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Determination of the Molecular Structure of Interphases Between Epoxy/4,4'-Diaminodiphenylsulfone Adhesives and Silver Substrates Using SERS and XPS

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The molecular structure of interphases formed by curing an epoxy/4,4'-diaminodiphenylsulfone (DADPS) adhesive against rough silver substrates was determined using surface-enhanced Raman scattering (SERS) and x-ray photoelectron spectroscopy (XPS). SERS spectra obtained from the adhesive deposited onto silver island films were very similar to SERS spectra obtained from the DADPS curing agent spun onto silver island films, indicating that DADPS in the adhesive system segregated to the interphase and was preferentially adsorbed onto the silver substrate. Differences in the relative intensity of several bands in the normal Raman and SERS spectra of DADPS were observed. For example, the band near 1603 cm^{-1} was stronger in SERS spectra of DADPS than in normal Raman spectra. The band near 1150 cm^{-1} was weaker in SERS spectra of DADPS than in normal Raman spectra. These results implied that DADPS was adsorbed through one of the NH_2 groups with an end-on conformation. Consistent results were also obtained from XPS spectra. C(1s) spectra of the adhesive and silver fracture surfaces of specimens prepared by curing the adhesive against silver substrates were more similar to the C(1s) spectra of DADPS than to those of the bulk adhesive. These results confirmed the preferential adsorption of DADPS onto the silver substrate from the adhesive system. The similarity of the C(1s) spectra obtained from adhesive and silver fracture surfaces indicated that a thin DADPS-rich interphase was formed between the bulk adhesive and the silver substrate and that the locus of failure was partially within this layer. However, less nitrogen and sulfur were detected on the silver fracture surface than on the adhesive fracture surface. A large amount of silver was observed on the substrate fracture surface and a trace was found on the adhesive fracture surface. These results indicated that failure of the adhesive joints was within the interphase but near the silver substrate. No evidence of chemisorption of DADPS onto the substrate was observed.

KEY WORDS Epoxy adhesive, diaminodiphenylsulfone curing agent, interphase, surface segregation, silver, surface-enhanced Raman scattering, X-ray photoelectron spectroscopy.

I INTRODUCTION

The term "interphase" is frequently used to describe the transition zone between the adhesive and the substrate.¹ In this zone, the chemical and physical properties of the adhesive may be considerably different than in the bulk. It is generally believed that the interphase controls the durability and strength of adhesive joints.

The interphase is primarily responsible for the transference of stress from one adherend to another in adhesive joints and is frequently the site of environmental attack. The initial strength and stability of the adhesive joint depend on the molecular structure of the interphase after processing and environmental exposure. As a result, characterization of the molecular structure of interphases in adhesive joints is essential for improving the performance of an adhesive system. However, few investigations regarding the molecular structure of interphases in adhesive joints have been reported.

Kim et al² investigated polyimide/metal interphases formed by spin-coating polyamic acid from solution onto copper surfaces followed by thermal curing to form the polyimide. Cross-section transmission electron microscopy (TEM) results showed that very fine copper-rich particles were distributed in the polyimide matrix 80 to 200 nm away from the copper boundary. It was suggested that the polyamic acid reacted with copper to form a complex which decomposed during subsequent thermal curing, resulting in the formation of copper-rich particles in the polyimide. When copper was deposited on the polyimide film, TEM results showed the interphase was very sharp, and that Cu-rich particles were not found in the polyimide even after thermal curing. It was also found that the adhesion of polyimide-on-metal joints was much greater than that of metal-on-polyimide joints, since the former case involved chemical bonding between copper and polyimide.

Carter et al³ investigated the surface chemical effects between an epoxy/dicyandiamide adhesive and adherends such as electrogalvanized steel (EGS) and low carbon steel (LCS). It was found that lap joints made with EGS adherends were more durable than joints made with LCS adherends during cyclic corrosion testing. Reflection-adsorption infrared (RAIR) spectra of epoxy/dicyandiamide adhesive deposited onto steel, zinc, and zinc oxide substrates were also obtained. These spectra showed that the substrates exerted a strong influence on the molecular structure of the interphase. They suggested that a redox reaction between metallic zinc and dicyandiamide resulted in formation of a unique molecular species in the interphase. However, no reaction was noted between zinc oxide and dicyandiamide. It was concluded that zinc was oxidized and dicyandiamide was reduced when dicyandiamide was cured against metallic zinc.

Garton^{4,5} used attenuated total reflection infrared spectroscopy (ATR) to characterize the molecular structure of an anhydride/epoxy adhesive cured at 150°C for 3 hours against an oxidized germanium crystal primed with an aminosilane coupling agent. It was found that the amino groups of the primer reacted with the anhydride groups to form amides in the interface. However, there was no evidence of imide formation. He concluded that the water produced in the imidization reaction was not able to escape, thus resulting in an unfavorable equilibrium for imide formation.

Ondrus et al⁶ used RAIR to determine the molecular structure of adhesive/aluminum and adhesive/steel interphases. Two model adhesive systems, epoxy/anhydride and epoxy/tertiary amine, were used. When an epoxy/tertiary amine adhesive was cured against steel substrates primed with an aminosilane coupling agent, the oxidation of aminosilane to form an imine occurred at the interphase.

When an epoxy/anhydride adhesive was cured against aluminum substrates also primed with an aminosilane coupling agent, a complex molecular structure in the interphase was obtained. The anhydride reacted with the silane to form amide and

imide groups in the interphase. Metal cations from the aluminum substrate also reacted with the anhydride to form carboxylate salts at the metal surface.

Ondrus et al⁷ also determined the molecular structure of interphases formed by curing epoxy/anhydride adhesives against unprimed copper and copper-containing aluminum substrates. X-ray photoelectron spectroscopy (XPS) and RAIR showed that the anhydride curing agent reacted with the cuprous oxide on the copper substrates. Cuprous ions were removed from the oxide and oxidized, resulting in the formation of a layer of cupric carboxylate salt in the interphase.

For the case of copper-containing aluminum (2024 aluminum) substrates, the anhydride was adsorbed onto the surface oxide (Al_2O_3) of the substrate to form a surface carboxylate. However, no metal ions were removed from the oxide and no layer of metal carboxylate was formed. Copper in the 2024 aluminum was mostly in the form of an aluminide below the surface oxide and did not react with the anhydride.

Boerio and Hong⁸ used a novel technique known as surface-enhanced Raman scattering (SERS) to determine the molecular structure of interphases between a silver island film and a model anaerobic acrylic adhesives system. SERS is a phenomenon in which the Raman scattering cross section of molecules adsorbed onto the roughened surfaces of certain metals such as silver, copper, and gold is enhanced by as much as 10^6 relative to the cross section for normal Raman scattering from the bulk. However, the enhancement is short-range and is restricted to the first few layers of molecules adjacent to the surface. As a result, SERS can be used for non-destructive characterization of interphases as long as the polymer films are not so thick that normal Raman scattering from the bulk of the film is more intense than SERS from the interphase.

