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Low-temperature graft copolymerization of 1-vinyl imidazole on polyimide films with simultaneous lamination to copper foils—effect of crosslinking agents

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Abstract

A simple technique of thermal graft copolymerization of 1-vinyl imidazole (VIDZ) in the presence of a small amount of a crosslinking agent (XLA) on plasma-pretreated polyimide (PI or Kapton HN®) films with simultaneous lamination of copper foils was demonstrated. The simultaneous thermal grafting and lamination process was carried out in the temperature range of 80–150°C under atmospheric conditions and in the complete absence of a polymerization initiator. Significant improvement in adhesion was achieved by the presence of a XLA, such as 2,4,6-triallyloxy-1,3,5-triazine (TATZ), or 1,3,5-triallyl benzene tricarboxylate (TBTC), in VIDZ during the thermal graft copolymerization and lamination process. T-peel adhesion strength exceeding 17 N/cm can be readily achieved for the polyimide–copper interface for grafting and lamination carried out at the reduced temperature of 100°C. The T-peel adhesion strengths are reported as a function of the cooling rate, the argon plasma pre-treatment time of the polyimide films, the thermal lamination temperature, and the thermal lamination time. The polyimide–copper interface graft copolymerized and laminated in the presence of a XLA also exhibited substantially improved resistance to moisture. The surface compositions of the polyimide films and copper foils from the delaminated interfaces were studied by X-ray photoelectron spectroscopy (XPS). The enhanced interfacial adhesion has resulted in cohesive failure deep inside the PI film as is also revealed by the scanning electron micrograph (SEM). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Grafting; Lamination; Crosslinking agent

1. Introduction

Polyimides (PI) are widely used in the microelectronics packaging industry especially in printed circuit board (PCB) because of its superior mechanical properties, high temperature resistance, solvent resistance and low dielectric constant [1–3] Copper is used as the metal in PCB due to its excellent electrical conductivity and low electromigration property. One of the methods in making PCB is by curing polyamic acid precursors coated on copper metal at a temperature above 250°C to form polyimides–copper composite. Alternatively, in making flexible PCB, copper is coated on polyimides via the techniques of vacuum evaporation, metal sputtering, ion plating, etc. The polyimide–copper composites or laminates so obtained have limited adhesion strength, which is a key issue to be resolved currently. A great deal of effort has been devoted to the surface modification of polyimides for adhesion improvement to metals [4–8].

Earlier fine works [9,10] have shown that the adhesion of polyimides and copper can be achieved and enhanced by first through plasma graft copolymerization of 1-vinyl imidazole (VIDZ) on polyimides, followed by metallization of copper on the graft modified polyimides surface and thermal treatment at 80°C. The imino groups of the grafted VIDZ polymer form charge-transfer complexes with copper metal, thus enhancing the adhesion strength. Xue et al. [11] reported that the imino groups of benzimidazole interacted with copper metal at zero oxidation state to form a complex. Lee et al. [12] evaluated the simultaneous passivation and adhesion experiment by incorporating triazole or imidazole functionalities into the polyimide to improve lamination with copper. In another development, Rånby et al. [13,14] demonstrated that initiator-promoted surface graft copolymerization, when carried out at the interface between two contacting polymer films, was accompanied by the simultaneous lamination of the polymer films. Surface modification

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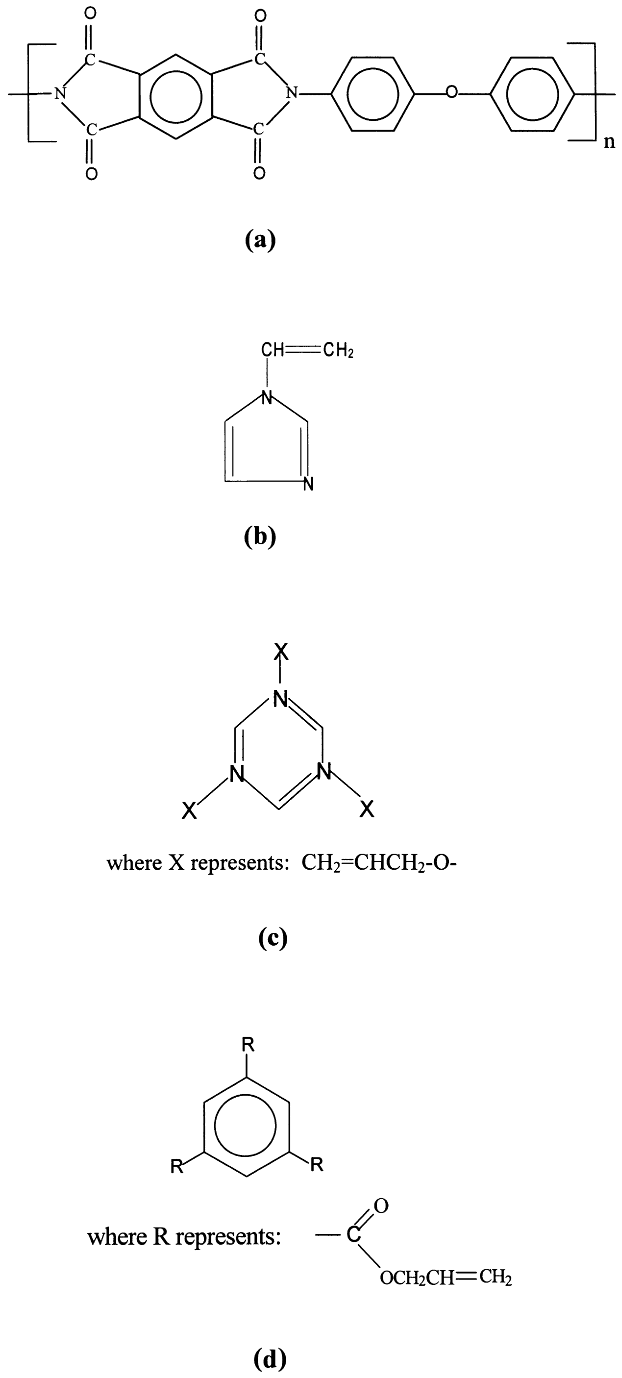

