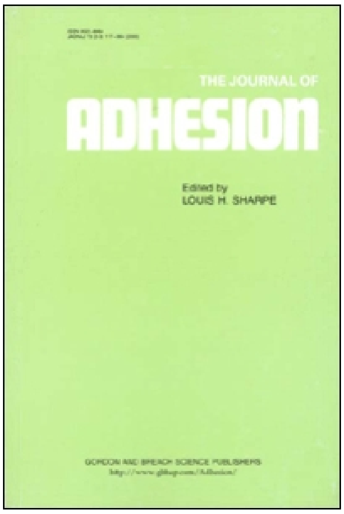

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Surface-Enhanced Raman Scattering from Polyimide Model Compounds on Functionalized Metal Surfaces. Part II: Phthalic Anhydride/meta-Aminothiophenol/Silver

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Surface-Enhanced Raman Scattering from Polyimide Model Compounds on Functionalized Metal Surfaces. Part II: Phthalic Anhydride/meta-Aminothiophenol/Silver

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The interphase between a polyimide and a metal substrate was modeled by depositing phthalic anhydride (PA) onto a silver substrate pretreated with meta-aminothiophenol (m-ATP) 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 determine the molecular structure of the interphase. It was found that m-ATP was adsorbed dissociatively onto silver substrates through the thiol groups. The tilt angle for m-ATP molecules adsorbed on silver substrates was determined using RAIR to be approximately 39°. However, there was no preferred rotational angle of the adsorbed APDS molecules about the molecular axes. When PA was deposited onto m-ATP pretreated silver substrates, anhydride groups of PA reacted with amino groups of m-ATP to form amic acids. When PA/m-ATP/Ag samples were chemically cured in acetic anhydride and pyridine or triethylamine, isoimide was the predominant product regardless of the use of pyridine or triethylamine as catalyst. These results were different from those obtained from PA/APDS/Au systems in which imide was the major product in the presence of triethylamine. These differences in the relative composition of cured products between two model systems were explained by the effect of substituents attached to APDS and m-ATP benzene rings.

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

I. INTRODUCTION

Polyimides are a class of high-temperature polymers frequently used as thin layers of dielectric insulation between wiring networks in multilevel VLSI packages and as matrix materials in graphite or glass reinforced composites due to their excellent thermal and mechanical stability, low dielectric constant, and chemical resistance. Strong and durable bonds between polyimides and substrates such as metal, silica, and graphite are stringently required in these applications. In order to optimize the performance and stability of polyimide/substrate joints, it is essential to determine and tailor the molecular structure of interphases between polyimides and substrates. It is also important to develop analytical techniques for the characterization of polymer/substrate interphases.

In a previous paper[1], we reported the use of surface-enhanced Raman scattering (SERS) and reflection-absorption infrared spectroscopy (RAIR) to determine the molecular structure of a model polyimide/metal interphase formed by depositing phthalic anhydride (PA) onto an 4-aminophenyldisulfide (APDS) functionalized gold substrate and then curing in acetic anhydride and pyridine or triethylamine. We also showed that organosulfur compounds such as aminophenyldisulfide and aminothiophenol may be effective as adhesion promoters for polyimide-to-metal bonding. This is because chemical bridges were formed between the metal and the polymer through the organosulfur coupling agents.

The purpose of this paper is to describe results we have obtained using SERS and RAIR to determine the molecular structure of another model polyimide/metal interphase which was prepared by depositing phthalic anhydride onto a silver substrate pretreated with meta-aminothiophenol (m-ATP) and then curing in acetic anhydride and pyridine or triethylamine. This system will be referred to as the PA/m-ATP/Ag system.

m-ATP was selected as a coupling agent between the model polyimide and the silver substrate in the present investigation. This is because amino groups of APDS easily form azo groups on the silver surface during the SERS experiments. Bands characteristic of azo groups were observed near 1460, 1400, and 1150 cm^{-1} in the SERS spectra of APDS monolayers adsorbed on the silver. This silver-catalyzed and laser-induced reaction has been reported for several chemical compounds adsorbed on the silver surface during SERS experiments. These compounds included p-nitrobenzoic acid,[2] p-aminobenzoic acid,[3] and 1,4-dinitrobenzene.[4]

In order to prevent the formation of azo groups, m-ATP was used for coupling polyimide to silver. It has been found that p-aminobenzoic acid was reduced to form azodibenzoate at the silver surface during SERS experiments, but m-aminobenzoic acid was not.[3] This difference was due to the interaction of the COOH group with silver causing electron withdrawal from the para substituent but not from the meta substituent. Thus, azo groups were not expected to form in the case of m-ATP adsorbed on the silver surface during SERS experiments. Indeed, bands related to azo groups were not observed in the SERS spectra obtained from m-ATP monolayers adsorbed on silver substrates (shown below).