SERS spectra obtained from thin films of neat adhesive spin-coated from 1% and 5% solutions in acetone were very similar. The intensities of bands in SERS spectra of films of neat adhesive were independent of the film thickness, demonstrating that the observed SERS signal was characteristic of the interphase and not of the bulk films. Moreover, SERS spectra of the adhesive system were very similar to SERS spectra of *o*-benzoic sulfimide (saccharin), a component of the curing system of the adhesive, and to normal Raman spectra of the sodium salt of saccharin. It was thus concluded that saccharin in the adhesive segregated to the interface and adsorbed by dissociation to form a salt.

Boerio and Hong⁹ also used SERS to characterize interphases between an epoxy/dicyandiamide (DDA) adhesive and silver substrates. Strong bands assigned to in-plane vibrations and very weak bands assigned to out-of-plane vibrations were observed in SERS spectra obtained from thin films of DDA. It was concluded that DDA was adsorbed with a vertical configuration involving coordination through the nitrilo nitrogen atom. SERS spectra of an adhesive system consisting of 8:1 mixtures diglycidyl ether of bisphenol-A (DGEBA) and DDA were identical to SERS spectra of DDA, indicating that DDA was preferentially adsorbed from the adhesive onto the silver substrate.

Some evidence for adsorption of both DGEBA and DDA was observed in SERS spectra obtained from 500:1 mixtures of DGEBA and DDA spun onto silver island films from dilute solutions. In those cases there was insufficient dicyandiamide available to occupy all the SERS-active surface sites.

The results described above indicate that interphases can have much different molecular structures than bulk adhesives and that SERS is a powerful technique for determining the molecular structure of adhesive/metal interphases. The purpose of this paper is to describe the use of surface-enhanced Raman scattering and x-ray photoelectron spectroscopy to determine the molecular structure of interphases formed when an epoxy/4,4'-diaminodiphenylsulfone (DADPS) adhesive was cured against silver substrates. The results obtained indicated that DADPS curing agent in the adhesive segregated to the interphase and was preferentially adsorbed onto silver substrates. However, no evidence was obtained showing that DADPS was chemisorbed onto silver substrates.

II EXPERIMENTAL

The epoxy/DADPS adhesive system used in this study was a commercial one-part filled adhesive system used in semiconductor applications. Information provided by the manufacturer indicated that the curing agent in the adhesive system was an aromatic amine. However, no other information regarding the composition of the adhesive was available. In order to conduct fundamental studies of the epoxy/metal interphase, it was necessary to identify the individual components in the adhesive system. Experimentation showed that methylethylketone (MEK) was a good solvent for the epoxy and the curing agent while toluene was a good solvent only for the epoxy. Accordingly, samples of adhesive was stirred into toluene and MEK to make 50% (by weight) suspensions. The soluble and insoluble portions were then separated using a centrifuge. Several drops of the solutions thus obtained were placed on KBr pellets which were dried under vacuum. Transmission infrared spectra were obtained using a Perkin-Elmer Model 1800 Fourier-transform infrared (FTIR) spectrophotometer interfaced with a Perkin-Elmer Model 7500 computer.

Substrates were prepared for SERS investigations as described below. Glass slides were cleaned by immersion in 0.1N NaOH for 1 hour, rinsed in 0.1N HCl aqueous solutions for another hour, rinsed briefly in distilled-deionized water in an ultrasonic cleaner, and blown dry with nitrogen. All of the above operations were carried out at room temperature. The clean slides were immediately placed in a vacuum chamber which was purged with nitrogen and pumped down to 10^{-6} Torr using sorption, sublimation, and ion pumps. Silver wire wrapped around a resistively heated tungsten filament was then slowly heated to evaporate island films onto the glass slides at a rate of about 1 Å per second. The thickness of the silver island films was controlled at about 40 Å using a quartz crystal oscillator thickness monitor.

Thin adhesive films were spun onto silver island films at room temperature from 2% solutions in MEK from which the insoluble filler had been removed. SERS spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, an ITT FW130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. The slit setting of the monochromator provided a spectral resolution of 10 cm^{-1} for the SERS spectra. The green line of the laser (5145 Å in wavelength) was incident on the sample at an angle of about 65° relative to the normal of the sample surface for SERS experiments and was s-polarized. Scattered light was collected using an f/0.95 collection lens and

focused onto the entrance slits of the monochromator. Spectra were obtained using a scan speed of 50 cm^{-1} per minute and a time constant of either 2 or 10 seconds. Plasma lines were removed from the spectra by placing a narrow-bandpass filter between the laser and sample.

Normal Raman spectra were obtained from small amounts of powdered sample supported in a glass capillary tube using the instrument described above and techniques which have been described elsewhere.¹⁰ All of the instrumental parameters were the same as for the SERS spectra except that the slits were set for a spectral width of 5 cm^{-1} .

Specimens for X-ray photoelectron spectroscopy (XPS) were prepared in the following manner. Commercially pure silver foil (2.0 mm thick) obtained from Aldrich was abraded with a series of dry silicon carbide abrasive papers ranging from 240 to 600 grit. After the surface was ground, wet polishing was performed using 14, 0.3, and $0.05 \mu\text{m}$ alumina on Microcloths (Buehler, Inc.) using deionized water as the lubricant. Finally, the resulting mirrors were rinsed in deionized water and blow dry with a stream of nitrogen.

Thick films of adhesive were thermally cured against polished silver substrates at 150°C for 1 hour. The adhesive joints were then immersed in liquid nitrogen, causing delamination to occur near the interface. The resulting substrate and adhesive fracture surfaces were examined by XPS. Two sets of fracture surfaces obtained from two separate joints were analyzed to ensure good reproducibility of the results.

The XPS spectra were acquired using a Perkin-Elmer PHI-5300 XPS spectrometer. Spectra were acquired using Mg $K\alpha$ radiation (15 kV; 20 mA) at a pass energy of 44.75 eV (0.5 eV step; 25 ms dwell time/step) for the survey spectra and 19.75 eV for the high resolution spectra (0.05 eV step; 50 ms dwell time/step). During analysis, the chamber pressure was maintained below 10^{-8} Torr and an electron take-off angle of 45° was used.

The spectra were corrected for charging effects by referencing the carbon 1s hydrocarbon peak to 284.6 eV. Elemental compositions of the various surfaces were determined by integration of the individual elemental peaks. High resolution spectra were analyzed in order to determine the various chemical species present. The individual components in each region were fitted using a 90%/10% Gaussian/Lorentzian peak shape.

In order to identify the positions of the various components in high resolution XPS spectra obtained from the bulk adhesive and fracture surfaces, neat 4,4'-diaminodiphenylsulfone powder (the curing agent) was also analyzed. This procedure allowed the components in the C(1s) peak due to the curing agent in the bulk adhesive to be identified. This information was then used to study the substrate and adhesive fracture surfaces obtained from the adhesive joints.

