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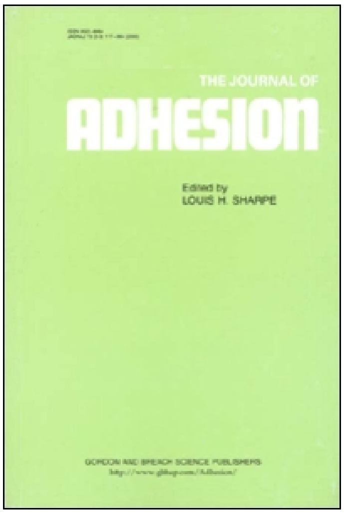

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Surface-Enhanced Raman Scattering from Polyimide Model Compounds on Functionalized Metal Surfaces. Part I: Phthalic Anhydride/ 4-Aminophenyldisulfide/Gold

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The interphase between a polyimide and a metal substrate was modeled by depositing phthalic anhydride (PA) onto a gold substrate pretreated with 4-aminophenyldisulfide (APDS) and then curing in a mixture of acetic anhydride and pyridine or triethylamine. Surface-enhanced Raman scattering (SERS) and reflection-absorption infrared spectroscopy (RAIR) were used to characterize the model interphases. It was found that APDS was adsorbed dissociatively onto Au substrates through the sulfur atoms. The average tilt angle for APDS molecules adsorbed onto gold substrates was determined, using RAIR, to be approximately 46°. However, there was no preferred rotational angle of the adsorbed APDS molecules about the long molecular axes. When PA was deposited onto APDS-primed Au substrates, anhydride groups of PA reacted with amino groups of APDS to form amic acids. Curing these thin amic acid films in acetic anhydride catalyzed with pyridine produced mainly isoimide species, while curing in the presence of triethylamine gave imide as the major product. The relative amount of isoimide and imide thus depended strongly on the catalyst used in the chemical curing processes.

KEY WORDS surface-enhanced Raman scattering; SERS; reflection-absorption infrared spectroscopy; interphase; 4-aminophenyldisulfide; phthalic anhydride; imide; isoimide.

INTRODUCTION

Polyimides are being increasingly used in microelectronics and composites due to their excellent thermal and mechanical stability, low dielectric constants, and chemical resistance. Good adhesion of polyimides to other materials such as metals and graphite is essential for these applications. It is generally believed that the performance and stability of polyimide composites and adhesive joints are closely related to the molecular structure of the polyimide/substrate interphase. As a result, there has been a great deal of interest in determining the structure of polyimide/substrate interphases.

However, there are few analytical techniques available for determining the structure of interphases that may be only a few molecular layers in thickness and buried between two phases that are thick on a macroscopic scale. One approach to this problem that is frequently taken is to separate the polymer from the substrate and to use surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) to examine the fracture surfaces. Another approach is to reduce the thickness of the polymer to such an extent that surface analysis techniques such as XPS, SIMS, and reflection-absorption infrared spectroscopy (RAIR) can be used to examine the interphase.

We have been interested in developing analytical techniques that can be used for *in-situ*, non-destructive characterization of polymer/substrate interphases. In that regard, surface-enhanced Raman scattering (SERS) is a technique that has interesting capabilities. SERS is a phenomenon in which the Raman scattering cross section of molecules adjacent to the roughened surfaces of metals such as silver, copper, and gold is enhanced as much as 10^6 compared with its value for normal Raman scattering. The enhancement is very large at the metal surface but decreases rapidly as a function of distance away from the surface and there is litttle enhancement for molecules that are more than a few molecular layers away from the metal surface. As a result, SERS is surface-selective and can be used for non-destructive characterization of polyimide/metal interphases.

We have already used SERS to investigate the molecular structure of interphases formed by curing the polyamic acid of pyromellitic dianhydride (PMDA) and oxydianiline (ODA)[1], and the polyamic acid of PMDA and 2,2-bis[4(4-aminophenoxy)-phenyl]-hexafluoropropane (4-BDAF)[2] against silver substrates. It was concluded that acid groups in the PMDA moieties of both polyamic acids formed carboxylate salts with silver ions from the substrate, thus inhibiting curing of the polymer adjacent to the substrate. Subsequently, we reported SERS and RAIR results obtained from polyimide/Au and polyimide/Cu systems[3]. These results indicated that large amounts of carboxylate salts were formed on the copper surface, resulting in a partial cure of polyamic acid films on copper substrates. However, only trace levels of carboxylates were detected on the gold surface and the polyamic acid was highly cured. The extent of carboxylate formation on silver substrates was intermediate between those on copper and gold substrates.

The purpose of this paper is to investigate the interaction between polyimide model compounds and organosulfur functionalized metal surfaces using SERS and RAIR. A few investigations using RAIR and XPS to study interactions between polyamic acids and aminosilane-primed substrates have been reported.[4-9] Grunze also reported somewhat related studies using second harmonic generation to characterize interphases between polyamic acids from PMDA and 4-aminophenyldisulfide and metals.[10] However, to our best knowledge, there have been no previous SERS investigations of interphases between polyamic acids or their model compounds and derivatized metal substrates.

In this research, phthalic anhydride (PA) was selected as a polyimide model compound, while 4-aminophenyldisulfide (APDS) was used to introduce amino groups onto gold surfaces. Thus, the model system discussed in the present paper consists of a top layer of PA, intermediate layer of APDS, and a gold substrate and it will be referred to as the PA/APDS/Au system.

Results obtained from SERS and RAIR indicated that APDS was adsorbed dissociatively onto Au substrates. The orientation of adsorbed APDS molecules was determined quantitatively using infrared spectroscopy. When PA was deposited onto APDS-treated gold substrates, anhydride groups of PA reacted with amino groups of APDS to form amic acids. Chemical curing of these amic acid films in mixtures of acetic anhydride and pyridine or triethylamine resulted in formation of isoimide and imide. The relative amounts of isoimide and imide formed on gold substrates depended strongly on the catalyst used for the chemical curing.