SERS and RAIR results presented in this paper indicated that m-ATP was adsorbed dissociatively onto silver substrates. The orientation of adsorbed m-ATP molecules was determined quantitatively using infrared spectroscopy. When PA was deposited onto m-ATP pretreated silver substrates, anhydride groups of PA reacted with amino groups of m-ATP to form amic acids. Chemical curing of these amic acid films gave mostly isoimide species regardless of whether pyridine or triethylamine were used. These results were different from those obtained from PA/APDS/Au systems. Curing PA/APDS/Au samples in acetic anhydride catalyzed with pyridine produced mainly isoimide groups, while imide was the major product when curing with the triethylamine catalyst. These differences in relative amounts of isoimide and imide formed on metal substrates were explained by the effect of substituents attached to APDS and m-ATP benzene rings.

II. EXPERIMENTAL

Silver substrates were prepared for SERS investigations as described below. Glass slides were cleaned using the same procedures as described in the previous study.[1] Clean glass slides were then immediately placed in a vaccum chamber which was purged with nitrogen and pumped down to 10^{-6} Torr using sorption, sublimation, and ion pumps. Silver wires wrapped around resistively-heated tungsten filaments were then slowly heated to evaporate metal island films onto the glass slides at a rate of approximately 1Å/s. The thickness of the silver island films was controlled at about 40 Å using a quartz crystal oscillator thickness monitor.

Meta-aminothiophenol (m-ATP), phthalic anhydride (PA), acetic anhydride, pyridine, and triethylamine were obtained from Aldrich Chemical Co. and used as-received. Monolayers of m-ATP were prepared by immersing a Ag island film in a 0.01% dilute solution of m-ATP in acetone for 10 minutes and then rinsing extensively with acetone. After that, m-ATP-coated substrates were immersed in a 0.1% solution of PA in acetone for 24 hours and then rinsed with acetone again. PA-coated specimens were then chemically cured in a mixture 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 the same instrument described in the previous paper.[1] The slit setting of the monochromator provided a spectral resolution of about $10\,cm^{-1}$ for the SERS spectra. The green line of the laser (Spectra-Physics Model 165 argon-ion laser, 5145 Å in wavelength) 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 was between 10 and 25 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 m-ATP were obtained from small amounts of m-ATP 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 metal films were used instead of metal island films. Thick metal films (several thousand angstroms) were prepared by thermally evaporating silver onto the clean glass slides. RAIR spectra were also obtained using the same apparatus described in the previous paper.[1] 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 m-ATP were obtained using the same spectrophotometer. Specimens of m-ATP were prepared by placing a small amount of m-ATP liquid between two KBr pellets.

The thickness of the organic films deposited onto silver substrates was determined by ellipsometry. Organic films were deposited onto thick silver films using the same procedures as those used to prepare SERS and RAIR samples. 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. The thickness of m-ATP monolayers deposited onto Ag substrates was measured to be about 7 Å which is approximately the same as the theoretical length of m-ATP molecules, indicating that there was a monolayer coverage of m-ATP on Ag.

III. RESULTS AND DISCUSSION

The normal Raman spectrum obtained from m-ATP is shown in Figure 1. The observed bands and their assignments are summarized in Table I. The band near 1637 cm^{-1} was assigned to the deformation mode of NH_2 groups.[5] Bands near 2580 and 934 cm^{-1} were attributed to the stretching and the bending mode of S—H groups, respectively. The remaining bands were related to vibrational modes of meta-substituted benzene rings and were assigned using the Wilson numbering system.[6,7] For example, strong bands near 1608, 1085, 1007, and 703 cm^{-1} were assigned to the C—C stretching mode ν(8b), C—H bending mode ν(18a), and ring breathing modes ν(12) and ν(1), respectively. No distinct aryl-S vibrations were observed due to coupling of C—S modes with ring modes.

SERS spectra obtained from m-ATP monolayers adsorbed onto Ag island films are presented in Figure 2. Differences were observed between the normal Raman and SERS spectra of m-ATP. Bands associated with S—H groups near 2580 and 934 cm^{-1} disappeared in the SERS spectra of m-ATP. Bands near 1608 and 1095 cm^{-1}, which were assigned to the C—C stretching mode ν(8b) and the C—X in-plane bending mode

TABLE I
Tentative band assignments for meta-aminothiophenol (m-ATP)

