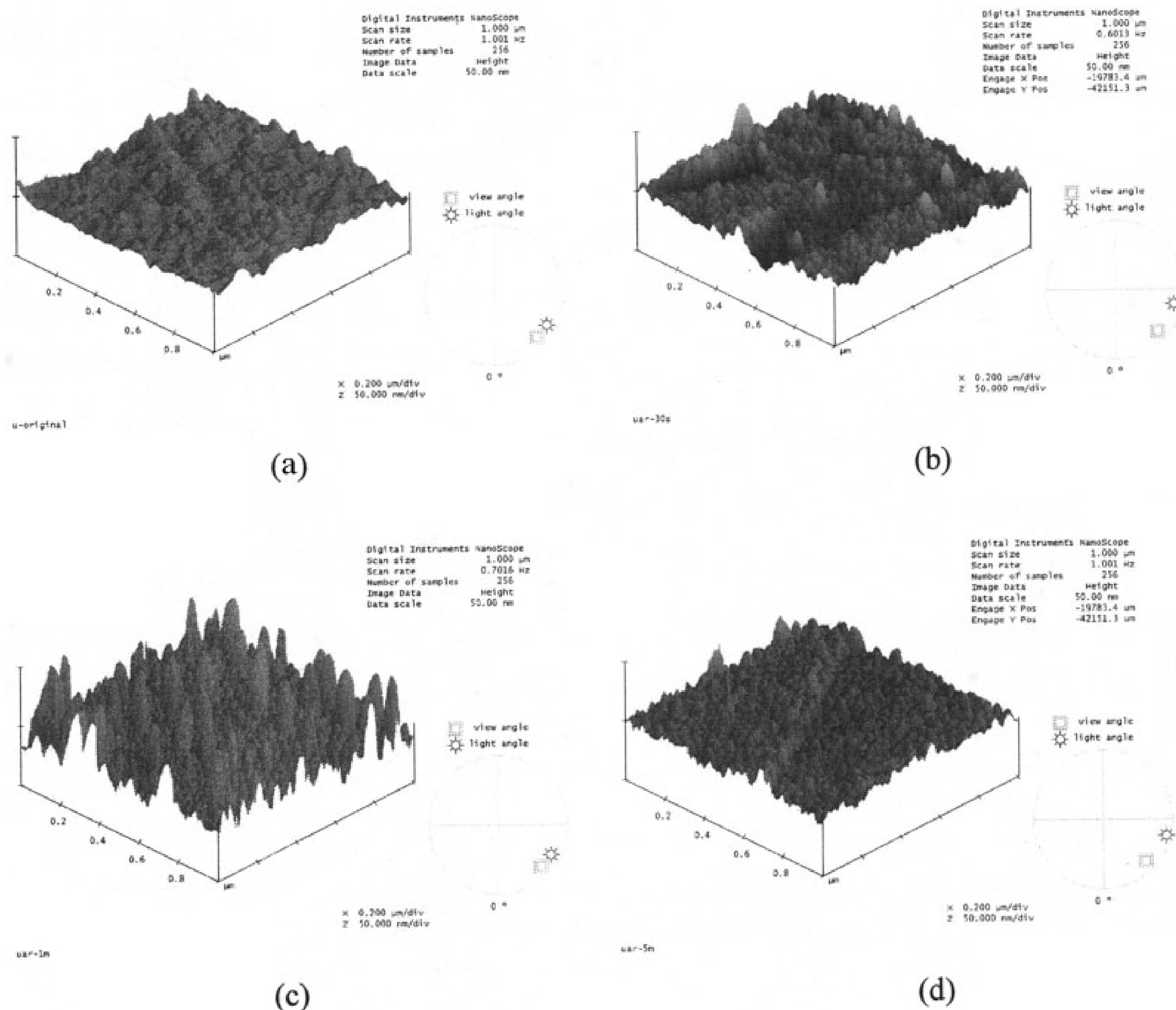

Figure 9 Three-dimensional AFM pictures of (a) unmodified Upilex S, (b) 0.5 min of argon plasma–modified Upilex S, (c) 1 min of argon plasma–modified Upilex S, and (d) 3 min of argon plasma–modified Upilex S. The other plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

of argon plasma modification. When the duration of argon plasma modification of Kapton E(N) was increased to 1 min, the total surface energy of Kapton E(N) was further increased to 75.2 mN/mm. No obvious additional increases in the total surface energy were found in Kapton E(N) modified by argon plasma for durations of 3 and 5 min, with a total surface energy of 73.5 and 73.7 mN/mm, respectively.