III RESULTS AND DISCUSSION

The commercial adhesive used in this study was a one-part adhesive system containing an epoxy resin, curing agent, and fillers. In order to identify the epoxy resin and curing agent, the adhesive was extracted with toluene and methylethylketone (MEK). The epoxy was soluble in toluene whereas the epoxy and curing

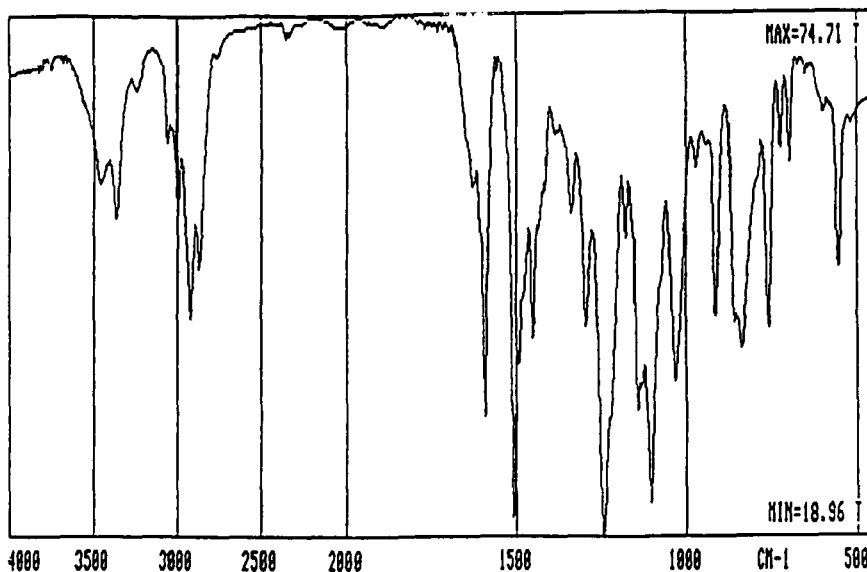


FIGURE 1 Infrared spectrum of compounds extracted from the commercial adhesive using methyl-ethylketone (MEK).

agent were both soluble in MEK. Infrared spectra were obtained from the compounds extracted from the adhesives by toluene and MEK. The spectrum of the toluene extract was mostly that of the epoxy. When the spectrum of the epoxy was subtracted from that of the MEK extract, the spectrum of the curing agent was obtained. The epoxy and curing agent were identified by comparison of their infrared spectra with published spectra of epoxy resins and curing agents.

The transmission infrared spectra of components extracted from the commercial adhesive using MEK and toluene are shown in Figures 1 and 2, respectively. Figure 3 is the difference spectrum obtained by subtracting the spectrum in Figure 2 from that in Figure 1. Since MEK could extract the epoxy and the aromatic amine curing agent but not the fillers, the spectrum in Figure 1 was considered to be characteristic of a mixture of epoxy resins and curing agents. Toluene was a good solvent for epoxy resins but was poor for amine curing agents. The spectrum in Figure 2 was characteristic of the epoxy resin while the difference spectrum in Figure 3 was mostly characteristic of the aromatic amine curing agent.

The infrared spectrum of the epoxy resin in the adhesive system (see Figure 2) was very similar to the infrared spectrum of polyglycidyl ether of phenol-formaldehyde novolac¹¹ and the infrared spectrum of the curing agent was very similar to that of 4,4'-diaminodiphenylsulfone (DADPS) (see Figure 4). These results indicated that the adhesive system consisted of an epoxy/novolac resin and a curing agent identified as 4,4'-diaminodiphenylsulfone (DADPS).

The infrared spectrum of DADPS was dominated by bands assigned to vibrations of the SO_2 bonds and benzene rings (see Figure 4). Tentative assignments of bands in the infrared spectrum of DADPS are summarized in Table I. Strong bands near 1290, 1147, and 552 cm^{-1} were assigned to the asymmetric stretching, symmetric stretching, and deformation modes of SO_2 bonds, respectively.^{12,13} The band near 1108 cm^{-1} was due to the stretching mode of aryl-S bonds. Bands related to benzene

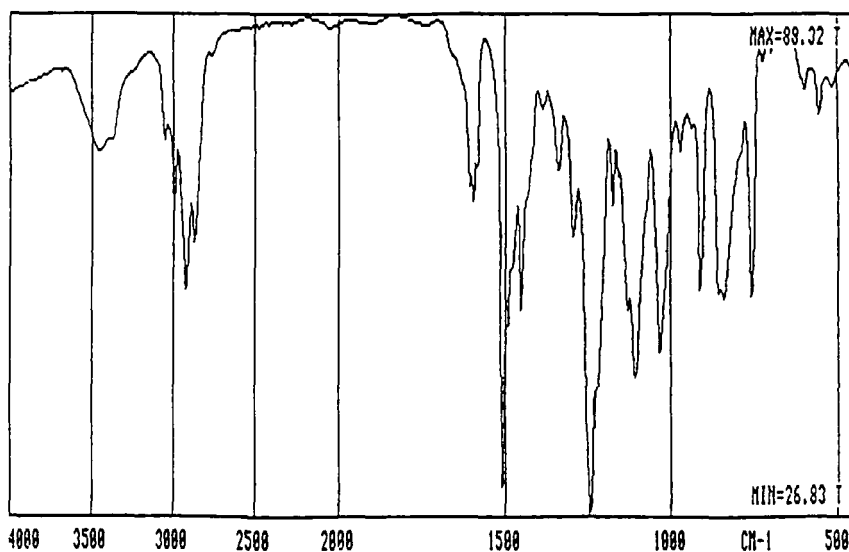


FIGURE 2 Infrared spectrum of compounds extracted from the commercial adhesive using toluene.

rings were assigned by the Wilson numbering system.^{13,14} The strongest band near 1595 cm^{-1} was related to the tangential ring stretching mode $\nu(8a)$ of the benzene rings. Other bands associated with NH_2 bonds were observed near 3464 , 3368 , 3265 , and 1635 cm^{-1} .¹²

The normal Raman spectrum of DADPS is shown in Figure 5 and the tentative band assignments are also summarized in Table I. The normal Raman spectrum of

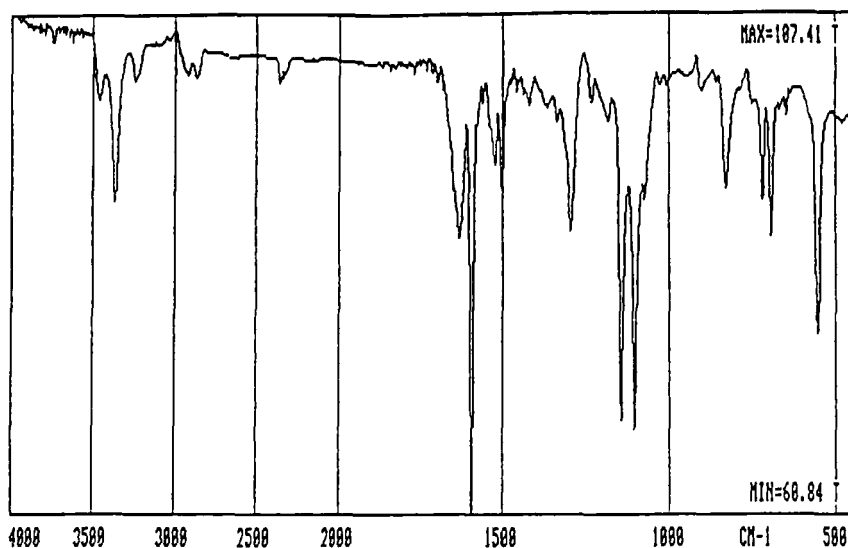


FIGURE 3 Difference spectrum obtained by subtracting the spectrum in Figure 2 from that in Figure 1.