Fig. 1. Chemical structures of (a) poly[N,N′-(oxydiphenylene) pyromellitimide], (b) 1-vinyl imidazole, (c) 2,4,6-triallyloxy-1,3,5-triazine and (d) 1,3,5-triallyl benzene tricarboxylate.

of polymers via grafting and graft copolymerization has also been reviewed [15,16]. Ikada et al. [16–19], for instance, have successfully incorporated a large number of functional groups onto polymer surfaces via graft copolymerization, usually in the absence of a polymerization initiator. In our previous work [8], we combined the above techniques to show that strong adhesion between polyimide film (Kapton HN®) and Cu foil could readily be achieved through thermal graft copolymerization of VIDZ on the surface of plasma-pretreated polyimide film in contact with a Cu foil, at a low temperature of 120°C under atmospheric conditions and in the complete absence of an added polymerization initiator. In the present work, we demonstrate in detail that the adhesion of polyimide film on copper foil via the simultaneous grafting and lamination technique can be further improved by the presence of a crosslinking agent, and can readily exceed the fracture strength of the polyimide film for grafting and lamination carried out at a reduced temperature of 100°C under atmospheric conditions and in the complete absence of a polymerization initiator. The strong adhesion between the polymer and the metal always gives rise to cohesive failure of the interface, with fragments of fracture polyimide substrate covering the entire surface of the copper substrate. The surface compositions of the polyimide film and copper foil after delamination by T-peel were characterized by XPS. The surface morphologies of polyimides and Cu substrates after peel test were revealed by SEM.

2. Experimental

2.1. Materials

The polyimide (PI) film used in the present study is poly[-N,N′-(oxydiphenylene) pyromellitimide] with the chemical structure shown in Fig. 1(a). It was purchased from Goodfellow, Inc. of Cambridge, UK as Kapton HN® in sheets of 150 mm × 150 mm in area and 75 μm in thickness. The surface of the film was cleaned with doubly distilled water, followed by acetone in an ultrasonic water bath before being used. Copper foils (99.9% purity) of 100 mm × 100 mm in area and 0.1 mm in thickness were also purchased from Goodfellow, Inc.. The surface of the copper foil was cleaned with a mixture of aqueous 0.01 M HCl/0.01 M HNO_3/0.01 M H_2SO_4 in the volume proportion of 6:1:1, respectively, before use. The monomer, 1-vinyl imidazole (VIDZ, 99 + % purity), and the crosslinking agents, 2,4,6-triallyloxy-1,3,5-triazine (TATZ, 97% purity) and 1,3,5-triallyl benzene tricarboxylate (TBTC, 98% purity) with chemical structures shown in Figs.1(b), (c) and (d), respectively, were purchased from Aldrich Chemical Co. of Milwaukee, USA and were used as received.

2.2. Simultaneous graft copolymerization and lamination

The PI film strips were pretreated with argon plasma before the thermal graft copolymerization with concurrent lamination experiment. The Ar plasma pretreatment was carried out in an Anatech SP100 plasma system, equipped with a cylindrical quartz reactor chamber. The glow discharge was produced at a plasma power of 35 W, an applied oscillator frequency of 40 kHz and an argon pressure of 0.6 Torr. The duration of the glow discharge pretreatment for the present study was set at between 5

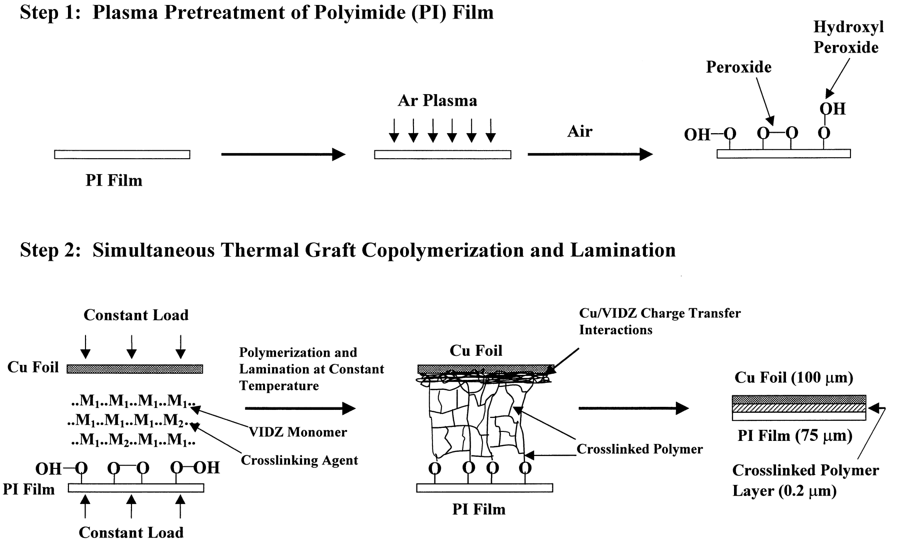

Fig. 2. Schematic diagram showing the procedure and mechanism for the simultaneous thermal graft copolymerization and lamination process.

and 30 s. The plasma-pretreated films were subsequently exposed to the atmosphere for 5–10 min for the generation of surface peroxide and hydroxyl peroxide species [19] before the thermal grafting and lamination experiment. In the simultaneous grafting and lamination experiment, a small quantity of a mixture of VIDZ consisting 2 vol.% of the crosslinking agent (XLA) was introduced between the PI film and the copper foil. Thermal graft copolymerization with concurrent lamination of Cu was achieved by heating the PI/VIDZ–XLA/Cu assembly under a constant load of about 20 kg/cm^2. The samples were introduced into the hot press only after the temperature set point was reached and maintained at a steady state. After the grafting and lamination experiments, the samples were cooled to room temperature either by quench-cooling or by annealing. For the quench-cooling method, the samples were removed from the hot press after the thermal grafting and lamination experiment and were allowed to cool in the ambient to the room temperature of 25°C. For the annealing method, the samples were cooled slowly in the hot press after the thermal grafting and lamination experiment until the samples returned to room temperature. In this case, the average cooling rate was in the order of 9–10°C/h.