EXPERIMENTAL

Gold substrates were prepared for SERS investigations as described below. Glass slides were cleaned by immersion in 0.1N NaOH aqueous solutions for 1 hour and rinsed in 0.1N HCl aqueous solutions for another hour. These glass slides were then rinsed ultrasonically in distilled-deionized water, blown dry with nitrogen, cleaned ultrasonically in absolute ethanol several times, and again blown dry with nitrogen.

The clean glass 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. Gold wires wrapped around resistively-heated tungsten filaments were then slowly heated to evaporate gold island films onto the glass slides at a rate of approximately 0.2 Å/s. The thickness of the gold island films was controlled at about 65 Å using a quartz crystal oscillator thickness monitor.

4-Aminophenyldisulfide (APDS), phthalic anhydride (PA), acetic anhydride, pyridine, and triethylamine were obtained from Aldrich Chemical Co. and used as-received. Monolayers of APDS were prepared by immersing a gold island film into a 0.01% solution of APDS in ethanol for 10 minutes, followed by rinsing with ethanol extensively. After that, organosulfur-coated gold substrates were immersed in a 0.1% solution of PA in ethanol for 24 hours and then rinsed with ethanol again. PA-coated specimens were then immersed in mixtures of acetic anhydride and pyridine or triethylamine (1:1 ratio by volume) for 24 hours.

All SERS spectra were obtained in a nitrogen atmosphere using a spectrometer equipped with a Spex 1401 double monochromator, a Hamamatsu R943-02 photomultiplier, a Stanford Research Model 400 gated photon counter interfaced to a Hewlett–Packard Vectra computer, and a Lexel 3000 krypton-ion laser. The slit setting of the monochromator provided a spectral resolution of about 10 cm^{-1} for the SERS spectra. The red line of the laser (6471 Å) was incident on the sample at an angle of about 65° relative to the normal to the sample surface for SERS experiments and was s-polarized. The laser power used for SERS experiments was between 10 and 50 mW. 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 23 cm^{-1} per minute. Plasma lines were removed from the spectra by placing a narrow-bandpass filter between the laser and sample. Normal Raman spectra of APDS were obtained from small amounts of APDS supported in a glass capillary tube using the instrument described above. All of the instrumental parameters were the same as used for the SERS spectra except that the slits were set for a spectral width of 5 cm^{-1}.

Similar procedures were used to prepare samples for RAIR experiments except that thick Au films were used as substrates instead of Au island films. Thick Au films (several thousand angstroms) were prepared by thermally evaporating Au onto clean glass slides. RAIR spectra were obtained using a Perkin–Elmer Model 1800 Fourier-transform infrared spectrophotometer and external reflection accessories provided by

Harrick Scientific Co. One reflection at an angle of 78° was used in all cases. Spectra were collected in the quantitative mode at a resolution of 4 cm^{-1}. Seven hundred and fifty scans were averaged for each spectrum collected. The spectra presented in this paper are difference spectra obtained by subtracting spectra of bare substrates from spectra of film-covered substrates.

Transmission infrared spectra of APDS were obtained using the same spectrophotometer. Samples were prepared by mixing a small amount of APDS powder with KBr powder and then pressing the mixture into a clear pellet under high pressure.

The thickness of the organic films deposited on gold substrates was determined by ellipsometry. Organic films were deposited onto thick gold films using the same procedures as those used to prepare SERS and RAIR specimens. The thickness of the films was measured using a Rudolph Research Model 436 ellipsometer to examine the metal substrates before and after deposition of the organic films.

RESULTS AND DISCUSSION

The normal Raman spectrum obtained from 4-aminophenyldisulfide (APDS) is shown in Figure 1. For convenience, the observed bands and their assignments are summarized in Table I. The strong band near 480 cm^{-1} was assigned to the S—S stretching mode, while the weak band near 1637 cm^{-1} was assigned to the deformation mode of NH_2 groups.[11] The remaining bands were related to vibrational modes of para-substituted benzene rings and were assigned using the Wilson numbering system.[12-13] Storng bands near 1100 and 1603 cm^{-1} were due to the ring breathing mode $\nu(1)$ and the C—C stretching mode $\nu(8a)$, respectively. Weak bands near 1506, 1302, 1189, 1018,

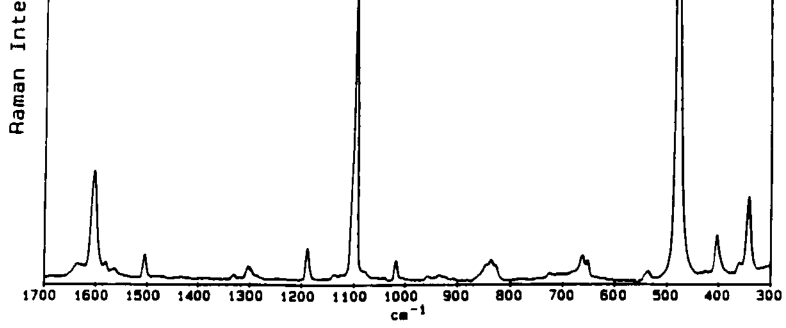

FIGURE 1 Normal Raman spectrum obtained from 4-aminophenyldisulfide (APDS).

TABLE I
Tentative band assignments for 4-aminophenoldisulfide (APDS)

NR (cm^{-1})	IR (cm^{-1})	SERS (cm^{-1})	RAIR (cm^{-1})	Assignments
	3418 (M)			$\nu_{as}(NH_2)$
	3335 (M)			$\nu_S(NH_2)$
1637 (W)	1626 (M)		1623 (M)	$\beta_S(NH_2)$
1603 (M)	1592 (S)	1600 (S)	1586 (S)	ν(8a), C—C stretching
1582 (W)				ν(8b), C—C stretching
1506 (W)	1491 (S)	1505 (W)	1490 (S)	ν(19a), C—C stretching
	1423 (W)		1423 (W)	ν(19b), C—C stretching
1302 (W)	1280 (M)		1288 (M)	ν(13), C—X stretching
1189 (W)	1176 (M)	1185 (W)	1177 (W)	ν(9a), C—H in-plane bending
	1123 (W)			ν(18b), C—X in-plane bending
1100 (S)	1085 (W)	1090 (S)	1075 (W)	ν(1), radial skeletal vib.
1018 (W)	1008 (W)	1020 (W)	1008 (W)	ν(18a), C—X in-plane bending
836 (W)	832 (W)	836 (W)	840 (W)	ν(6a), radial skeletal vib.
	822 (M)		821 (W)	ν(17b), C—H out-of-plane vib.
660 (W)		663 (W)		ν(12), radial skeletal vib.
480 (S)	517 (S)			ν(S—S)
403 (W)		404 (W)		ν(7a), C—X stretching + $\nu(NH_2)$
342 (W)				ν(10b), out-of-plane vib.