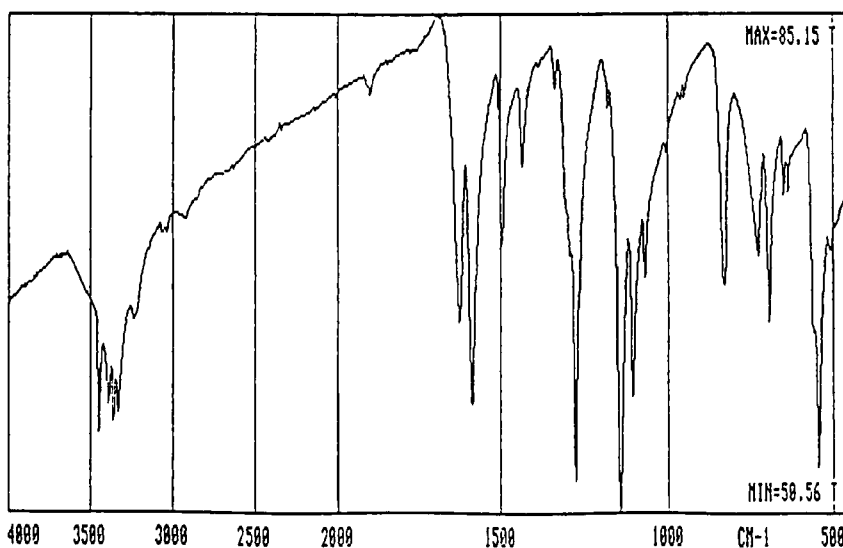


FIGURE 4 Infrared spectrum of 4,4-diaminodiphenylsulfone (DADPS).

DADPS was dominated by two strong bands near 1150 and 1603 cm^{-1} . The band near 1150 cm^{-1} was attributed to the symmetric stretching mode of SO_2 bonds while the strong band near 1603 cm^{-1} was assigned to the $\nu(8a)$ mode of benzene rings. Medium intensity bands near 1118 , 1081 , 846 , and 832 cm^{-1} were related to the stretching mode of aryl-S bonds and to the ring breathing mode $\nu(1)$, the radial ring stretching mode $\nu(6a)$, and the CH out-of-plane bending mode $\nu(17b)$ of benzene

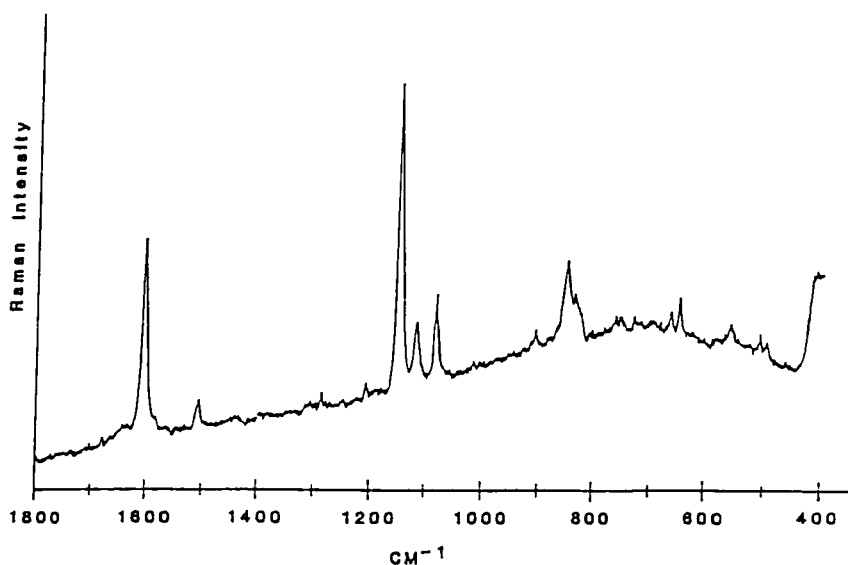


FIGURE 5 Normal Raman spectrum obtained from 4,4-diaminodiphenylsulfone (DADPS).

TABLE I
Tentative band assignments for 4,4'-diaminodiphenylsulfone (DADPS)

IR	NR	SERS	Assignment
3464 (W)			ν_a (NH ₂)
3368 (M)			ν_a (NH ₂)
3268 (W)			ν_s (NH ₂)
1595 (S)	1603 (S)	1602 (S)	ν (8a)
1503 (M)	1504 (W)	1500 (W)	ν (19a)
		1400 (W)	
1295 (M)			ν_a (SO ₂)
	1286 (W)	1280 (W)	
1146 (S)	1149 (S)	1160 (S)	ν_s (SO ₂)
1108 (S)	1117 (W)	1118 (W)	aryl-S
	1081 (M)	1080 (W)	ν (1)
1074 (W)			β (NH ₂)
		980 (W)	sulfate contaminants
		940 (W)	sulfite contaminants
	846 (M)	850 (W)	ν (6a)
830 (M)	832 (W)		ν (17b)
	728 (W)	730 (W)	
721 (W)			ν (4)
694 (M)			ν (12)
	646 (W)	650 (W)	γ_s (NH ₂) and sulfite contaminants
552 (S)	555 (W)	545 (W)	γ_s (SO ₂)

S: strong; M: medium; W: weak.

rings, respectively. Weak bands near 646 and 555 cm⁻¹ were assigned to deformation modes of NH₂ and SO₂ groups, respectively. No effort was made to assign the remaining weak bands in the normal Raman spectrum of DADPS.

Figure 6 shows the SERS spectrum of DADPS spin-coated onto silver island films from 1% solutions in MEK. Generally speaking, the SERS and normal Raman spectra were very similar. The strong band near 1150 cm⁻¹ in the normal Raman spectrum shifted upward to about 1155 cm⁻¹ in the SERS spectrum. Another strong band near 1603 cm⁻¹ in the normal Raman spectrum appeared relatively strong in the SERS spectrum. The signal-to-noise ratio in our SERS spectra was not good enough to distinguish all weak bands from noise. However, most of the weak bands in SERS spectra of DADPS such as those near 1504, 1286, 1117, 1080, 846, 730, 646, and 545 cm⁻¹ were related to vibrational modes of DADPS. The corresponding bands were also present in the normal Raman spectrum of DADPS (see Figure 5 and Table I). A new weak band appeared near 1400 cm⁻¹ in the SERS spectrum. Bands near 640 and 940 cm⁻¹ in SERS spectra of DADPS were probably due to sulfite species which were reduced from residual sulfate ions on the glass during deposition of the silver or during subsequent SERS experiments.¹⁵ When these samples were exposed to the laser, sulfite species were oxidized to form sulfates, resulting in the appearance of the band near 980 cm⁻¹ in SERS spectra.