2.3. Adhesion strength measurements and surface characterization

The T-peel adhesion strengths were determined using an Instron Model 5540, tensile strength tester. All measurements were performed at a crosshead speed of 0.5 cm/min. Each adhesion strength reported was the average of at least three sample measurements. For the peel strength measurement, the sizes of the samples were kept at 0.2–0.3 cm wide and 0.8–1.0 cm long. XPS measurements were made on a VG ESCALAB MKII spectrometer with a Mg K_α X-ray source (1253.6 eV photon) at a constant retard ratio of 40. The polyimide films and copper foils were mounted on the standard sample studs by means of double-sided adhesive tape. The X-ray source was operated at a reduced power of 120 W (12 kV and 10 mA). The operating pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during the measurements. The core-level spectra were obtained at photoelectron take-off angle (α, measured with respect to the sample surface) of 75°, unless otherwise specified. All binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV, so as to compensate for the effects of charging. In peak synthesis, the line width (full width at half maximum, FWHM) for the Gaussian peaks was maintained constant for all components in a particular spectrum of a particular sample. The compositions of both the PI and Cu surfaces were analyzed after mechanical delamination. SEM micrographs were obtained from the Hitachi Scanning Electron Microscope, Model S-2150. The samples were attached to the sample stud by means of double-sided adhesive tape.

3. Results and discussion

Plasma generated from various gases and under various glow discharge conditions have been widely used for the surface modification of polymers [20–26]. The simultaneous graft copolymerization and lamination process used in the present work is shown schematically in Fig. 2. The T-peel adhesion strength of the present PI/Cu interface as a function of the Ar plasma pretreatment time of the PI film from the simultaneous thermal grafting and lamination carried out at 120°C for 4 h is shown in Fig. 3. In all cases, the assemblies were cooled by the annealing method after the thermal grafting and lamination process. Three adhesion strength curves are reported. For plasma pretreatment time below 25 s, the adhesion strengths obtained from

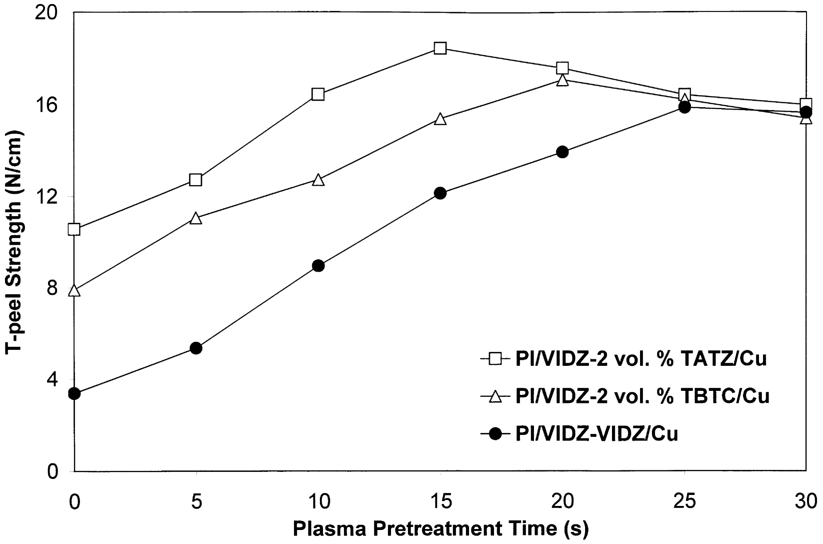

Fig. 3. Dependence of the peel adhesion strength on the Ar plasma pretreatment time of the polyimide film. All samples were subjected to thermal grafting/lamination at a temperature of 120°C for 4 h.

lapped assemblies using the VIDZ–TATZ monomer mixture for graft copolymerization are always higher than those using the VIDZ–TBTC mixture. The adhesion strengths are lowest for assemblies graft copolymerized and laminated using VIDZ monomer alone under the corresponding experimental conditions. Peel strengths above 8 N/cm were obtained for assemblies laminated in the presence of a XLA and with no Ar plasma pretreatment of the PI film. These adhesion strengths are more than twice that obtained using VIDZ alone. For graft copolymerization and lamination carried out with VIDZ only, the adhesion strength approaches an asymptotic value of about 16 N/cm after 30 s of Ar plasma pretreatment time for the PI film. In contrast, maximum peel strengths of 19 and 17 N/cm are achieved, respectively, for the PI/VIDZ–TATZ/Cu and PI/VIDZ–TBTC/Cu assemblies at a substantially reduced plasma pretreatment time for the PI film. It is noted that for all the lapped assemblies with adhesion strengths greater than 14 N/cm, delamination occurs by cohesive failure, which involves fracturing of the PI film and incomplete peeling of the polymer film from the copper surface. Thus, cohesive failure is observed for PI films with plasma pretreatment time greater than 10, 15 and 20 s for the graft copolymerization and lamination with copper foil carried out in the presence of VIDZ–TATZ, VIDZ–TBTC and VIDZ alone, respectively (see also Fig. 8 below). Further, when a small quantity of VIDZ monomer is sandwiched between a plasma-pretreated PI film and an inert poly(tetrafluoroethylene) film, graft copolymerization of VIDZ proceeded readily on the PI surface at temperatures above 100°C. The presence of tethered VIDZ chains on the PI surface was confirmed by the persistence of distinct N 1s components associated with the VIDZ polymer, even after the PI film had been subjected to exhaustive washing and extraction. The susceptibility of the plasma and ozone pretreated PI film surfaces to graft copolymerization with vinyl monomers has also been demonstrated in the earlier studies [24]. The presence of a finite adhesion strength between the pristine PI film and Cu in Fig. 3, however, indicates that the VIDZ homopolymer at the lapped interface probably has also contributed to the observed adhesion phenomenon.