NR (cm^{-1})	IR (cm^{-1})	SERS (cm^{-1})	RAIR (cm^{-1})	Assignments
	3432 (M)			$\nu_{as}(NH_2)$
3370 (M)	3356 (M)			$\nu_S(NH_2)$
3080 (M)	3053 (W)	3080 (W)		ν(2), C—H stretching
2580 (M)	2556 (W)			ν(S—H)
1630 (W)	1618 (M)	1630 (W)	1618 (M)	$\beta_s(NH_2)$
1608 (M)	1595 (S)	1597 (S)	1590 (S)	ν(8b), C—C stretching
	1478 (S)		1478 (S)	ν(19b), C—C stretching
1460 (W)	1445 (W)	1460 (W)	1445 (W)	ν(19a), C—C stretching
	1321 (W)		1320 (W)	
1317 (W)	1301 (W)	1315 (W)	1297 (M)	ν(14), C—C stretching
1285 (W)	1269 (W)		1269 (W)	ν(13), C—X stretching
	1166 (W)		1166 (W)	ν(9b), C—H in-plane bending
1095 (W)	1081 (W)	1085 (M)	1077 (W)	ν(18a), C—X in-plane bending
1007 (S)	992 (W)	1005 (S)	992 (W)	ν(12), radial skeletal vib.
934 (W)	924 (W)			β(S—H)
899 (W)	880 (W)	896 (W)	880 (W)	ν(6b), radial skeletal vib.
	850 (W)			ν(17b), C—H out-of-plane vib.
785 (W)	771 (W)		769 (W)	ν(11), C—H out-of-plane vib.
703 (W)	685 (W)	700 (W)	685 (W)	ν(1), radial skeletal vib.
549 (W)				ν(16a), out-of-plane skeletal vib.
422 (W)		424 (W)		ν(7b), C—X stretching

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

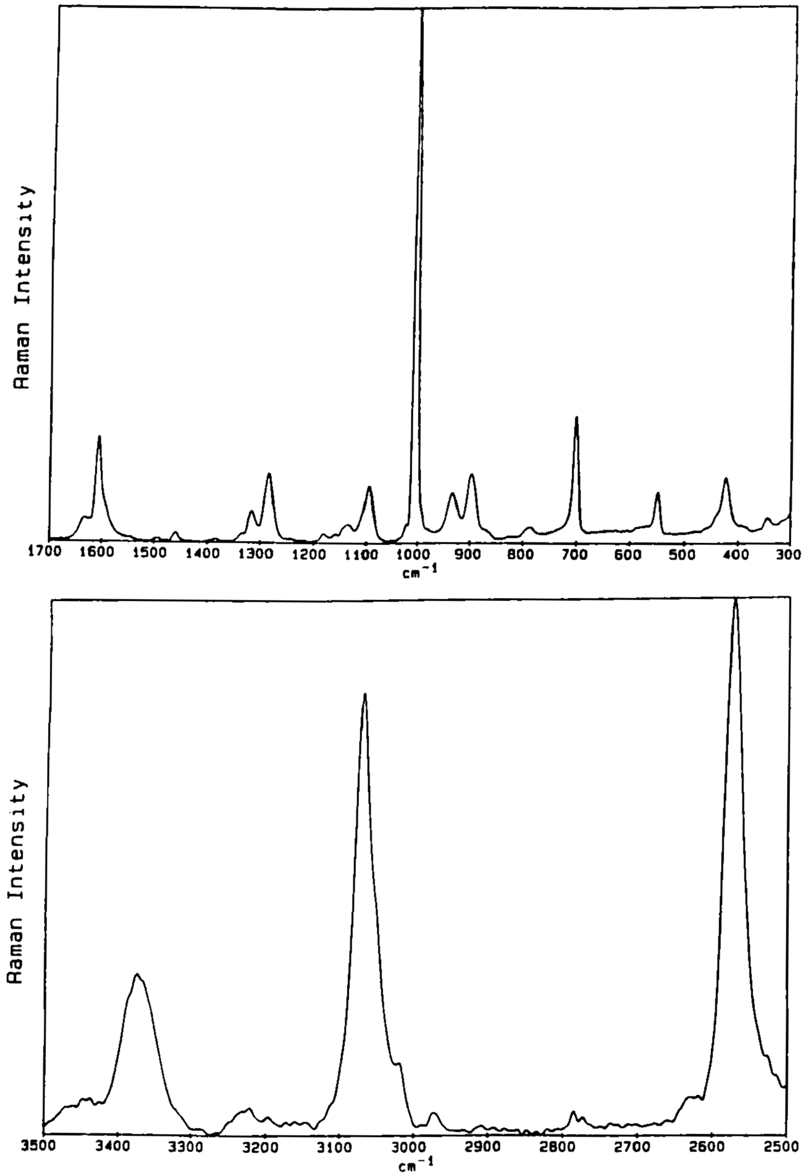

FIGURE 1 Normal Raman spectra obtained from meta-aminothiophenol (m-ATP) between (A)-300–1700 cm^{-1} and (B)-2500–3500 cm^{-1}.

ν(18a), shifted to about 1597 and 1085 cm^{-1}, respectively, and increased in intensity in SERS spectra of m-ATP. The band near 422 cm^{-1}, assigned to the C—X stretching mode ν(7b), also increased in intensity. These results indicated that cleavage of S—H bonds occurred and that m-ATP was adsorbed dissociatively onto Ag substrates through the thiol groups. The shift in position of substituent-sensitive ring modes was attributed to a change of environment for adsorbed molecules.