Figure 7 is the SERS spectrum of the adhesive spun onto silver island films from 2% solutions in MEK from which the insoluble fillers had been removed. This spectrum was obviously dominated by strong bands near 1155 and 1603 cm⁻¹. The SERS spectrum of the adhesive was very similar to the SERS spectrum of DADPS (see Figure 6), implying that DADPS molecules in the adhesive system segregated

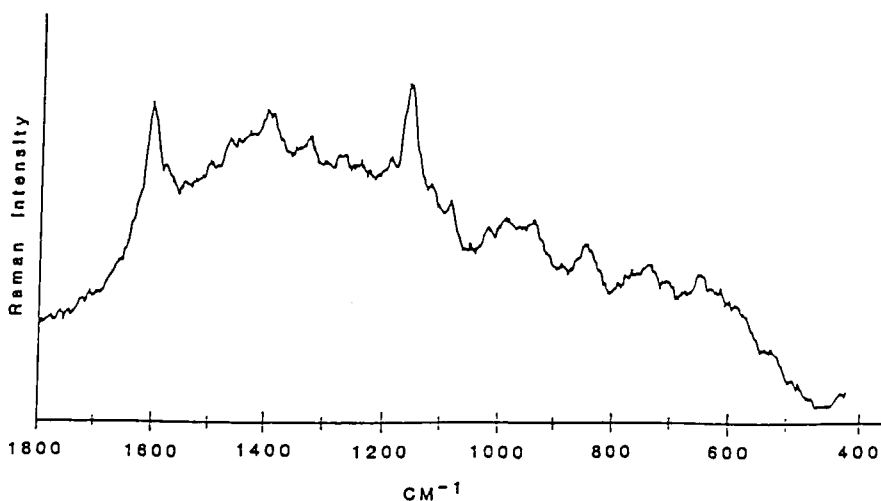


FIGURE 6 SERS spectrum obtained from 4,4-diaminodiphenylsulfone (DADPS) spun onto a silver island film from a 1% solution in MEK.

to the adhesive/silver interphase and were preferentially adsorbed onto the silver substrate. However, very weak bands near 1275 and 925 cm^{-1} , which were likely due to epoxy resins, were observed in SERS spectra of the adhesive, perhaps indicating that minor levels of epoxy resin were also adsorbed on the silver island films. The weight percent of DADPS in the adhesive was less than 5%.¹⁶ This might

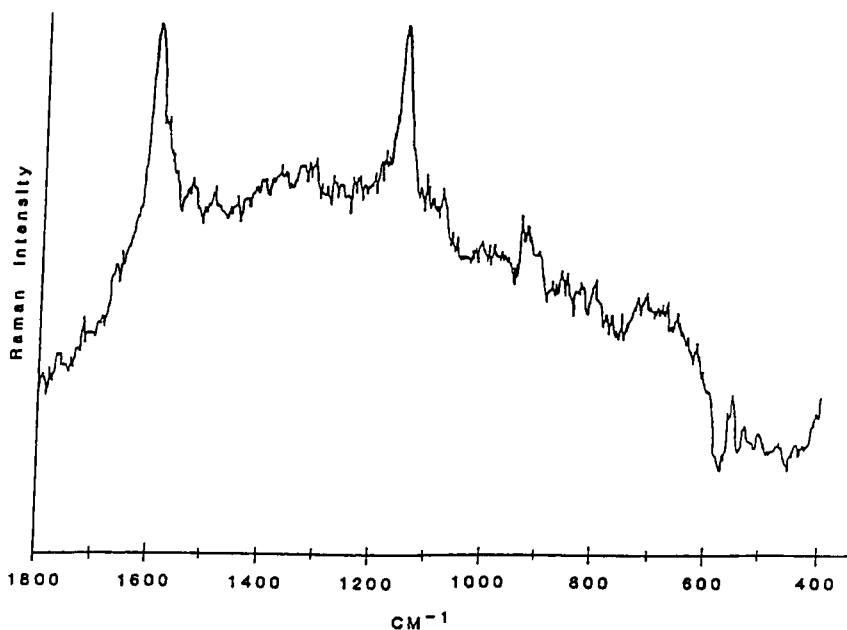


FIGURE 7 SERS spectrum obtained from the commercial adhesive deposited onto a silver island film from a 2% solution in MEK.

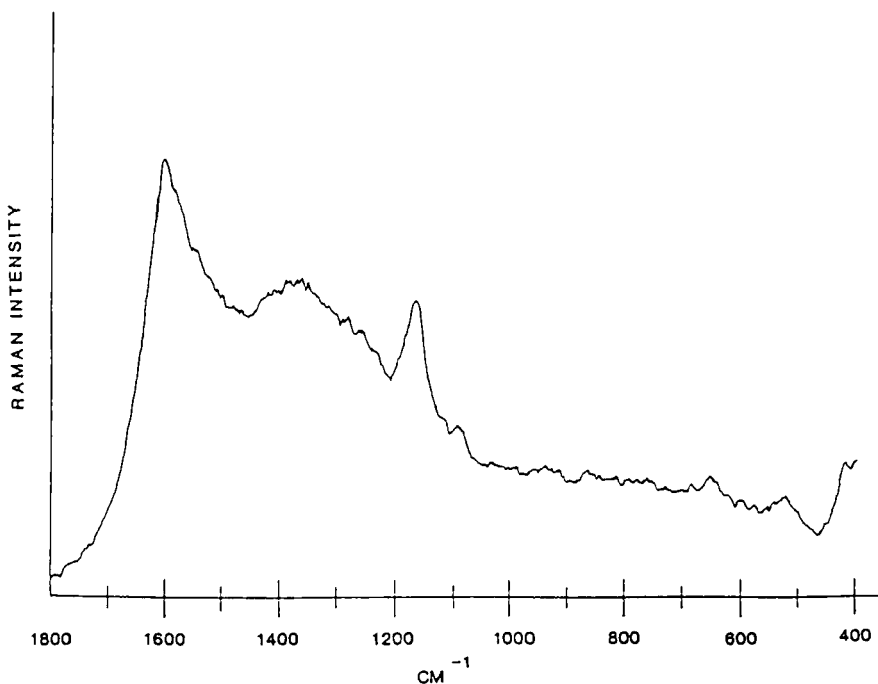


FIGURE 8 SERS spectrum obtained from the commercial adhesive deposited onto a silver island film from a 2% solution in MEK and then cured at 150°C for 1 hour.

indicate that there was insufficient DADPS available to occupy all the SERS-active surface sites, when the thin adhesive films were spun onto silver substrates from a dilute solution (2% by weight).

SERS spectra of thin adhesive films were generally similar to the normal Raman spectrum of DADPS. No significant band shifts or bands related to new chemical species were observed in SERS spectra of the adhesive spun onto silver island films, indicating that there was no strong chemical interaction between adsorbed DADPS and silver substrates. This result was confirmed by XPS as discussed below.