Due to the vast difference in the thermal conductivities between polymers and metals, annealing or slow cooling is crucial to the development and maintenance of a high adhesion strength for the polymer–metal interface. Direct exposure of the thermally graft copolymerized and laminated assembly at hot press temperature, e.g. 120°C, to room temperature in a quenching process will result in severe thermal stress at the polymer–metal interface. To illustrate this thermal stress effect, the PI/Cu laminates were subjected to various extents of thermal quenching in the “interrupted quench-cooling” process. In this process, the PI/Cu laminate was first cooled very slowly (by annealing, see Section 2) from the hot press or lamination temperature to a pre-determined set-point temperature. It was then quench-cooled from the set-point temperature to room temperature. The degree of quench-cooling from the set-point temperature to room temperature (ΔT) is expected to have a significant effect on the resulting adhesion strength of the PI/Cu laminate. A laminate with the largest degree of interrupted quench-cooling (the largest ΔT) is expected to exhibit the lowest adhesion strength. Fig. 4 demonstrates the effect of various degrees of interrupted quench-cooling on the T-peel strengths of the PI/Cu laminates after the simultaneous thermal grafting and lamination at 120°C for 4 h with the 20 s Ar plasma-pretreated PI films. For the PI/VIDZ/Cu assemblies graft copolymerized and laminated with VIDZ alone, the T-peel strengths decrease from about 14 N/cm for the completely annealed PI/Cu interface

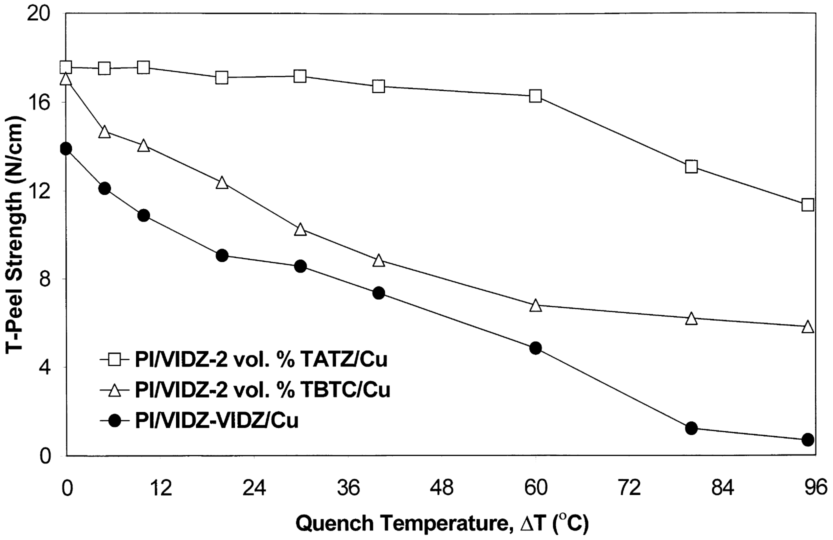

Fig. 4. Dependence of the peel adhesion strength on the interrupted quench-cooling of the PI/Cu interface. All samples were subjected to thermal grafting/lamination at a temperature of 120°C for 4 h and with 20 s of Ar plasma pretreatment time for the polyimide films.

($\Delta T = 0$°C) to less than 1 N/cm for the sample which has been quenched by the ambient atmosphere from 120–25°C ($\Delta T = 95$°C). Even a mere 5°C quenching ($\Delta T = 5$°C, or slow cooling from 120–30°C, followed by atmospheric quenching to 25°C), can result in a significant loss in the peel strength of the polymer–metal interface. The quench-cooling curve from PI/VIDZ–TBTC/Cu assembly shows the same trend as that of the PI/VIDZ/Cu assembly, except for the generally higher adhesion strengths observed. However, the cooling curve for the PI/VIDZ–TATZ/Cu assembly suggests that the adhesion strength of the polymer–metal interface is not drastically affected by quench-cooling, as shown by the persistence of a peel strength of 11 N/cm after a 95°C quenching. This peel strength is more than 10 times that of the residual strength in the similarly quench-cooled PI/VIDZ/Cu assembly. The adhesion curve for the PI/VIDZ–TATZ/Cu assembly remains almost unaffected when the extent of quench-cooling is less than 60°C (i.e. $\Delta T < 60$°C, or slow cooling from 120–85°C or below, followed by atmospheric quenching to 25°C).

The data in Figs. 3 and 4 readily suggest that the grafted VIDZ polymer on the PI film acts as an effective adhesive for both the Cu/VIDZ polymer and VIDZ polymer/Cu interfaces. Thus, the mechanical properties of the VIDZ polymer "adhesive" layer are expected to play an important role in the adhesion strength of the PI/Cu laminates. The strengthening of the mechanical properties of the VIDZ polymer by crosslinking has a marked effect on the resulting adhesion strength, as shown in Fig. 3. Further, the enhanced mechanical properties of the VIDZ polymer through crosslinking have significantly increased the ability of the PI/Cu laminate in withstanding large thermal stresses, as illustrated by the thermal quenching data in Fig. 4.