Figure 11(b) shows a trend for the total surface energy of Upilex S with various durations of argon plasma modification similar to that of Kapton E(N), shown in Figure 11(a). The total surface energy of unmodified Upilex S was 38.52 mN/m, which increased to 67.84 mN/mm with the application of 0.5 min of argon plasma modification. When the duration of argon plasma modification increased to 1 min, the total surface energy of Upilex S was further increased to 78.82 mN/mm. Further increases in the duration of argon plasma modification to 3 and 5 min did not show additional increases in the total surface energy of Upilex S, which was 75.13 and 73.7 mN/mm, respectively.

From Figure 11(a,b) it can be seen that the increased surface energy of Kapton E(N) and Upilex S by argon plasma modification was mainly the result of increases in the proportion of polar surface energy. Argon plasma modification of Kapton E(N) and Upilex S did not induce any obvious changes in the portions of dispersed surface energy.

On the basis of the results observed in Figures 4 and 11, the enhanced peel strength of sputtered copper on Kapton E(N) and Upilex S by argon plasma modification was strongly affected by the surface energy of Kapton E(N) and Upilex S. The much increased sur-

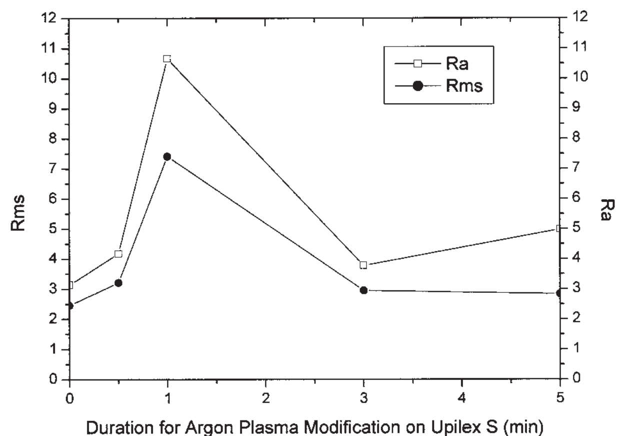

Figure 10 Surface roughness such as Rms and Ra of unmodified and argon plasma–modified Kapton E(N) plotted with various duration times for argon plasma modification of Upilex S. The other plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

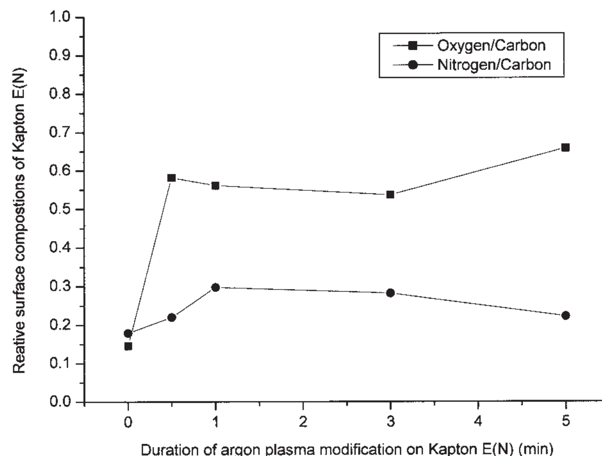

Figure 12 Relative surface compositions of unmodified and argon plasma–modified Kapton E(N). The plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