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

836, 660, 403, and 342 cm^{-1} were assigned to ν(19a), ν(13), ν(9a), ν(18a), ν(6a), ν(12), ν(7a), and ν(10b), respectively. Vibrational modes associated with aryl-S bonds were coupled with ring modes so that no distinct aryl-S vibrations were observed.

SERS spectra obtained from APDS monolayers adsorbed onto gold island films are shown in Figure 2. Significant differences were observed when the normal Raman and

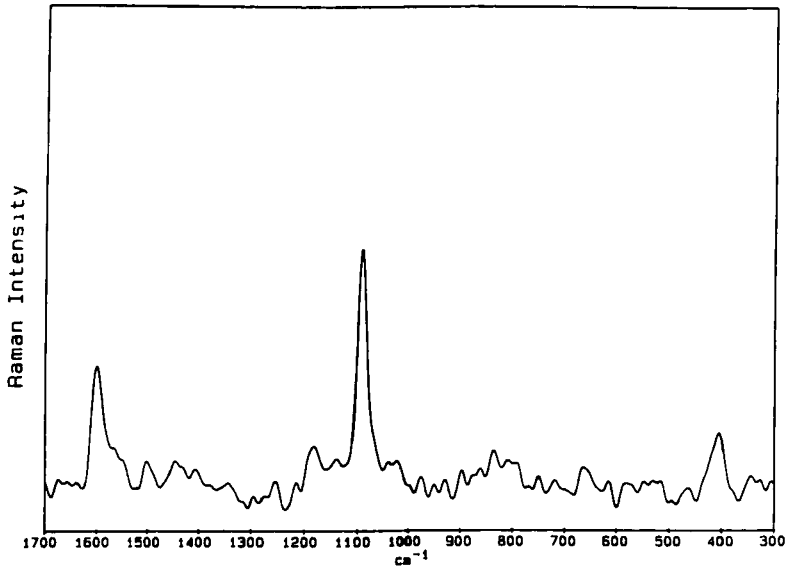

FIGURE 2 SERS spectrum obtained from an APDS monolayer adsorbed onto a gold island film.

SERS spectra of APDS were compared. The strong band near 480 cm^{-1}, which was assigned to the S—S stretching mode, disappeared in the SERS spectrum, indicating that S—S scission occurred upon adsorption of APDS onto Au. The band due to $\nu(1)$ shifted downward from 1100 to 1090 cm^{-1}. These results indicated that APDS was adsorbed dissociatively through the S atom.

No band due to S—Au bonds was observed between 150–400 cm^{-1} in SERS spectra of APDS. However, formation of S-metal bonds between organic sulfides and metals such as Au and Ag has been reported by several authors using SERS[14–16] and XPS.[17–18] These authors also observed the cleavage of S—S bonds and the shift of substituent-sensitive ring vibrations such as the ring breathing mode $\nu(1)$ in their SERS spectra.[14–16] The shift in position of substituent-sensitive ring modes was usually explained as due to a change of environment for adsorbed molecules.

The transmission infrared spectrum obtained from APDS is shown in Figure 3. The observed bands and their assignments are also summarized in Table I. The band near 1626 cm^{-1} was assigned to the bending mode of NH_2 groups.[11] Other bands were related to vibrational modes of para-substituted benzene rings and were also assigned using the Wilson numbering system[12–13] (see Table I). Again, no distinct bands related to C—S bonds could be assigned in the infrared spectra.

A RAIR spectrum obtained from an APDS monolayer deposited onto a Au substrate is shown in Figure 4. When this spectrum was compared with the transmission infrared spectrum of APDS, some differences were observed. Several substituent-sensitive ring modes shifted in frequency. For example, the band near 1280 cm^{-1}, which was assigned to $\nu(13)$, the C—X in-plane bending mode, shifted upward to about 1288 cm^{-1} in the RAIR spectra of APDS. Bands near 1085 and 832 cm^{-1}, which were assigned to $\nu(1)$ and $\nu(6a)$, shifted to about 1075 and 840 cm^{-1}, respectively. These results again suggested that cleavage of S—S bonding took place and the APDS was chemisorbed through the S atom.

The orientation of APDS molecules adsorbed onto the Au substrate was determined by comparing the relative intensities of several bands in the normal Raman and SERS

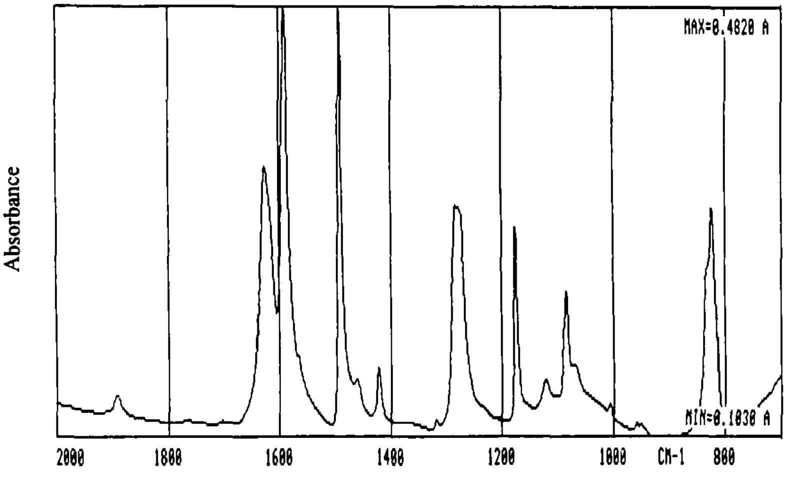

FIGURE 3 Transmission infrared spectrum obtained from APDS.