In an earlier fine work of Inagaki et al. [10], the VIDZ graft copolymerized polyimide film surface was metallized by vacuum deposition of copper metal in a separate step. The maximum T-peel strength of the resulting polymer–metal interface was in the order of 6.4 N/cm. This adhesion strength is less than half of that of the present PI-film/Cu-foil joint formed from the thermal graft copolymerization with concurrent lamination technique. Nevertheless, both techniques involve the imidazole groups which are capable of forming strong charge-transfer complexes with copper. Earlier work of Xue et al. [11] has also reported on the interaction of copper metal at zero oxidation state with benzimidazole. In fact, new polyimide containing imidazole units in the main chain to improve copper adhesion has been prepared [27] The polymer exhibits good adhesion with copper but is too brittle for microelectronics packaging applications.

Fig. 5 summarizes the dependence of T-peel strengths of PI/Cu laminates on the temperature of thermal graft copolymerization/lamination for PI films with 20 s of Ar plasma pretreatment time and 4 h of thermal grafting/lamination time. Again, significantly higher adhesion strengths are observed for the samples laminated in the presence of the XLAs. The peel strength curve for assemblies laminated in the presence of VIDZ alone starts to increase from 4 N/cm at a temperature of 90°C and reach an optimum value of 14 N/cm at a temperature of 120°C, after which the peel strength decreases with the increase in lamination temperature. The peel strength curve for assemblies graft copolymerized and laminated using the VIDZ–TBTC monomer mixture follows the same trend as that using the pure VIDZ monomer, except for the improved adhesion strength and the attainment of the maximum adhesion strength at a lower temperature of 100°C. The peel strength curve for the PI/VIDZ–TATZ/Cu assembly, on the other hand, increases monotonously from 12 N/cm at a grafting/

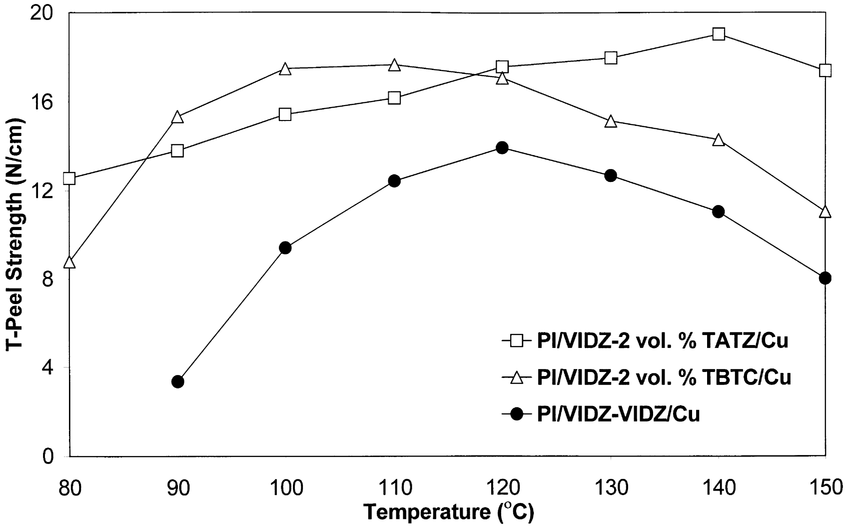

Fig. 5. Dependence of the peel adhesion strength on the thermal grafting/lamination temperature. All samples were subjected to 4 h of thermal grafting/lamination and with 20 s of Ar plasma pretreatment time for the polyimide films.

lamination temperature of 80°C to 18 N/cm at a temperature of 140°C, with the adhesion strength decreases slightly at higher temperatures. The adhesion strengths of the assemblies laminated at 90°C using the VIDZ–XLA monomer mixture are already greater than the optimum value attainable using the VIDZ monomer alone at a higher lamination temperature of 120°C. The decrease in adhesion strength for grafting/lamination using the VIDZ–TBTC monomer mixture or pure VIDZ monomer at elevated temperatures could be due to the thermal degradation of grafted polymer at the PI/Cu interface. However, in the presence of the VIDZ–TATZ monomer mixture, the adhesion strength for the lapped assembly increases steadily with temperature, suggesting that the crosslinked graft layer so obtained may be more resistant to thermal degradation.

Finally, Fig. 6 shows the effect of thermal grafting/lamination time on the observed T-peel adhesion strength of the PI/Cu laminates for PI films with 20 s of Ar plasma pretreatment time and for lamination carried out at 120°C. Thus, the optimum adhesion strengths for all the samples with and without using the XLAs are achieved after 4 h of thermal grafting/lamination time. Increase in grafting/lamination time to above 4 h does not result in an appreciable increase in the adhesion strength.

In microelectronics packaging applications, moisture resistance of the polymer–metal interface is an important issue. Thus, the moisture resistance of the PI/Cu junction, obtained from the present simultaneous grafting and lamination technique, is also evaluated. Fig. 7 shows the changes in T-peel strengths as a function of water immersion time

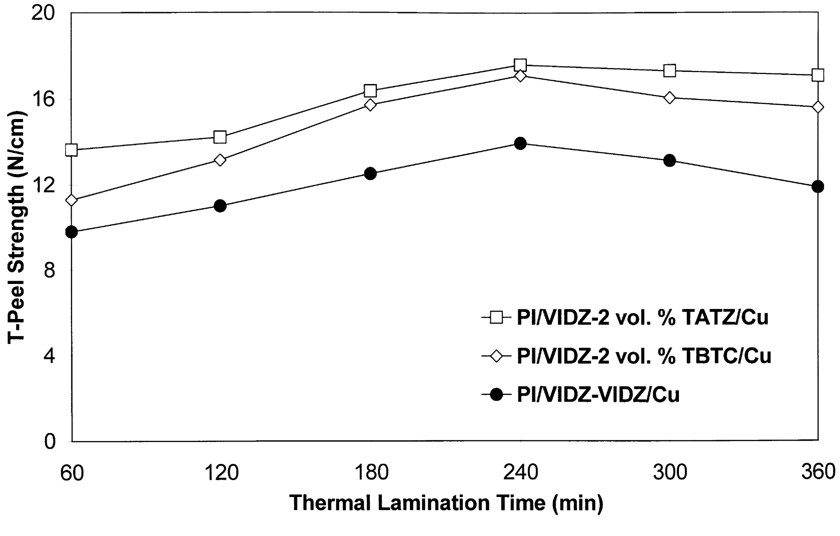

Fig. 6. Dependence of the peel adhesion strength on the thermal grafting/lamination time. All samples were subjected to thermal grafting/lamination at a temperature of 120°C and with 20 s of Ar plasma pretreatment time for the polyimide films.