The SERS spectrum obtained from adhesive spun from 2% solution onto silver island films and then thermally cured at 150°C for 1 hour is shown in Figure 8. This spectrum was very similar to the SERS spectrum of the adhesive before thermal treatment (see Figure 7), implying that DADPS molecules were still preferentially adsorbed onto silver island films upon thermal curing. The observation of broad bands near 1380 and 1580 cm^{-1} in this spectrum was attributed to the formation of amorphous graphite species during thermal curing.¹⁷ The band near 1603 cm^{-1} due to $\nu(8a)$ of benzene rings was superimposed on the broad band near 1580 cm^{-1} .

Some information regarding the orientation of DADPS molecules adsorbed onto silver substrates could also be obtained by comparing the relative intensities of some bands in the normal Raman and SERS spectra of DADPS (see Figures 5 and 6) using the surface selection rules for Raman scattering. Several authors have investigated the selection rules for Raman scattering by molecules adsorbed onto metal substrates. Moskowitz developed a theory that was based strictly on electromagnetic effects.¹⁸ According to the theory, modes which are normally allowed for the free

molecule may appear in surface spectra with considerably different intensities. The strongest lines in the Raman spectra of molecules adsorbed onto metal substrates should correspond to modes transforming the same as α_{zz} where z is the coordinate perpendicular to the metal surface. The next most intense lines should correspond to modes transforming the same as α_{xz} and α_{yz} . The weakest lines should correspond to modes transforming as α_{xy} , α_{xx} , and α_{yy} . Modes transforming as α_{zz} and involving atomic motions mostly perpendicular to the surface were predicted to be especially intense.

Modes which are normally forbidden may appear in the Raman spectra of molecules adsorbed on the surfaces of reflecting substrates for two reasons. One is that the high symmetry molecule may become a lower symmetry surface complex. The other is that quadrupole terms may contribute to the molecular polarizability.¹⁹

Differences in relative intensity of several bands in the normal Raman and SERS spectra of DADPS were observed and these differences may be related to the orientation effect of the adsorbed DADPS molecules. DADPS belongs to the point group D_{2h} in which α_{zz} belongs to the symmetry species A_g . The strongest lines in the SERS spectra should correspond to species A_g and involve motions that are largely parallel to the twofold axis $C_2(z)$.

No out-of-plane vibrations were observed to appear with significant intensity in the SERS spectrum of DADPS. As a result, DADPS was not likely to be adsorbed flat down. The strongest band near 1150 cm^{-1} in the normal Raman spectrum appeared relatively weak in the SERS spectrum. This band was assigned to the symmetric stretching mode of SO_2 bonds. If DADPS were adsorbed end-on with an NH_2 group adjacent to the silver surface, the band near 1150 cm^{-1} would not involve motion perpendicular to the surface and would be relatively weak. The band near 1603 cm^{-1} in the normal Raman spectrum was assigned to the mode $\nu(8a)$. This mode would belong to the symmetry species A_g of the point group D_{2h} if DADPS were adsorbed end-on and would be relatively strong in the SERS spec-

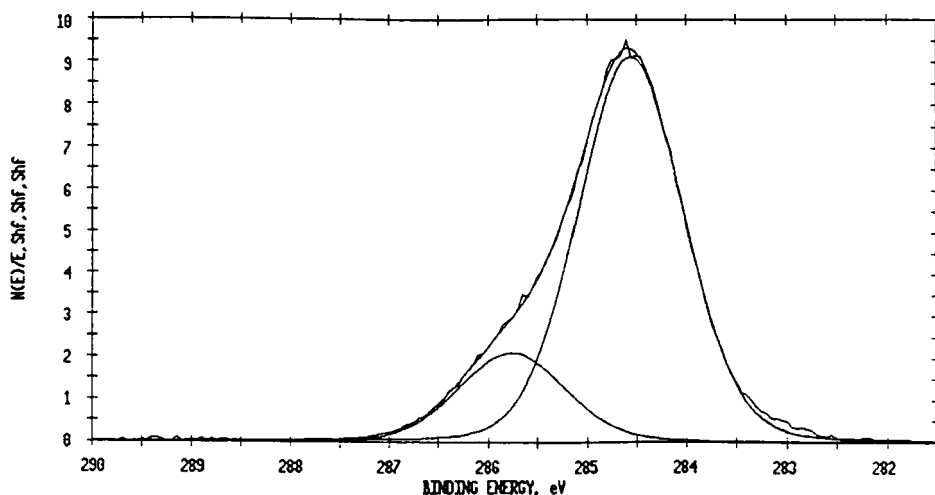


FIGURE 9 C(1s) XPS spectrum obtained from 4,4'-diaminodiphenylsulfone (DADPS).

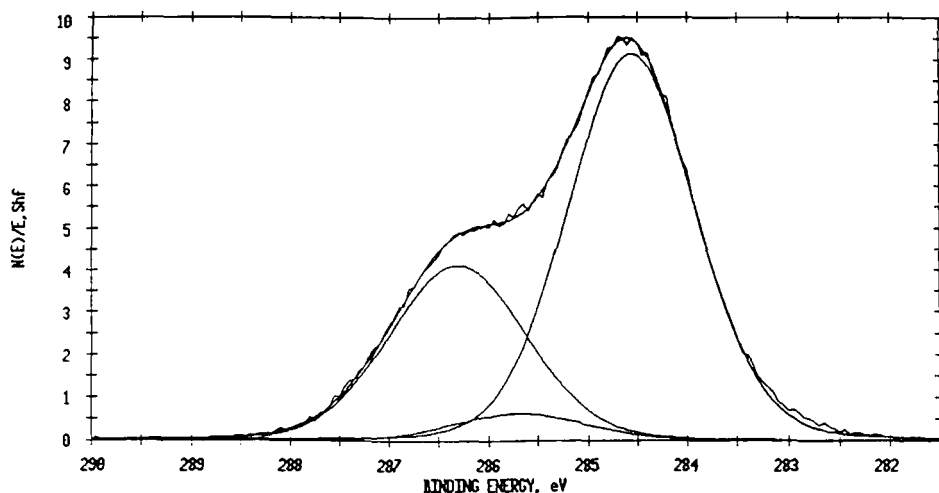


FIGURE 10 C(1s) XPS spectrum obtained from the bulk adhesive.

trum. In fact, the band near 1602 cm^{-1} was one of the strongest bands in the SERS spectrum. These results indicated that DADPS was adsorbed through one NH_2 group with an end-on conformation.

X-ray photoelectron spectroscopy was used to obtain complementary information. The C(1s) spectrum of neat DADPS powder is presented in Figure 9. Considering the chemical structure of DADPS, three carbon species, carbon bonded to carbon, sulfur, and nitrogen, were expected. However, Clark and Thomas²⁰ showed that the substituent effect of sulfur on the C(1s) core levels was quite small (0.4 eV) compared with that of oxygen (1.6 eV). As a result, we assumed that the C(1s) spectrum of the curing agent consisted of only two components, one near 284.6 eV due to carbon bound to carbon and to sulfur and another near 285.8 eV due to carbon bound to nitrogen.