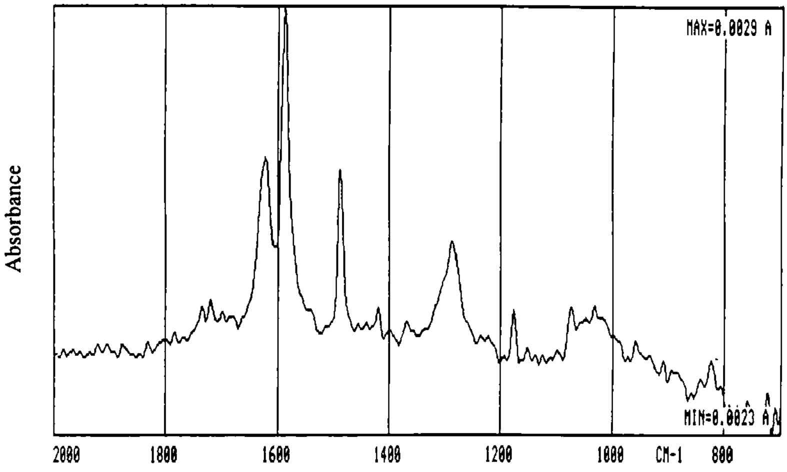

FIGURE 4 RAIR spectrum obtained from an APDS monolayer adsorbed onto a thick gold film.

spectra of APDS using the surface selection rules. Several authors have investigated the selection rules for Raman scattering by molecules adsorbed onto metal substrates.[19-21] Moskovits developed a theory that was based strictly on electromagnetic mechanisms.[19] According to the theory, modes involving atomic motions mostly perpendicular to the surface were predicted to be stronger in the surface spectra, while those involving atomic motions mostly parallel to the surface were expected to become weaker.

The band near 342 cm^{-1} in the normal Raman spectrum of APDS was assigned to ν(10b), the out-of-plane vibrational mode of benzene rings. This band became much weaker in the SERS spectra of APDS, indicating that APDS was probably adsorbed through the S atom with a conformation in which the long molecular axis tilted away from the perpendicular to the metal surface by a certain angle. However, no significant differences in relative intensity of the remaining bands in the normal Raman and SERS spectra of APDS were observed. Thus, no further information regarding the orientation could be obtained from SERS spectra. RAIR was used to determine the tilt angle of APDS adsorbed on the gold surface.

RAIR can be used for quantitative determination of the orientation of molecules adsorbed on reflective surfaces. Bands corresponding to vibrational modes having transition moments perpendicular to the substrate appear with enhanced intensity in RAIR spectra, while those with transition moments parallel to the surface appear with reduced intensity. The band intensities are thus orientation-dependent and can give information about the tilt and rotation angles of molecules adsorbed on metal substrates.

Let us define laboratory coordinates (see Chart I) so that z is the direction perpendicular to the surface, while x and y represent directions in the plane parallel to the surface. The angle between the long axis of the adsorbed molecules and the z coordinate is then defined as θ (*i.e.*, tilt angle of the long molecular axis away from the surface normal). ϕ is the angle between the molecular plane and the x-z plane (*i.e.*, rotation

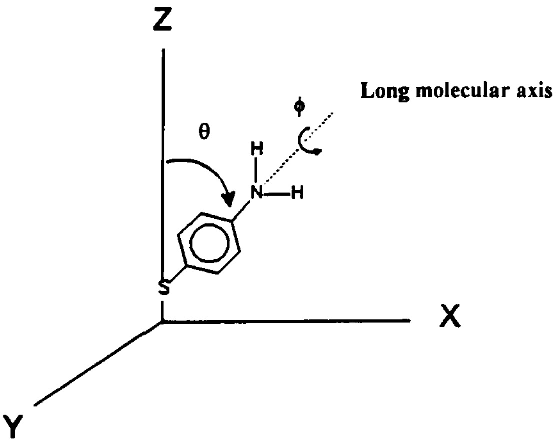

CHART I The tilt angle θ and rotation angle ϕ of 4-aminophenyldisulfide (APDS) molecules adsorbed on the gold surface.

angle of the molecule about the long molecular axis). By calculating the intensity ratios of some bands in RAIR and transmission IR spectra, θ and ϕ can be obtained using equations (1) and (2).[22-23]

$$A_{\parallel}(R)/A^{i}_{\perp}(R) = [A_{\parallel}(T)/A^{i}_{\perp}(T)]\ [\cot^2\theta/\cos^2\phi] \tag{1}$$

$$A_{\parallel}(R)/A^{0}_{\perp}(R) = [A_{\parallel}(T)/A^{0}_{\perp}(T)]\ [\cot^2\theta/\sin^2\phi] \tag{2}$$

where

$A_{\parallel}(R)$: absorbance of a band in RAIR spectra having the dipole moment parallel to the long molecular axis.

$A^{i}_{\perp}(R)$: absorbance of a band in RAIR spectra having the dipole moment perpendicular to the long molecular axis and in the molecular plane.

$A^{0}_{\perp}(R)$: absorbance of a band in RAIR spectra having the dipole moment perpendicular to the long molecular axis but out of the molecular plane.

$A_{\parallel}(T)$: absorbance of a band in the transmission IR spectra (isotropic spectra) having the dipole moment parallel to the long molecular axis.

$A^{i}_{\perp}(T)$: absorbance of a band in transmission IR spectra (isotropic spectra) having the dipole moment perpendicular to the long molecular axis and in the molecular plane.

$A^{0}_{\perp}(T)$: absorbance of a band in transmission IR spectra (isotropic spectra) having the dipole moment perpendicular to the long molecular axis but out of the molecular plane.