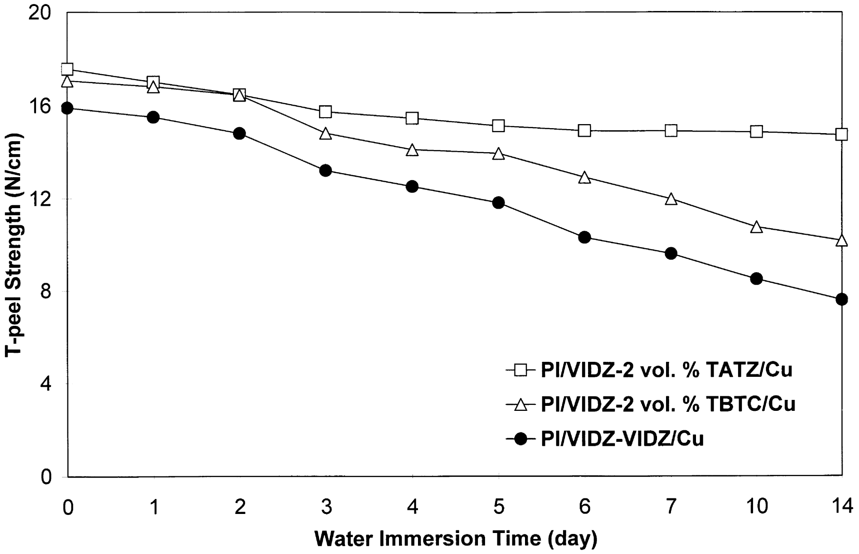

Fig. 7. Dependence of the peel adhesion strength on the duration of samples immersed in doubly distilled water. All samples were subjected to thermal grafting/lamination at a temperature of 120°C for 4 h and with 20 s of plasma pretreatment time for the polyimide films.

for the assemblies, obtained with and without using the XLAs, from grafting/lamination at 120°C for 4 h with the 20 s Ar plasma-pretreated PI film. For the assemblies using the VIDZ–TATZ monomer mixture for graft copolymerization, the PI/Cu interface still retains close to 80% of its original adhesion strength even after 14 days of immersion in water at room temperature. A drastic decrease of more than 50% in adhesion strength is observed for the assemblies graft copolymerized and laminated using VIDZ alone. The assemblies using the VIDZ–TBTC monomer mixture show moderate resistance to moisture and retain about 60% of its original adhesion strength after 14 days of immersion in water. The lack of complete moisture resistance of the present PI/Cu interfaces can be attributed to the fact that the graft copolymerized VIDZ polymer at the interface is itself a hydrophilic polymer. The polar and electron-rich imidazole group which gives rise to the hydrophilicity of the VIDZ polymer, however, also plays a crucial role in the charge-transfer interaction with Cu to account for the observed adhesion strength. Nevertheless, the crosslinked VIDZ polymer could act as a barrier or deterrent to water penetration into the PI/Cu interface.

Fig. 8(a)–(f) show the respective N 1s core-level spectra of the delaminated surfaces of Cu foils and PI films from the three types of assemblies prepared under the experimental conditions which give rise to the maximum adhesion strength in each type of assembly. Fig. 8(a) and (b) shows the N 1s core-level spectra of the delaminated Cu and PI surfaces, respectively, from the PI/VIDZ/Cu assembly which exhibits a T-peel strength of about 16 N/cm. The corresponding N 1s core-level spectra of the delaminated surfaces from the PI/VIDZ–TBTC/Cu assembly with a T-peel strength of 17 N/cm are shown in Fig. 8(c) and (d), and those from the PI/VIDZ–TATZ/Cu assembly with a T-peel strength of 19.5 N/cm are shown in Fig. 8(e) and

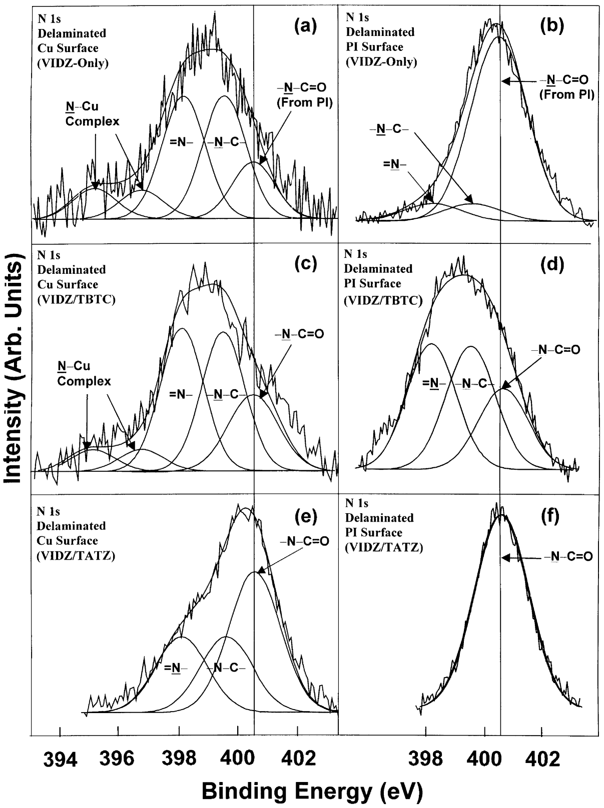

Fig. 8. XPS N 1s core-level spectra, obtained at $\alpha = 75°$, of: (a) copper surface and (b) polyimide surface after delamination of a PI/VIDZ/Cu assembly having a peel strength of 15.8 N/cm; (c) copper surface and (d) polyimide surface after delamination from of a PI/ VIDZ–TBTC/Cu assembly having a peel strength of 17.0 N/cm; and (e) copper surface and (f) polyimide surface after delamination from a PI/VIDZ–TATZ/Cu assembly having a peel strength of 19.5 N/cm.