Three components, near 284.6, 285.8, and 286.4 eV were used to fit the C(1s) spectrum of the neat adhesive shown in Figure 10. The component near 284.6 eV was related to carbon bound to carbon, hydrogen, and sulfur while those shifted upward by about 1.2 and 1.8 eV were related to carbon making single bonds with nitrogen and oxygen, respectively. C—O bonds were, of course, characteristic of the epoxy/novolac resin while C—N bonds were characteristic of the DADPS curing agent as discussed above.

XPS spectra of adhesive and substrate fracture surfaces, which were prepared by curing the adhesive against polished silver substrates and then delaminating the adhesive from the substrate by immersion in liquid nitrogen, were also obtained. The C(1s) spectrum obtained from the adhesive fracture surface is shown in Figure 11. This spectrum was considerably different from the C(1s) spectrum of the bulk adhesive (see Figure 10), whereas it was similar to the C(1s) spectrum of DADPS (see Figure 9), indicating that DADPS molecules in the adhesive system segregated to the adhesive/silver interphase and were preferentially adsorbed onto the silver substrate. This result was consistent with those obtained from SERS spectra.

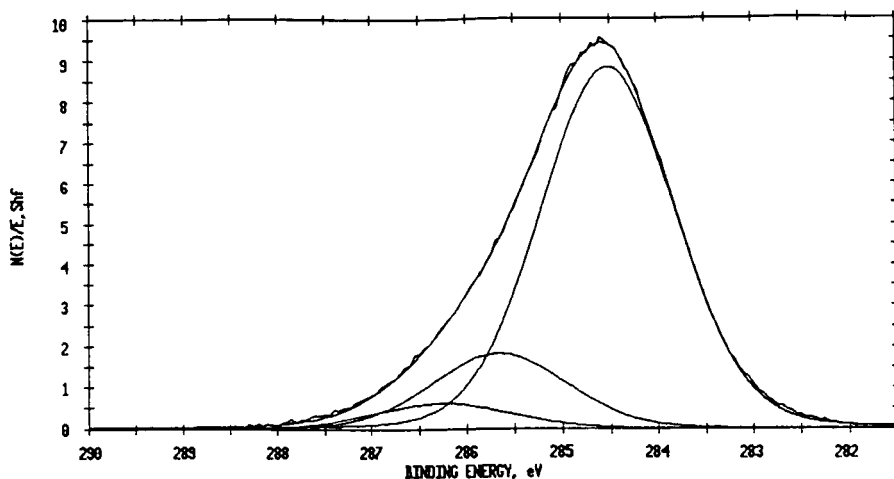


FIGURE 11 C(1s) multiplex spectrum obtained from adhesive fracture surfaces of specimens prepared by curing the adhesive against polished silver substrates.

Three components near 284.6, 285.8, and 286.4 eV were observed in the C(1s) spectrum of the adhesive fracture surface. As described above, the component near 286.4 eV which had a 1.8 eV separation was assigned to carbon bound to oxygen and was characteristic of epoxy resin. This component appeared with medium intensity in the C(1s) spectrum of bulk adhesive (see Figure 10), while it was very weak in the C(1s) spectrum of adhesive fracture surface (see Figure 11). The component near 285.8 eV was assigned to carbon bound to nitrogen and was characteristic of DADPS. This component was stronger in the C(1s) spectrum of the adhesive fracture surface than in the C(1s) spectrum of the bulk adhesive. These results demonstrated that there was a higher concentration of DADPS in the interfacial region than in the bulk of adhesive. However, the observation of the very weak peak near 286.4 eV implied that a trace amount of epoxy resin was likely still retained in the interphase.

As described above, SERS results indicated that an incomplete DADPS coverage on the silver surface had occurred when the thin adhesive films were spun from a dilute solution (2% by weight). However, in XPS investigations, specimens were prepared by curing thick films of as-received adhesives onto silver substrates and then delaminating the adhesive joints to obtain failure surfaces. It is impossible to determine whether the DADPS coverage on the silver surface was complete or not using XPS spectra obtained from the failure surfaces of adhesive joints. The conclusion which can be drawn here is that DADPS was the major component in the interphase and substantially covered the silver surface.

The preferential adsorption of DADPS onto silver substrates was also confirmed by results obtained from the C(1s) spectrum of the silver fracture surface (see Figure 12). Like the case of the adhesive fracture surface, the spectral features of the C(1s) spectrum of the silver fracture surface were more similar to the C(1s) spectrum of pure DADPS than to the C(1s) spectrum of the bulk adhesive. Three components near 284.6, 285.8, and 286.4 eV were observed in Figure 12. The intensity of the component near 285.8 eV, which was characteristic of C—N bonds in the curing

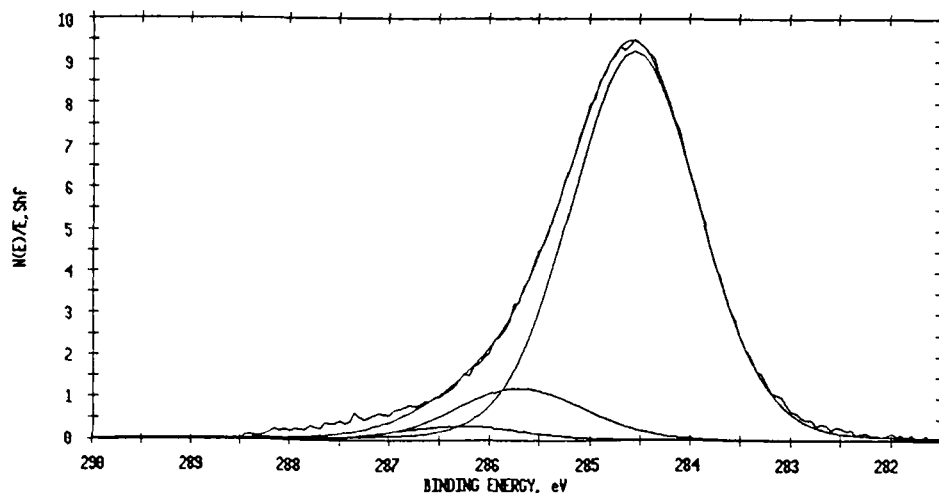


FIGURE 12 C(1s) multiplex spectrum obtained from silver fracture surfaces of specimens prepared by curing the adhesive against polished silver substrates.

agent, was much greater than that of the component near 286.4 eV, which was characteristic of the epoxy, indicating the segregation of DADPS molecules near the adhesive/silver interfacial region.

Because of the similarity of C(1s) spectra of pure DADPS, adhesive and substrate fracture surfaces (see Figures 9, 11, and 12, respectively), it was considered that a thin interfacial layer, which was enriched in DADPS molecules, was formed between the silver substrate and the bulk adhesive and that failure occurred within this interfacial layer. However, the component near 285.8 eV was weaker in the C(1s) spectrum of the silver fracture surface than in the C(1s) spectrum of the adhesive fracture surface, perhaps indicating that failure of the adhesive joints was close to the silver substrate.