In order to use equations (1) and (2) for the calculation of tilt and rotation angles, it is necessary to choose two pairs of bands in which the dipole moments of bands in each pair are perpendicular to each other (one parallel to the long molecular axis, the other perpendicular to the long axis). Bands near 1491, 1423, and 822 cm^{-1} were thus selected for the calculation of orientation. The band near 1491 cm^{-1} was assigned to the ring C—C stretching mode ν(19a) which has the dipole moment mostly parallel to the long molecular axis, whereas the band near 1423 cm^{-1} was assigned to another ring C—C stretching mode ν(19b) which has the dipole moment mostly perpendicular to the long molecular axis and in the molecular plane. Intensity ratios of these two bands (*i.e.*, $A_{\|}(R)/A^{i}_{\perp}(R)$ and $A_{\|}(T)/A^{i}_{\perp}(T)$) can be used for equation (1). The band near 822 cm^{-1} was attributed to the ring out-of-plane vibrational mode ν(17b) which has the dipole moment mostly perpendicular to the long molecular axis but out of the molecular plane. Intensity ratios of bands near 1491 and 822 cm^{-1} (*i.e.*, $A_{\|}(R)/A^{0}_{\perp}(R)$ and $A_{\|}(T)/A^{0}_{\perp}(T)$) can be used for equation (2).

A tangent-line technique was used to draw the base line for bands near 1491, 1423, and 822 cm^{-1} in both transmission IR and RAIR spectra of APDS. The absorbance ratios, including $A_{\|}(R)/A^{i}_{\perp}(R)$, $A_{\|}(T)/A^{i}_{\perp}(T)$, $A_{\|}(R)/A^{0}_{\perp}(R)$, and $A_{\|}(T)/A^{0}_{\perp}(T)$ were calculated to be approximately 5.06, 2.84, 3.58, and 1.94, respectively. The tilt and rotation angles were then calculated to be approximately 46° and 45°, respectivley. These results indicated that APDS was adsorbed through the S atom with the long molecular axis tilted away from the surface normal about 46°. However, the calculated rotation angle was equal to the average value (45°), probably indicating that there was no preferred rotational angle of adsorbed APDS about the long molecular axes.

It should be noted that the theoretical length of APDS molecules was estimated to be approximately 8 Å. However, taking into account the average tilt angle of APDS, the theoretical height of adsorbed APDS was about 6 Å. These values were very close to the thickness of APDS monolayers deposited onto Au substrates (approximately 7 Å as measured by ellipsometry), indicating that there was only a monolayer coverage of APDS on Au.

Figure 5 shows a SERS spectrum obtained from a sample prepared by immersing an APDS treated Au island film in a 0.1% phthalic anhydride (PA) solution for 24 hours and then rinsing with ethanol. Some differences were observed between this spectrum

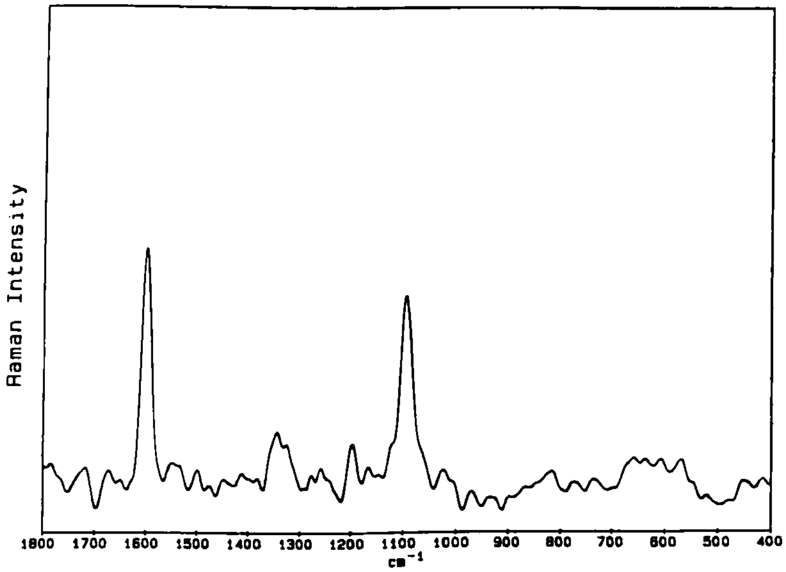

FIGURE 5 SERS spectrum obtained from a sample prepared by immersing an APDS pretreated gold island film into a 0.1% solution of phthalic anhydride (PA) for 24 hours and then rinsing with ethanol.

and the SERS spectrum of APDS monolayers (see Figure 2). A new band was observed near 1340 cm^{-1} in the SERS spectrum obtained from a PA/APDS/Au sample (see Figure 5). The band near 1600 cm^{-1} increased in intensity and became the strongest band in the SERS spectrum of the PA/APDS/Au system, while the band near 403 cm^{-1} decreased in intensity. These differences were attributed to the interaction between PA and APDS. Appearance of the band near 1340 cm^{-1}, which was assigned to the C—N stretching mode of amide groups,[1] indicated that anhydride groups of PA reacted with amino groups of APDS to form amic acids (see Chart II). The band near 1600 cm^{-1} was