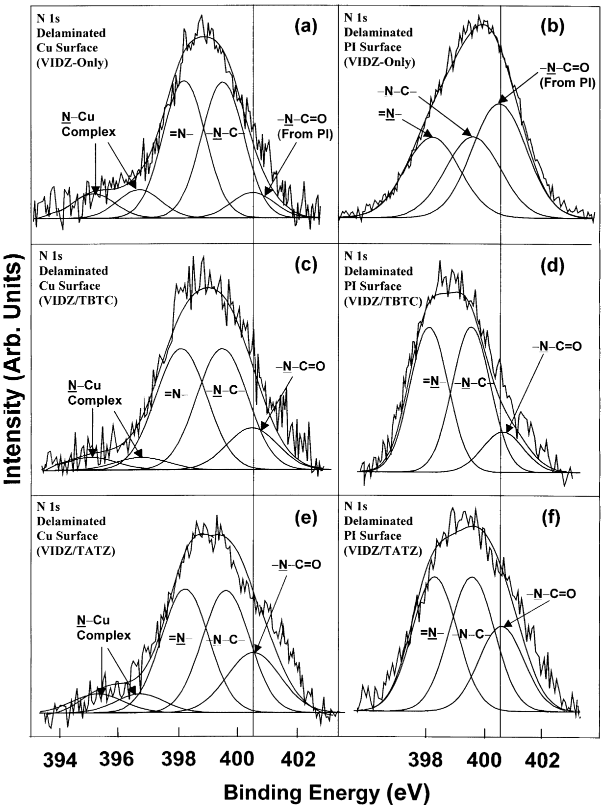

Fig. 9. XPS N 1s core-level spectra, obtained at $\alpha = 75°$, of (a) copper surface and (b) polyimide surface after delamination of a PI/VIDZ/Cu assembly having a peel strength of 4.0 N/cm; (c) copper surface and (d) polyimide surface after delamination of a PI/VIDZ–TBTC/Cu assembly having a peel strength of 6.0 N/cm; and (e) copper surface and (f) polyimide surface after delamination of a PI/VIDZ–TATZ/Cu assembly having a peel strength of 11.5 N/cm.

(f). The spectra of the copper surface can be curve-fitted with five peak components, based on the fixed FWHM approach in peak synthesis adopted in the present work, having binding energies (BEs) at about 400.5, 399.7, 398.5, 397.3 and 396.1 eV. The first BE component (400.5 eV) is attributable to the imide group (–*N*–C=O) of the PI film [28]. The next two high-BE components (399.7 and 398.5 eV) are attributable, respectively, to the amine (–*N*–C–) and imine (=*N*–) nitrogen of the VIDZ ring, while the two lower-BE components (397.3 and 396.1 eV) are attributable to the nitrogen atoms of the VIDZ ring charge-transfer-complexed with Cu [8,10]. The difference in component BEs between the amine (–*N*–C–) and imine (=*N*–) nitrogen species for the neutral and charge-transfer-complexed imidazole rings appears to be similar. This result suggests that both the amine (–*N*–C–) and imine (=*N*–) nitrogen in the imidazole ring participated in the charge-transfer complex formation with copper. First of all, the possibility of the imidazole ring to establish a resonance hybrid structure [29] such that the amine nitrogen also shares part of the double bond can be the reason for the slightly negative BE shift of the amine –*N*–C– species from 400 to 399.7 eV. The hybrid structure can also account for the observation that electron transferred from Cu is shared readily between the imine and amine nitrogen of the imidazole ring. The transfer of electrons from Cu to the imidazole rings readily results in a more electron-rich environment for the nitrogen species and thus gives rise to the two lowest BE N 1s components at 397.3 and 396.1 eV. The presence of a similar low BE shoulder has been suggested for the charge-transfer complex resulted from the deposition of copper on poly(vinyl imidazole) [10].