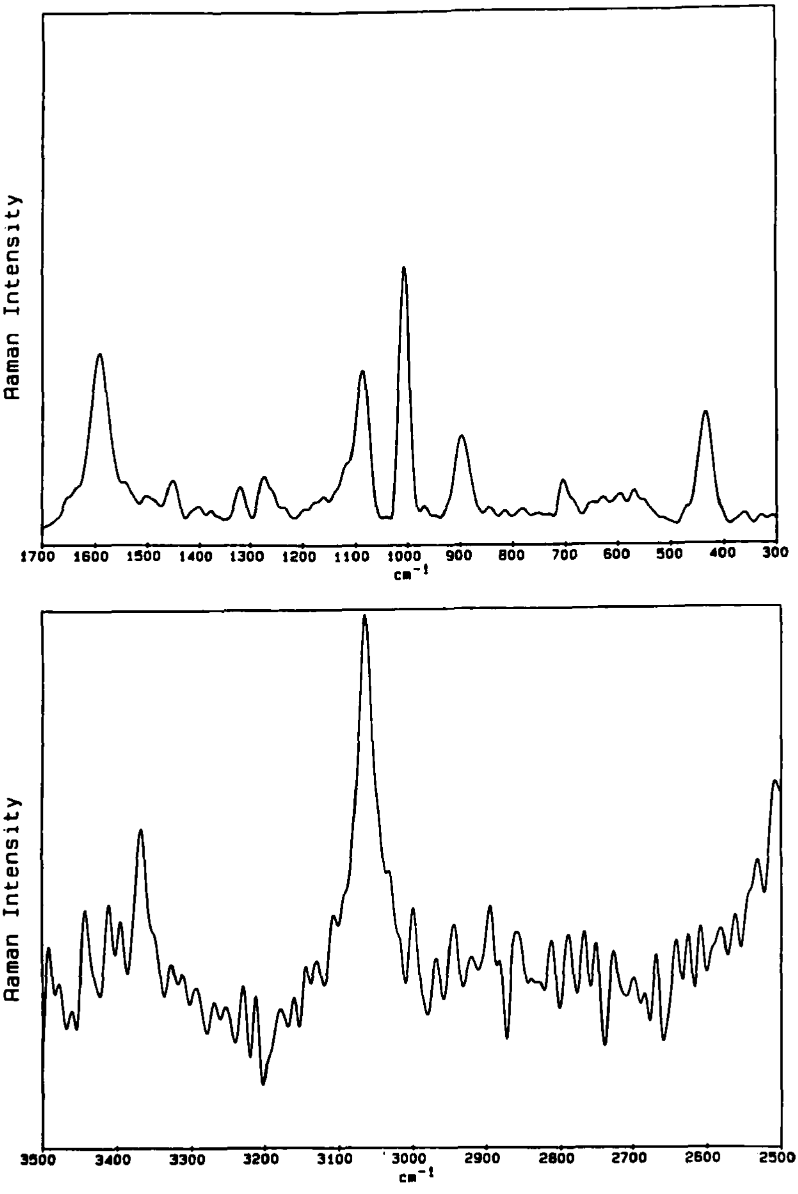

FIGURE 2 SERS spectra obtained from an m-ATP monolayer adsorbed onto a silver island film between (A)-300–1700 cm^{-1} and (B)-2500–3500 cm^{-1}.

RAIR results were in good agreement with SERS results. The transmission infrared and RAIR spectra of m-ATP are shown in Figures 3 and 4, respectively. The observed bands and their assignments are also summarized in Table I. The position of all bands observed in RAIR spectrum of m-ATP (see Figure 4) matched very well with that of the corresponding bands in the transmission infrared spectrum (see Figure 3). However,

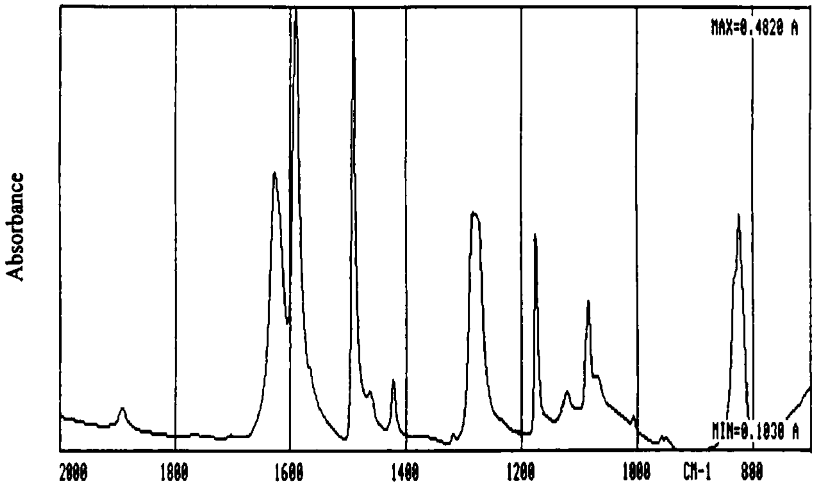

FIGURE 3 Transmission infrared spectrum obtained from m-ATP.