Consistent results were also obtained by comparing atomic concentrations for the bulk adhesive with those for the adhesive and silver fracture surfaces (see Table II). For the bulk adhesive, 69.2% C, 24.5% O, 5.0% Si, 0.9% N, and 0.4% S were detected. There were 74.3% C, 20.0% O, 1.3% Si, 2.7% N, 1.5% S, and 0.2% Ag on the adhesive fracture surface, while 53.6% C, 9.8% O, 1.6% N, 0.8% S, and 34.2% Ag were observed on the silver fracture surface. The N and S atomic concentrations for both the adhesive and silver fracture surfaces were greater than those

TABLE II
Atomic concentrations of the bulk adhesive and fracture surfaces of the adhesive cured against polished silver substrate. The take-off angle was 45°

	Atomic Concentration (%)					
	C	O	N	S	Si	Ag
Bulk Adhesive	69.2	24.5	0.9	0.4	5.0	—
Adhesive Fracture Surface	74.3	20.0	2.7	1.5	1.3	0.2
Silver Fracture Surface	53.6	9.8	1.6	0.8	—	34.2

for the bulk adhesive, indicating that the interphase had a composition that was enriched in DADPS.

For the silver fracture surface, 1.6% N and 0.8% S were detected. Less N and S were observed on the silver fracture surface than on the adhesive fracture surface (2.7% N and 1.5% S). It was thus considered that the locus of failure was partially within the DADPS-rich layer and very close to the silver substrate. This was supported by the observation of 0.2% Ag on the adhesive fracture surface and 34.2% Ag on the silver fracture surface (see Table II). The Ag atomic concentration for the polished silver substrate without coating any organic compounds was 35.3%.

As described above, SERS results indicated that there was no chemical interaction between preferentially adsorbed DADPS molecules and silver substrates. XPS spectra also showed consistent results. The overall line shapes of the C(1s) spectra of the adhesive and metal fracture surfaces were similar to that of pure DADPS. No band shifts or new bands due to new chemical species were observed in the C(1s) spectra of fracture surfaces, implying that no chemical interaction took place between DADPS and silver substrates. These results were also confirmed when the N(1s) and S(2p) spectra of pure DADPS and the fracture surfaces were compared. The N(1s) and S(2p) spectra of pure DADPS were identical to those of the fracture surfaces. A single component near 399.6 eV was observed in the N(1s) spectra and assigned to nitrogen bonded to carbon. A doublet near 167.4 and 168.6 eV with a separation of 1.2 eV was observed in the S(2p) spectra and assigned to sulfur doubly bound to two oxygen atoms. Moreover, there were no differences between the Ag Auger spectra of the silver fracture surface and the silver substrate without organic coating, further supporting the conclusion that DADPS was not chemisorbed on the silver substrate.

Another possible interpretation of the XPS data was considered. If strong interaction did occur between DADPS and silver but the number of strongly interacting species was small, the overall line shapes of the peaks in the XPS spectra might not be altered significantly. However, this possibility was excluded by considering XPS spectra obtained from a very thin film (about 10 Å as measured by ellipsometry) of neat DADPS spun onto a silver substrate from a very dilute solution. The N(1s) and S(2p) spectra obtained from the thin DADPS film were very similar to those of the neat DADPS. A single component near 399.5 eV was observed in the N(1s) spectra. A doublet near 167.6 and 168.8 eV with a separation of 1.2 eV was observed in the S(2p) spectra. There were also no differences between the Ag Auger spectra of the bare silver substrate and the substrate with the very thin film of DADPS. These results indicated again that no strong chemical interaction occurred between DADPS and silver substrates.

SERS data also supported the above conclusions. SERS is an interfacial effect and extremely surface-sensitive. Even if a monolayer of organic compounds were chemisorbed onto the silver surface, considerable changes due to such a strong interaction were expected to be observed in the SERS spectra. For example, Tsai et al²¹ used SERS to investigate the adsorption of model compounds for polyimides onto silver island films. One of the polyimide model compounds, pyromellitic diimide (PMDI), was found to be chemisorbed onto the silver substrate. This was evident from the observation of a strong band near 690 cm⁻¹ in the SERS spectrum

of ultra-thin PMDI films (less than 10 Å). This band was assigned to the deformation mode of CNC groups which shifted upward from near 650 cm^{-1} in the normal Raman spectrum of PMDI.

No significant band shifts or bands related to new chemical species were observed in our SERS spectra of the thin adhesive films (see Figures 7 and 8), indicating that there was no strong chemical interaction between adsorbed DADPS and silver substrates. It is likely that DADPS was physisorbed on the silver substrates. It is likely that DADPS was physisorbed on the silver substrates. It is also possible that DADPS interacted weakly with silver substrates, resulting in small position shifts of bands in XPS and SERS spectra. However, these changes were not discernable in our XPS and SERS measurements.

Absence of strong interaction between DADPS and silver may explain that fracture of the adhesive joints was near the interphase between the DADPS-rich layers and the silver substrates and partially within DADPS-rich layers.

IV CONCLUSIONS

SERS spectra obtained from an epoxy/DADPS adhesive deposited onto silver island films were identical to SERS spectra obtained from 4,4'-diaminodiphenylsulfone (DADPS) curing agent, indicating that DADPS in the adhesive segregated to the interphase and was preferentially adsorbed onto the silver substrate.

Differences in the relative intensity of several bands in the normal Raman and SERS spectra of DADPS were observed and were explained by the orientation effect of adsorbed DADPS molecules. The band near 1603 cm^{-1} , which was assigned to a tangential ring stretching mode of benzene rings, appeared relatively strong in SERS spectra of DADPS while the band near 1150 cm^{-1} , which was assigned to the symmetric stretching of SO_2 bonds, was relatively weak. These results implied that DADPS was oriented end-on with one of the NH_2 groups adjacent to the silver surface.

X-ray photoelectron spectroscopy (XPS) provided consistent results. The C(1s) spectra of the adhesive and silver fracture surfaces of specimens prepared by curing the adhesive against silver substrates were more similar to the C(1s) spectra of DADPS than to those of the bulk adhesive. This observation confirmed that preferential adsorption of DADPS from the adhesive system onto the silver substrate had occurred.

C(1s) spectra obtained from the adhesive fracture surface were similar to those of the silver fracture surface. It was thus concluded that a thin DADPS-rich interphase was formed between the bulk adhesive and the silver substrate and that the locus of failure was partially within this layer. The observation of less N and S atoms on the silver fracture surface than on the adhesive fracture surface, and the observation of 0.2% and 34.2% silver on the adhesive and silver fracture surfaces, respectively, indicated that failure of the adhesive joints was within the interphase but near the silver substrates.

No evidence for chemisorption of DADPS onto silver substrates was observed from SERS or XPS spectra, probably explaining that failure of the adhesive joints was close to the DADPS-rich layer/silver interphase.

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