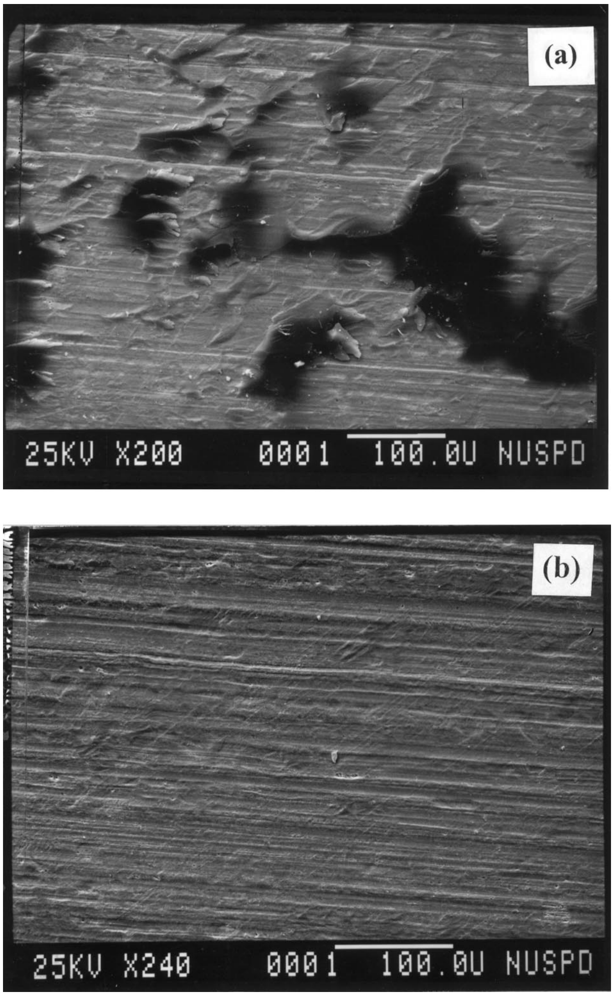

Fig. 10. Surface scanning electron micrographs of (a) delaminated copper surface from a PI/VIDZ/Cu assembly having a peel strength of 4.0 N/cm showing fragments of polymer and exposed copper surface due to fracturing of polyimide film and (b) delaminated copper surface from a PI/VIDZ–TATZ/Cu assembly having a peel strength of 19.5 N/cm showing the complete coverage of the copper surface by the polymer film.

The N 1s core-level lineshapes of the delaminated Cu surfaces from the PI/VIDZ/Cu assembly (Fig. 8(a)) and PI/VIDZ–TBTC/Cu assembly (Fig. 8 (c)) suggest the presence of nitrogen species from the polyimide film, in addition to those from the VIDZ polymer and their charge-transfer-complexed species with Cu. The corresponding N 1s spectra from delaminated PI surfaces show the presence of the imide group from PI in addition to the nitrogen species from VIDZ. However, the N 1s core-level spectra of the delaminated Cu and PI surfaces from the PI/VIDZ–TATZ/Cu assembly (Fig. 8(e)) are distinctively different from the two previous assemblies. The contribution of the complexed species arising from charge-transfer interaction with copper is not discernible due to the fact that the cohesively delaminated polyimide fragments were distributed uniformly across the copper surface. The thickness of the fragmented polymer layer is believed to be greater than the XPS sampling depth of about 7.5 nm. The N 1s core-level spectrum of the corresponding PI surface (Fig. 8(f)) shows predominantly the contribution from the imide group of the PI film. Thus, in the presence of the TATZ crosslinking agent and enhanced interfacial adhesion, cohesive failure deep inside the PI film has resulted in a more uniform coverage of thick polymer fragments on the delaminated Cu surface (see also the SEM micrographs in Fig. 10 below).

The N 1s core-level spectra of the delaminated Cu and PI surfaces from the weak joints of the corresponding PI/VIDZ/Cu, PI/VIDZ–TBTC/Cu and PI/VIDZ–TATZ/Cu assemblies are shown in Fig. 9(a)–(f). The corresponding T-peel adhesion strengths for the three assemblies are 4, 6 and 11.5 N/cm. The N 1s core-level spectra of the delaminated Cu surfaces of all the three assemblies show the presence of PI, VIDZ and the charge-transfer-complexed species, while those of the PI surfaces show the presence of PI and VIDZ species. The comparison of these N 1s core-level spectra with those from the stronger joints clearly suggests a more prominent contribution of VIDZ signal (or a reduced contribution of the PI signal) on both the delaminated Cu and PI surfaces for the weaker joints.

An earlier study [30] had outlined the different failure modes of the PI/Cu interface, prepared from metallization of the VIDZ graft copolymerized PI surface, having a peel strength of 6.4 N/cm and suggested that the interfacial failure was a combination of different modes, involving both cohesive failure in the bulk of PI and adhesional failure within the grafted polymer. Our XPS results suggest that the failure mode of the strong PI/Cu joint obtained from the present simultaneous grafting and lamination technique is distinctively cohesive in nature, with failure occurring predominantly inside the PI film. However, the adhesion failure of the weaker joints occurs by a combination of adhesional and cohesive failure.

The SEM micrograph of the delaminated Cu surface from the PI/VIDZ/Cu assembly having a weak adhesion strength of about 4 N/cm (Fig. 10(a)) reveals the presence of the polymer fragments and the fracturing of polyimide substrate on the Cu surfaces, resulting in non-uniform coverage of the copper surface by PI. The surface morphology as shown in Fig. 10(a) is consistent with the chemical composition of the delaminated Cu surface and the presence of the *N*–Cu charge-transfer complexes in the N 1s core-level spectrum of Fig. 9(a). However, the micrograph of the delaminated Cu surface from the PI/VIDZ–TATZ/Cu assembly having a strong adhesion strength of 19.5 N/cm (Fig. 10(b)) reveals the complete coverage of a polymer layer on the Cu surface. The surface morphology is consistent with the absence of the Cu signal and the *N*–Cu charge-transfer-complexed species in the N 1s core-level spectrum of Fig. 8(e). Thus, the thickness of the fractured polymer layer on the Cu surface must be greater than the XPS sampling depth of 7.5 nm. The stronger adhesion always results in a larger contribution of the PI signal on the Cu surface, while the weaker adhesion always results in a larger contribution of the grafted VIDZ polymer signal on the PI surface, as shown in the XPS spectra of Figs. 8 and 9.

4. Conclusion

A strong and improved adhesion between polyimide film and copper foil can be achieved by direct thermal graft copolymerization of a mixture of 1-vinyl imidazole and a crosslinking agent on a plasma pretreated PI film in the presence of a contacting Cu foil under atmospheric conditions and in the absence of an added polymerization initiator. The adhesion strengths are also affected by the rate of cooling of the simultaneously graft copolymerized and laminated polymer–metal interface. Adhesion strength above 17 N/cm can be readily achieved when the simultaneous grafting and lamination process was carried out at 100°C for 4 h with the PI films pretreated with 20 s of Ar plasma and using the annealing process for cooling. Strong adhesion between PI and Cu arises from the charge-transfer interactions between the nitrogen moieties of the grafted polymer and the Cu atoms, as well as the fact that the grafted polymer chains are tethered on the PI film as a result of the graft copolymerization process.

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