some differences were observed between the transmission infrared and RAIR spectra. Bands near 2556 and 924 cm^{-1} which were related to S—H groups disappeared in the RAIR spectra of m-ATP. Bands near 1595 and 1081 cm^{-1} in the transmission IR spectra of m-ATP shifted to about 1590 and 1077 cm^{-1}, respectively, in the RAIR spectra of m-ATP. These results revealed that m-ATP was chemisorbed on the Ag surface through the sulfur stoms. Formation of S-Ag bonding between m-ATP and Ag substrates was also confirmed by X-ray photoelectron spectroscopy (XPS). These XPS results will be published subsequently.[8]

The orientation of m-ATP adsorbed onto Ag substrates was also determined by comparing the relative intensity changes of several bands in SERS and RAIR spectra.

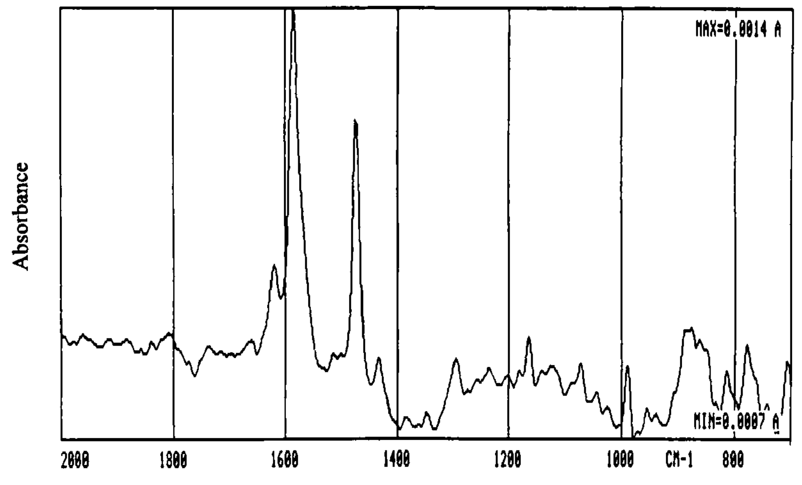

FIGURE 4 RAIR spectrum obtained from an m-ATP monolayer adsorbed onto a thick silver film.

Qualitative information can be obtained from the normal Raman and SERS spectra using the selection rules developed by Moskovits.[9] The band near 549 cm^{-1} in the normal Raman spectrum of m-ATP (see Figure 1) was assigned to ν(16a), the out-of-plane vibrational mode of benzene rings. This band became relatively weak in the SERS spectra of m-ATP (see Figure 2), indicating that m-ATP was adsorbed with a tilted, rather than flat, orientation. Several in-plane vibrational modes of benzene rings, which have atomic motions largely parallel to the molecular axis of m-ATP (defined in Chart I), were strong in the SERS spectra of m-ATP. These included bands near 1597, 1085, 1005, and 424 cm^{-1} which were assigned to ν(8b), ν(18a), ν(12), and ν(7b), respectively. All these bands were strong in the SERS spectrum obtained from m-ATP monolayers, also implying that m-ATP was adsorbed through the S atom with a tilted orientation. This tilted orientation was determined quantitatively using infrared spectroscopy as described below.

According to the method described in the previous paper,[1] three bands in the transmission and RAIR spectra of m-ATP (see Figures 3 and 4), which have dipole moments perpendicular to one another, were selected to calculate the tilt and rotation angles. The band near 1478 cm^{-1} assigned to ν(19b), a C—C stretching mode of benzene rings, has a dipole moment mostly parallel to the molecular axis (defined in Chart I). The band near 1445 cm^{-1} assigned to another C—C stretching mode ν(19a) has its dipole moment mostly perpendicular to the molecular axis and in the molecular plane. Intensity ratios of these two bands (*i.e.*, $A_{\parallel}(R)/A^{i}_{\perp}(R)$ and $A_{\parallel}(T)/A^{i}_{\perp}(T)$) can be used in equation (1) in the previous paper.[1] The band near 771 cm^{-1} related to the out-of-plane vibrational mode ν(11) of benzene rings exhibits a dipole moment perpendicular to the molecular axis but out of the molecular plane. Intensity ratios of bands near 1478 and 771 cm^{-1} (*i.e.*, $A_{\parallel}(R)/A^{0}_{\perp}(R)$ and $A_{\parallel}(T)/A^{0}_{\perp}(T)$) can be used in equation (2) shown in the previous paper.[1]

These intensity ratios, including $A_{\parallel}(R)/A^{i}_{\perp}(R)$, $A_{\parallel}(T)/A^{i}_{\perp}(T)$, $A_{\parallel}(R)/A^{0}_{\perp}(R)$, and $A_{\parallel}(T)/A^{0}_{\perp}(T)$ were measured to be approximately 4.93, 1.75, 3.83, and 1.25, respectively. The tilt angle θ and the rotation angle ϕ were then calculated using equations (1) and (2)