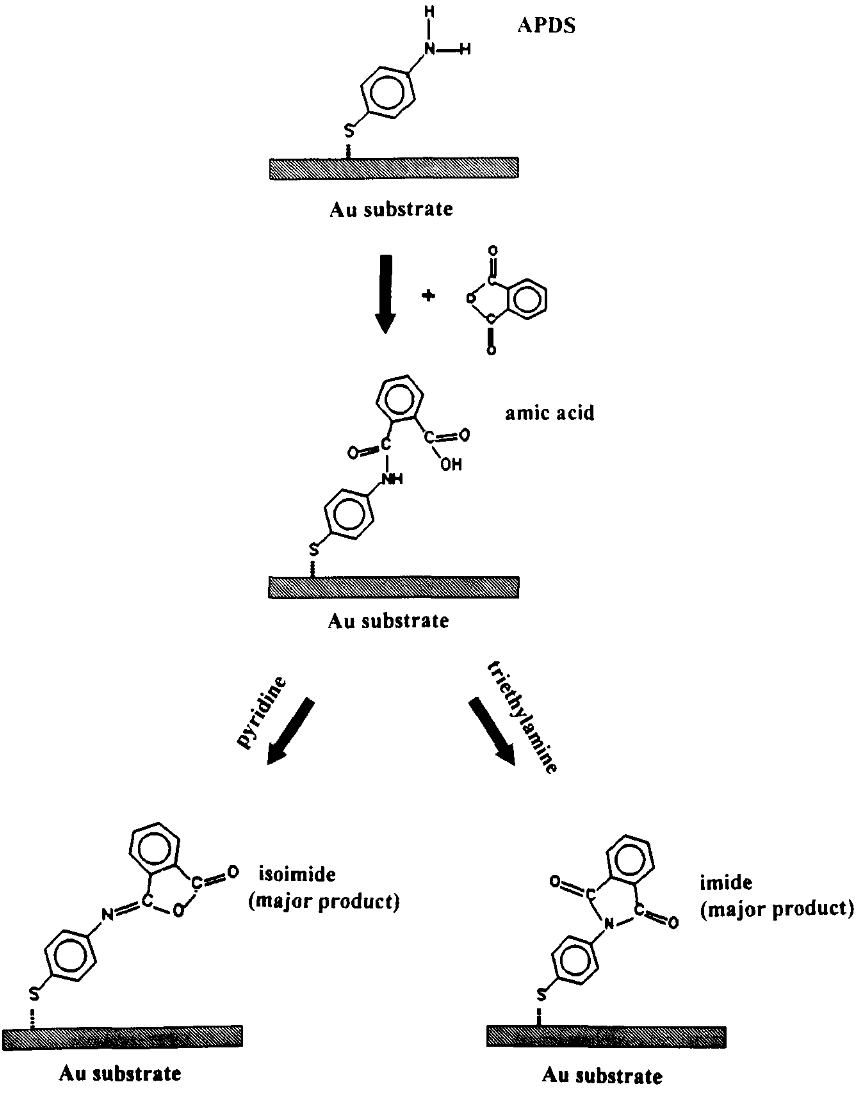

CHART II Represtation of proposed structures of adsorbed molecules on phthalic anhydride/4-aminophenyldisulfide/gold (*i.e.*, PA/APDS/Au) samples before and after chemical curing.

assigned to the C—C stretching mode ν(8a) of APDS and PA aromatic rings. The incorporation of PA increased the concentration of aromatic rings on the metal surface, resulting in the increase in intensity of the band near 1600 cm^{-1}. The band near 403 cm^{-1} was attributed to the ν(7a) mode of APDS benzene rings and the ν(C—NH$_2$) mode. This band became weaker in the SERS spectrum of PA/APDS/Au because APDS reacted with PA, consuming NH$_2$ groups.

Formation of amic acids on Au substrates was confirmed by RAIR results. The RAIR spectrum obtained from PA deposited onto an APDS-treated Au film using the same procedures as those for SERS experiments is shown in Figure 6. Several new bands were observed when this spectrum was compared with the RAIR spectrum of APDS monolayers (see Figure 4). Bands near 1525 and 1320 cm^{-1} were due to amide groups, while the band near 1718 cm^{-1} was due to acid groups.[1] Appearance of these bands and disappearance of the band due to NH$_2$ near 1618 cm^{-1} suggested that amic acids were formed by reacting anhydride groups of PA with amino groups of APDS.

One might ask whether phthalic anhydride reacted with moisture to form phthalic acid during PA exposure of the APDS treated surface. If this reaction occurred, the acid groups of phthalic acid and the amino groups of APDS would combine to ammonium carboxylate species.[24] However, there was no evidence in our SERS and RAIR spectra showing that ammonium carboxylate was formed. Moreover, we have obtained a RAIR spectrum from a sample prepared by immersing an APDS-treated Au substrate in a dilute solution of pyromellitic dianhydride (PMDA) for 24 hours, and then rinsing the sample extensively with ethanol.[25] It was found that one of the anhydride groups of PMDA reacted with an amino group of APDS, forming an amic acid. The other anhydride group of PMDA remained intact. This was evident from the observation of bands related to anhydride near 1870, 1800 and 1250 cm^{-1} in the RAIR spectrum. These results indicated that either anhydride-moisture interaction did not occur in our model systems or the interaction was too little to be detected by our instruments.

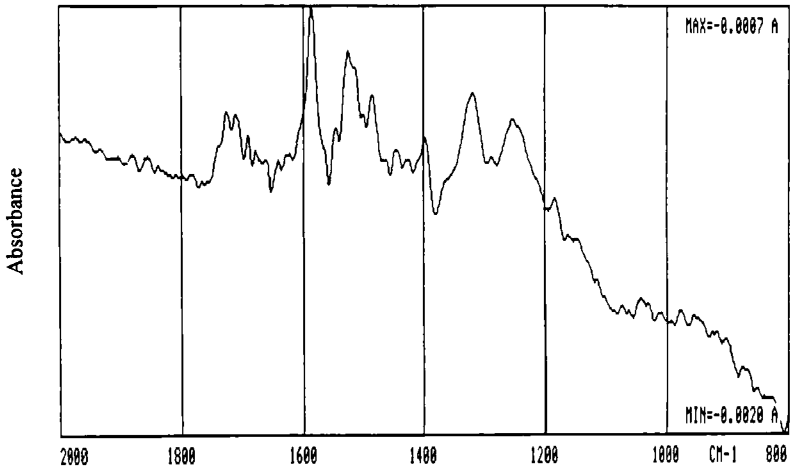

FIGURE 6 RAIR spectrum obtained from a sample prepared by immersing an APDS pretreated gold film into a 0.1% solution of PA for 24 hours and then rinsing with ethanol.