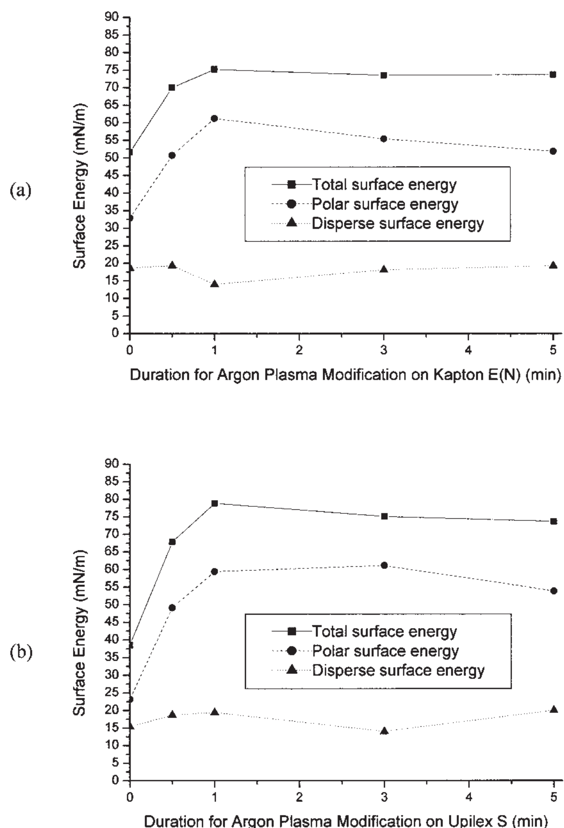

Figure 11 Surface energy of unmodified and argon plasma–modified (a) Kapton E(N) and (b) Upilex S plotted with various duration times for argon plasma modification of Kapton E(N) and Upilex S. The other plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

face energy of Kapton E(N) and Upilex S modified by argon plasma showed a greatly increased peel strength with sputtered copper.

Surface compositions of Kapton E(N) and Upilex S

The relative surface compositions of unmodified and argon plasma–modified Kapton E(N) and Upilex S are shown in Figures 12 and 13. Figure 12 indicates that the relative surface compositions of oxygen to carbon and of nitrogen to carbon on the surfaces of unmodified Kapton E(N) were 0.15 and 0.18, respectively. When argon plasma modification was applied to Kapton E(N) for 0.5 min, the relative surface compositions of oxygen to carbon and of nitrogen to carbon were

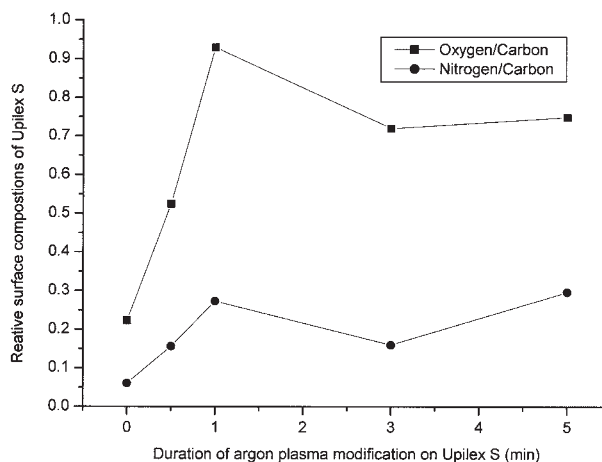

Figure 13 Relative surface compositions of unmodified and argon plasma–modified Upilex S. The plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

TABLE I
Mechanical Properties of Kapton E(N) and Upilex S.

Property	Test method	Kapton E(N)	Upilex S
Density (g/cm3)	ASTM D1505	1.46	1.47
T_g (°C)	DMA	359	>500
CTE (ppm/°C) 20–100 °C	TMA	12	8
Tensile strength (MPa)	ASTM D882	306	392
Elongation (%)	ASTM D882	45	30
Tensile modulus (GPa)	ASTM D882	5.1	8.6

Note: CTE = coefficient of thermal expansion; DMA = dynamic mechanical analysis; TMA = thermal mechanical analysis.

increased to 0.58 and 0.22, respectively. With a further increase in the duration of argon plasma modification of Kapton E(N) to 1 min, the relative surface compositions of oxygen to carbon and of nitrogen to carbon were slightly decreased to 0.56 and increased to 0.30, respectively. When argon plasma modification was applied to Kapton E(N) for 3 min, the relative surface compositions of oxygen to carbon and of nitrogen to carbon were slightly decreased to 0.54 and 0.28, respectively. When argon plasma modification was applied to Kapton E(N) for 5 min, the relative surface composition of oxygen to carbon was highly increased to 0.66, and the relative surface composition of nitrogen to carbon was slightly decreased to 0.22.

Figure 13 shows that the relative surface compositions of oxygen to carbon and of nitrogen to carbon on the surfaces of unmodified Upilex S were 0.22 and 0.06, respectively. When argon plasma modification are applied to Upilex S for 0.5 min, the relative surface compositions of oxygen to carbon and of nitrogen to carbon were increased to 0.52 and 0.16, respectively. With a further increase in the duration of argon plasma modification of Upilex S to 1 min, the relative surface compositions of oxygen to carbon and of nitrogen to carbon were increased a great deal, to 0.93 and 0.27, respectively. When argon plasma modification was applied to Upilex S for 3 min, the relative surface compositions of oxygen to carbon and of nitrogen to carbon were greatly decreased, to 0.71 and 0.16, respectively. When argon plasma modification was applied to Upilex S for 5 min, the relative surface composition of oxygen to carbon was slightly increased to 0.74, and the relative surface composition of nitrogen to carbon was greatly increased, to 0.30.