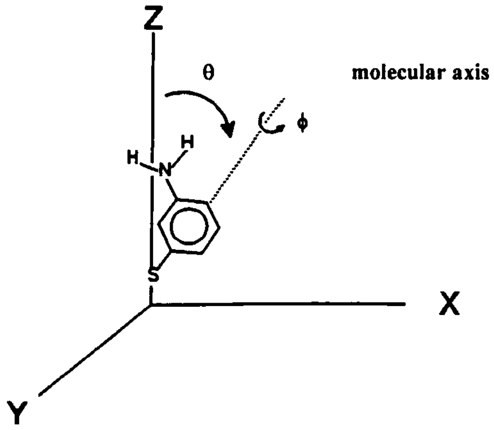

CHART I The tilt angle θ and rotation angle ϕ of meta-aminothiophenol (m-ATP) molecules adsorbed on the silver surface.

to be about 39° and 44°, respectively. The calculated rotation angle was very very close to the average value (45°), perhaps indicating that there was no preferred rotation angle for m-ATP molecules adsorbed on silver substrates. It was concluded that m-ATP was adsorbed onto Ag substrates through the S atom with a conformation in which the molecular axis tilted away from the surface normal approximately 39° (see Chart I). However, there was no preferred rotational angle of the adsorbed m-ATP molecules.

Figure 5 shows the SERS spectrum obtained from a sample prepared by immersing a m-ATP pretreated Ag island film in a 0.1% solution of PA for 24 hours and then rinsing with acetone. Some differences were observed between this spectrum and the SERS spectrum of m-ATP (see Figure 2). The band near 1597 cm^{-1} increased in intensity and a new band was observed near 1340 cm^{-1} in Figure 5. The band near 1340 cm^{-1} was assigned to the C—N stretching mode of amide groups,[10] indicating that amic acids were formed by reacting anhydride groups of PA with amino groups of m-ATP (see Chart II). The C—C stretching mode ν(8b) of m-ATP benzene rings was combined with the ν(8a) mode of PA benzene rings, resulting in the increase in intensity of the band near 1597 cm^{-1}.

Consistent results were observed in the RAIR spectrum obtained from a sample prepared by immersing a m-ATP pretreated Ag substrate into a 0.1% solution of PA for 24 hours and then rinsing with acetone (see Figure 6). Upon comparing this RAIR spectrum with the RAIR spectrum of m-ATP monolayers (see Figure 4), some differences were observed. The band near 1618 cm^{-1} due to amine groups became very weak in Figure 6, while new bands were observed near 1716, 1673, 1521, 1400, and 1317 cm^{-1}. The bands near 1716 and 1400 cm^{-1} were assigned to acid groups. Bands near 1673, 1521, and 1317 cm^{-1} were related to amide groups.[10] Observation of bands due to acid

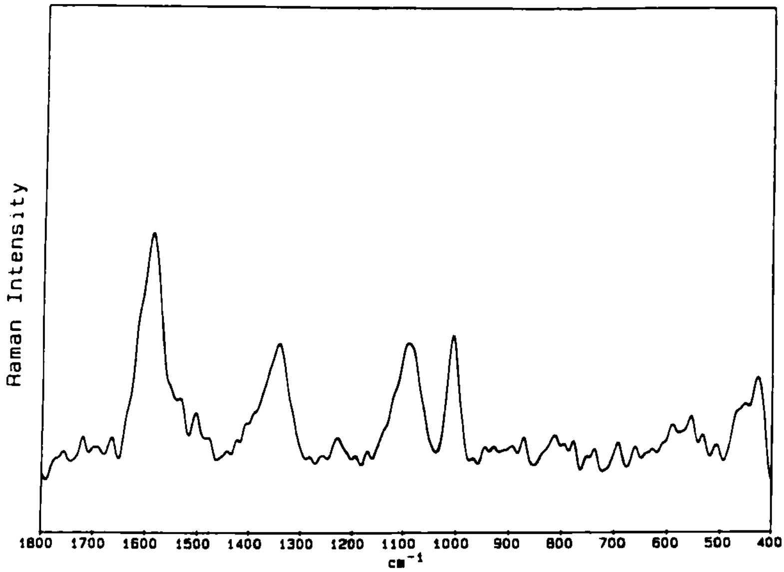

FIGURE 5 SERS spectrum obtained from a sample prepared by immersing a m-ATP pretreated silver island film into a 0.1% solution of phthalic anhydride (PA) for 24 hours and then rinsing with acetone.