The SERS spectrum obtained after chemical curing of a PA/APDS/Au sample in a solution of acetic anhydride and pyridine (1:1 ratio by volume) for 24 hours is shown in Figure 7. When this spectrum was compared with the SERS spectrum of PA/APDS/Au before curing (see Figure 5), significant differences were observed. The band near 1340 cm^{-1} assigned to the C—N stretching mode of amide groups disappeared in the SERS spectrum of PA/APDS/Au after curing, while new bands near 1700 and 1230 cm^{-1} were observed. Bands near 1700 and 1230 cm^{-1} can be assigned to the C=N stretching and the C—O—C stretching modes of isoimide groups. Assignment of these Raman bands to isoimide structures has been proposed by Young *et al.*[1] and Tsai *et al.*[2] They observed a strong band near 1700 cm^{-1} in Raman spectra of polyamic acids from PMDA/ODA and PMDA/4-BDAF cured against silver substrates and assigned this band to isoimide species. Bands characteristic of imide structures were also observed near 1380 and 1800 cm^{-1} in Figure 7.[26] The absence of the band due to amide and the observation of bands due to isoimide and imide indicated that chemical curing of amic acid groups adsorbed on Au substrates in a solution of acetic anhydride and pyridine gave mixtures of isoimide and imide. However, the bands near 1230 and 1700 cm^{-1} were much stronger than those near 1380 and 1800 cm^{-1}, suggesting that isoimide was the predominant product (see Chart II).

Different results were observed when amic acid films were cured in acetic anhydride using triethylamine as a catalyst. Figure 8 shows the SERS spectrum obtained from a PA/APDS/Au sample after curing in a mixture of acetic anhydride and triethylamine (1:1 ratio by volume) for 24 hours. Bands due to imide groups near 1380 and 1800 cm^{-1} became stronger relative to bands due to isoimide groups near 1700 and 1230 cm^{-1}. This indicated that chemical curing of amic acid films in acetic anhydride/triethylamine

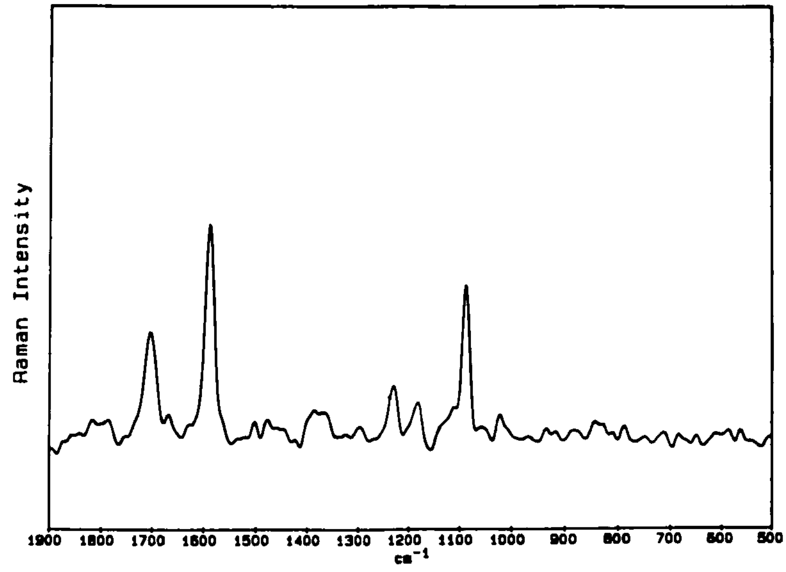

FIGURE 7 SERS spectrum obtained from a sample prepared by immersing an APDS pretreated gold island film into a 0.1% solution of PA for 24 hours, rinsing with ethanol, and then curing the films in a mixture of acetic anhydride and pyridine.

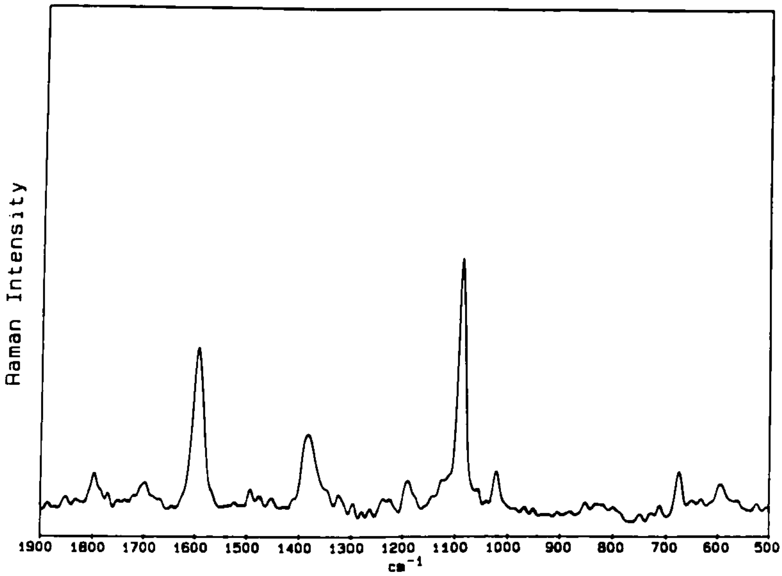

FIGURE 8 SERS spectrum obtained from a sample prepared by immersing an APDS pretreated gold island film into a 0.1% solution of PA for 24 hours, rinsing with ethanol, and then curing the films in a mixture of acetic anhydride and triethylamine.

solutions produced mainly imide species (see Chart II). These results also indicated that the relative amounts of isoimide and imide depended strongly on the catalyst used for the chemical curing.

RAIR results were consistent with SERS results. RAIR spectra obtained from PA/APDS/Au samples after curing in acetic anhydride and pyridine or triethylamine are shown in Figures 9 and 10, respectively. Bands due to both isoimide and imide groups were observed in Figure 9. Bands near 920, 1224, and 1690 cm^{-1} were associated with vibrational modes of isoimide groups,[27-29] while bands near 1380, 1710, and 1780 cm^{-1} were related to imide groups.[26] Observation of these bands indicated that mixtures of isoimide and imide were obtained by curing with pyridine catalyst. However, bands near 1380 and 1780 cm^{-1} due to imide groups became stronger in Figure 10 and the band near 920 cm^{-1} due to isoimide was very weak, implying that imide was the predominant product when curing with triethylamine catalyst.