Figures 12 and 13 show that it was easier to modify Kapton E(N) by argon plasma as the relative surface composition of oxygen to carbon approached a very high level, which occurred with an argon plasma modification of duration of 0.5 min. This is because Kapton E(N) has a lower tensile modulus than Upilex S, as shown in Table I. A softer material is easier to surface-modify by argon plasma.[16] Hence, Kapton E(N) was easier to modify with argon plasma to enhance peel strength with sputtered copper. However, a softer material such as Kapton E(N) is more sensitive to argon plasma modification, which caused a big decrease in peel strength with sputtered copper as the duration of argon plasma modification was increased to 3–5 min, as shown in Figure 4(a).

According to the results shown in Figures 11–13, the much increased surface energy of Kapton E(N) and Upilex S from argon plasma modification at optimal plasma settings such as a duration of 1 min was a result of the much increased relative compositions of oxygen to carbon and of nitrogen to carbon.

Chemical bonds of Kapton E(N) and Upilex S

The binding energies of chemical bonds such as C—C/C—H at 284.6 eV, C—O at 286.29 eV, C═O at 288.61 eV, and C—N at 285.68 eV for the C_{1s} of Kapton E(N) and Upilex S were investigated in this study. Figures 14 and 15 show typical C_{1s} spectra of unmodified and argon plasma–modified Kapton E(N) and Upilex S. From Figures 14 and 15, the chemical bond of C—C/C—H at 284.6 eV for Kapton E(N) and Upilex S was decreased as argon plasma modification was applied. To interpret the effects of chemical bonds

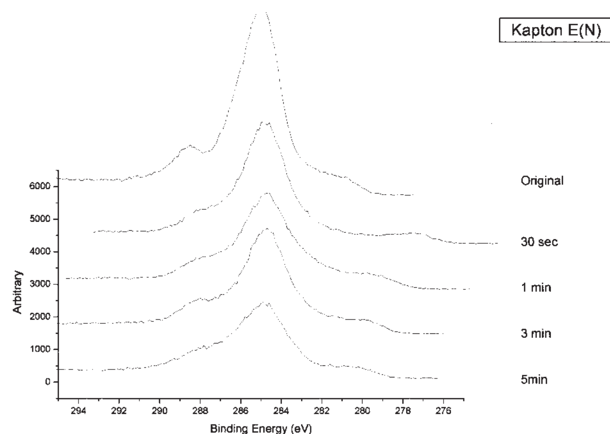

Figure 14 Typical C_{1s} spectra of unmodified and argon plasma–modified Kapton E(N). The plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

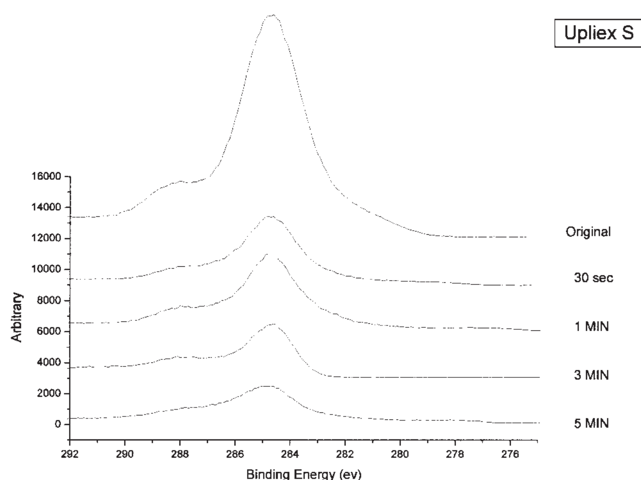

Figure 15 Typical C_{1s} spectra of unmodified and argon plasma–modified Upilex S. The plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