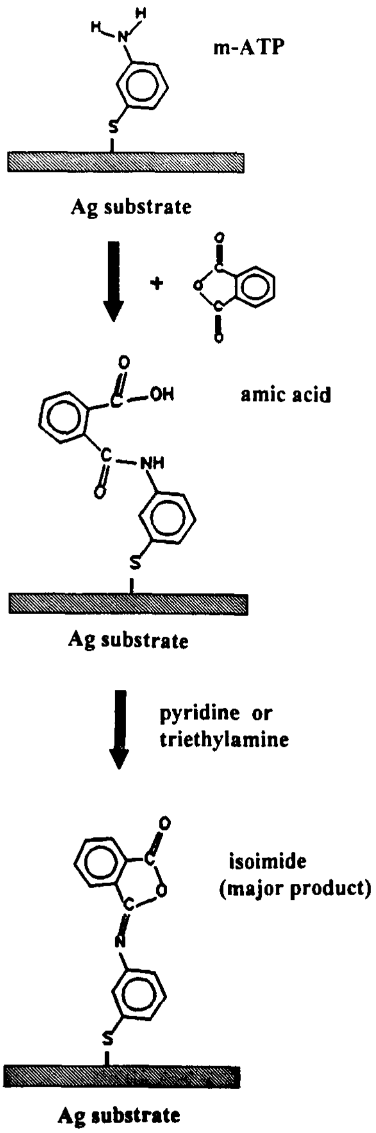

CHART II Representation of proposed structures of adsorbed molecules on phthalic anhydride/meta-aminothiophenol/silver (*i.e.*, PA/m-ATP/Ag) samples before and after chemical curing.

and amide groups and the decrease in intensity of the band due to amino groups again suggested that amic acids were formed on Ag substrates.

It should be noted that the intensities of the bands near 1673, 1521, and 1317 cm^{-1} were weak relative to those of bands due to m-ATP near 1592 and 1478 cm^{-1}. Especially, the band near 1317 cm^{-1} was overlapped with the band near 1320 cm^{-1} due to the ring vibrational mode of m-ATP. However, a difference spectrum, which was obtained by subtracting the spectrum in Figure 4 from that in Figure 6, showed a

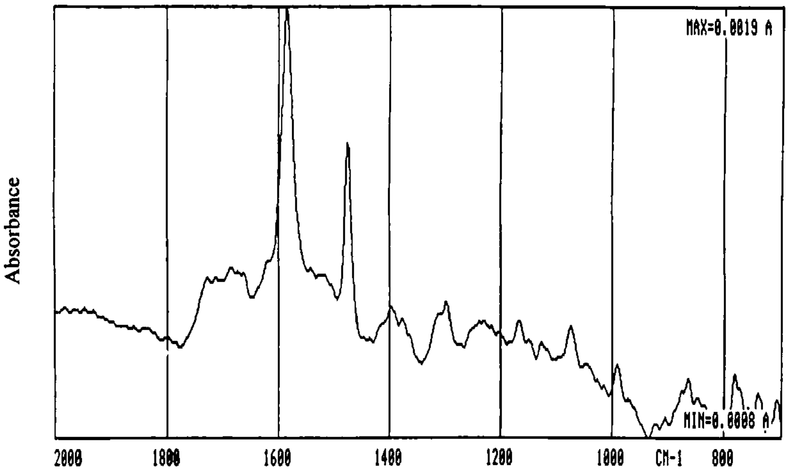

FIGURE 6 RAIR spectrum obtained from a sample prepared by immersing a m-ATP pretreated silver substrate into a 0.1% solution of PA for 24 hours and then rinsing with acetone.

strong band near 1670 cm^{-1}, weak bands near 1521 and 1320 cm^{-1}, and a strong negative band near 1620 cm^{-1}. These results confirmed that amic acids were formed on the Ag surface at the expense of NH_2 groups.

One might ask whether the anhydride group or the acid group formed near the interphase interacted with Ag substrates to form carboxylate salts. Strong bands characteristic of silver carboxylate salts usually appear near 1580–1600, 1380–1420, and 830–850 cm^{-1} in the Raman spectra. In our SERS spectra of PA/m-ATP/Ag (see Figure 5), strong broad bands were observed near 1600 and 1340 cm^{-1} which were assigned to the C—C stretching modes of benzene rings and the C—N stretching mode of amide groups. However, no band was observed between 830–850 cm^{-1}, indicating that m-ATP substantially covered the silver surface and that carboxylates were not formed at the interphase.

The SERS spectrum obtained from a sample prepared by immersing a m-ATP pretreated Ag island film in a 0.1% solution of PA for 24 hour, rinsing with acetone, and then curing in a mixture of acetic anhydride and pyridine for 24 hours is shown in Figure 7. Significant differences were observed when this spectrum was compared with the SERS spectrum obtained from PA/m-ATP/Ag samples before curing. The band due to the amide vibrational mode near 1340 cm^{-1} decreased in intensity, while bands characteristic of isoimide near 1700 and 1230 cm^{-1}[10–11] and imide near 1800 and 1380 cm^{-1}[12] were observed in the SERS spectrum of PA/m-ATP/Ag after curing. These results indicated that mixtures of isoimide and imide groups were formed when PA/m-ATP/Ag samples were chemically cured in a solution of acetic anhydride and pyridine. However, bands due to isoimide were much stronger than those due to imide, implying that chemical curing of amic acid films in a mixture of acetic anhydride and pyridine produced mostly isoimide species (see Chart II).