Two reactions may take place during the chemical curing of polyamic acids or their model compounds, such as N-aryl phthalamic acid and N-aryl pyromellitamic acid, in acetic anhydride solutions.[27, 30-33] One is the formation of imide, while the other is the formation of isoimide. The relative amounts of imide and isoimide depend strongly on curing conditions. It has generally been found that dehydration of amic acids in acetic anhydride catalyzed by pyridine gave mixtures of isoimide and imide. In the initial stages of this reaction, formation of isoimide was faster than formation of imide.[33] As the reaction proceeded, the rate of isoimide formation decreased gradually and mixtures of isoimide and imide were obtained eventually.[27,33] However, when amic acids were cured in acetic anhydride with triethylamine or sodium acetate, imide species were generally the major products. This is because the presence of a stronger

FIGURE 9 RAIR spectrum obtained from a sample prepared by immersing an APDS pretreated gold substrate into a 0.1% solution of PA for 24 hours, rinsing with ethanol, and then curing the films in a mixture of acetic anhydride and pyridine.

base such as triethylamine generated acetate ions, which induced isomerization of isoimide to imide. This isoimide-imide rearrangement in the presence of acetate ions has been reported by several groups.[32-34]

In the case of our model systems, only monolayers of amic acids were available to react. Since the rate of isoimide formation was greater at the beginning of the reaction, most amic acids formed isoimide structures on Au substrates when the curing was performed in mixtures of acetic anhydride and pyridine. When triethylamine was used

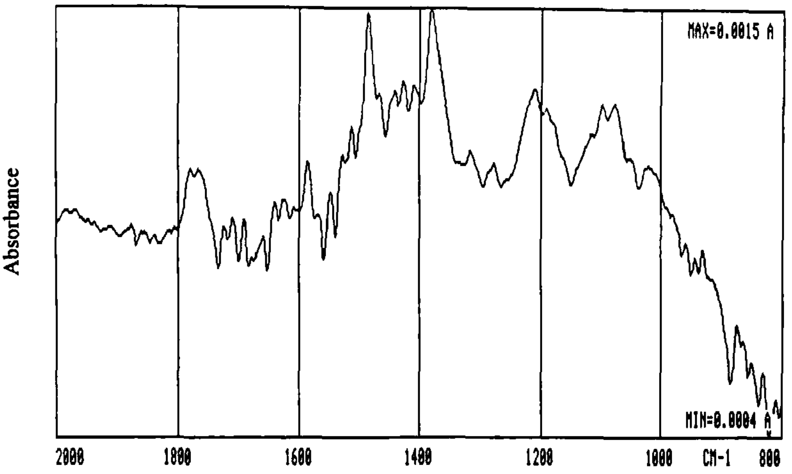

FIGURE 10 RAIR spectrum obtained from a sample prepared by immersing an APDS pretreated gold substrate into a 0.1% solution of PA for 24 hours, rinsing with ethanol, and then curing the films in a mixture of acetic anhydride and triethylamine.

for the curing, imide groups created by the dehydration process and by the rearrangement of isoimide to imide were the main products.

It should be noted that orientaions of amic acid, isoimide, and imide moieties of adsorbed molecules were not determined quantitatively since transmission infrared spectra could not be obtained. However, qualitative information about the orientation of these groups can be obtained by comparing the relative intensities of some bands in RAIR and SERS spectra. In the RAIR spectra of PA/APDS/Au (see Figure 4), bands near 1321 and 1520 cm^{-1} were assigned to the C—N stretching and N—H bending modes of amide groups, respectively. Another band due to the carbonyl stretching mode of amide groups was usually observed near 1670 cm^{-1}. Bands near 1321 and 1520 cm^{-1} were very strong in Figure 6, while the band near 1670 cm^{-1} was not observed. These results suggested that amic acid moieties were likely oriented with C=O bonds mostly parallel to the surface and with C—N bonds perpendicular to the surface (see Chart II).

In the RAIR spectra obtained from PA/APDS/Au samples cured in mixtures of acetic anhydride and pyridine (see Figure 9), bands near 1690, 1224, and 920 cm^{-1} were assigned to the C=N stretching, the asymmetric C—O—C stretching, and the symmetric C—O—C stretching modes, respectively. The band near 920 cm^{-1} was relatively stronger than bands near 1690 and 1224 cm^{-1}, indicating that isoimide moieties were oriented with the C=N bonds largely parallel to the surface (see Chart II).

In the RAIR spectra of PA/APDS/Au samples after curing in mixtures of acetic anhydride and triethylamine (see Figure 10), the band near 1380 cm^{-1} assigned to the axial C—N—C stretching mode of imide was much stronger than bands near 1710 and 1780 cm^{-1} assigned to imide C=O stretching modes. In the corresponding SERS spectra shown in Figure 8, the C—N—C stretching mode near 1380 cm^{-1} was also stronger than the C=O stretching mode near 1800 cm^{-1}. These results indicated that imide groups were oriented with C=O bonds largely parallel to the surface (see Chart II). Obviously, further work is needed for the quantitative determination of orientations of these groups.

CONCLUSIONS

The molecular structure of interphases between a model polyimide and an organosulfur-functionalized metal substrate was determined using SERS and RAIR. It was concluded that APDS was chemisorbed onto Au substrates through the sulfur atoms. The tilt and rotation angles for APDS adsorbed onto Au substrates were determined to be approximately 46° and 45° using RAIR, indicating that APDS was adsorbed with a conformation in which the long molecular axis was tilted away from the surface normal about 46°. However, there was probably no preferred rotation angle of the adsorbed APDS about the long molecular axis. When PA was deposited onto APDS-pretreated Au substrates, anhydride groups of PA reacted with amino groups of APDS, resutling in the formation of amic acids. Mixtures of isoimide and imide were obtained by curing these amic acid films in acetic anhydride solutions using either pyridine or triethylamine as a catalyst. However, the relative amount of isoimide and imide depended strongly on the catalyst used. Curing the amic acid films on PA/APDS/Au samples in a solution of acetic anhydride and pyridine produced mainly isoimide species, while curing in the presence of triethylamine catalyst gave imide species as the major products. It was also shown that chemical linkages were formed between the PA and the Au substrate through the APDS. Formation of chemical bridges may improve the adhesion between polyimides and metals. This indicated that organosulfur compounds such as APDS may be very useful as adhesion promoters for bonding polyimide to metal. Investigations regarding the use of organosulfur compounds as coupling agents in polyimide/metal and epoxy/metal adhesive systems have also been performed in our laboratory. The results will be published elsewhere.[24–25]

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