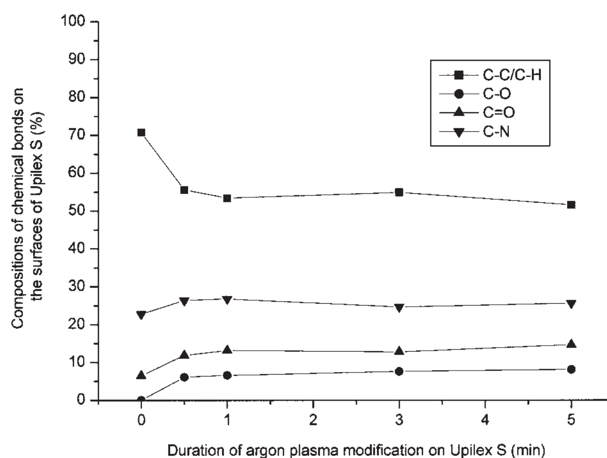

Figure 17 Chemical bonds of unmodified and argon plasma–modified Upilex S. The plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

on the enhanced peel strength from argon plasma modification, the relation between the chemical bonds of unmodified and argon plasma–modified Kapton E(N) and Upilex S with the duration of argon plasma modification was assessed, as shown in Figures 16 and 17. Figure 16 shows a decreased composition of C—C/C—H as argon plasma modification was applied to Kapton E(N). This decreased composition was then mainly transferred to the increased composition of the chemical bond C—O. As a duration of 1 min approached, a higher composition of C—O chemical bonds approached. The composition of C—O chemical bonds in Kapton E(N) remained at the same value even with further increases in the duration of argon plasma modification of Kapton E(N) to 3–5 min. Figure 17 also shows the trend of the composition of chemical bonds C—C/C—H and C—O in Upilex S was related to the duration of argon plasma modification, a trend similar to the composition of chemical bonds C—C/C—H and C—O in Kapton E(N).

It can be seen in Figures 12, 13, 16, and 17, which show the highly increased relative compositions of oxygen to carbon and of nitrogen to carbon in Kapton E(N) and Upilex S modified by argon plasma, that the highly increased level of oxygen in Kapton E(N) and Upilex S was mainly a result of the formation of C—O bonds on the surfaces of Kapton E(N) and Upilex S. The increased level of nitrogen in Kapton E(N) and Upilex S modified by argon plasma occurred because of the formation of C—N bonds on the surfaces of Kapton E(N) and Upilex S.

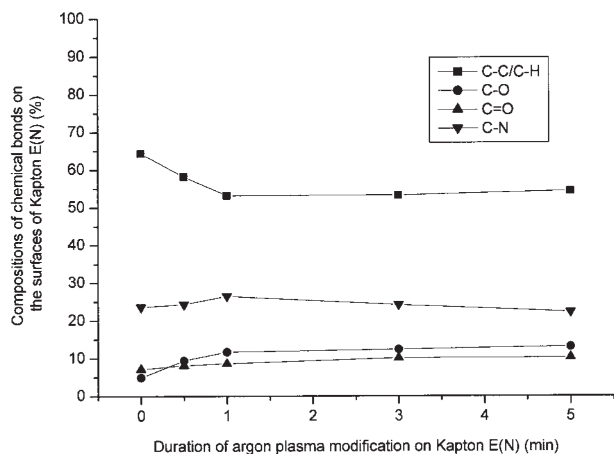

Figure 16 Chemical bonds of unmodified and argon plasma–modified Kapton E(N). The plasma settings were: power, 200 watts; chamber pressure, 60 mtorr; and argon flow rate, 10 sccm.

CONCLUSIONS

The results demonstrated that argon plasma modification is a good modification method that greatly increases the strength of the adhesion of sputtered copper to Kapton E(N) and Upilex S. The peel test results demonstrated an improvement from 1.2 g/mm and 0.7 g/m for untreated Kapton E(N) and Upilex S, respectively, to 110.3 g/mm and 98 g/mm for the surfaces of Kapton E(N) and Upilex S modified by argon plasma for a short duration of 1 min.

The enhanced strength of the adhesion sputtered copper to Kapton E(N) and Upilex S by argon plasma modification was strongly affected by the increased surface energy and surface roughness of the surfaces of Kapton E(N) and Upilex S as a result of argon plasma modification. When the optimal argon plasma settings—a 1-min duration, 200 W of power, and an argon flow rate of 10 sccm—were applied to Kapton

E(N) and Upilex S, higher surface energy and higher surface roughness of Kapton E(N) and Upilex S were observed, resulting in higher peel strength with sputtered copper.

The higher surface energy of Kapton E(N) and Upilex S modified by argon plasma was found to be a result of the higher surface composition of oxygen and nitrogen in Kapton E(N) and Upilex S. An increase in chemical bonds such as C—O and C═O with an increased surface composition of oxygen was observed with argon plasma modification of Kapton E(N) and Upilex S. An increase in chemical bonds such as C—N with an increased surface composition of nitrogen was observed with argon plasma modification of Kapton E(N) and Upilex S.

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