The SERS spectrum obtained from a sample prepared by immersing a m-ATP pretreated Ag island film in a 0.1% solution of PA for 24 hours, rinsing with acetone,

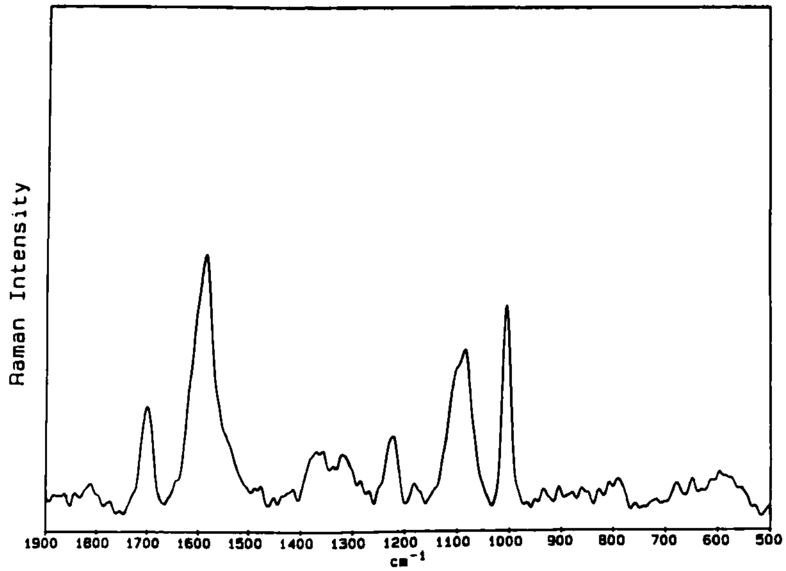

FIGURE 7 SERS spectrum obtained from a sample prepared by immersing a m-ATP pretreated silver island film into a 0.1% solution of PA for 24 hours, rinsing with acetone, and then curing the films in a mixture of acetic anhydride and pyridine.

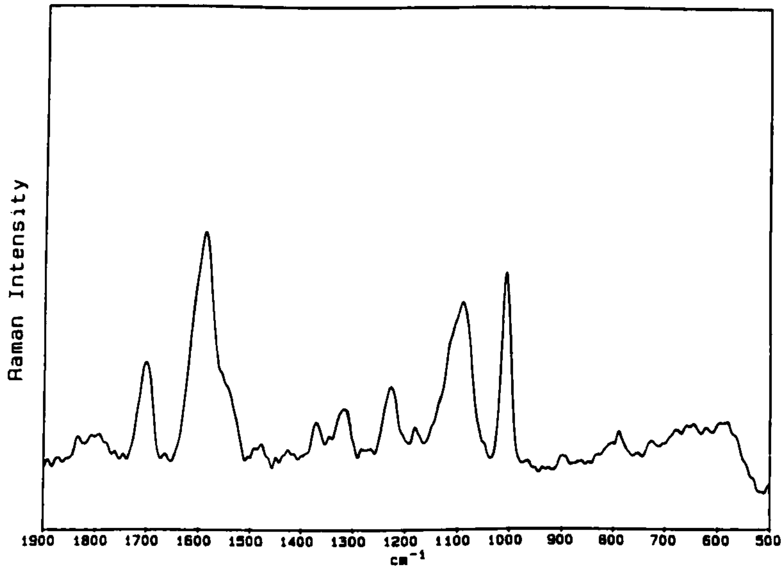

FIGURE 8 SERS spectrum obtained from a sample prepared by immersing a m-ATP pretreated silver island film into a 0.1% solution of PA for 24 hours, rinsing with acetone, and then curing the films in a mixture of acetic anhydride and triethylamine.

and then curing in a mixture of acetic anhydride and triethylamine for 24 hours is shown in Figure 8. Surprisingly, this spectrum was nearly identical to the SERS spectrum shown in Figure 7, suggesting that chemical curing of PA/m-ATP/Ag samples in a solution of acetic anhydride and triethylamine also produced isoimide as the predominant product. Previously, we have shown that curing PA/APDS/Au samples in a solution of acetic anhydride and triethylamine produced mostly imide groups.[1] This difference is probably due to different metal substrates and coupling agents used in these two model systems (described below).

RAIR spectra obtained from samples prepared by immersing m-ATP pretreated Ag substrates in 0.1% solutions of PA for 24 hour, rinsing with acetone, and then curing in mixtures of acetic anhydride and pyridine or triethylamine for 24 hours are shown in Figures 9 and 10, respectively. Generally speaking, these two spectra were very similar. Bands associated with isoimide near 1685 and 1234 cm^{-1} [13–16] and imide near 1373 cm^{-1} were observed in these spectra. The intensities of bands near 1685 and 1234 cm^{-1} were greater than that of the band near 1373 cm^{-1}, indicating that isoimide was the predominant product in both chemical curing processes. These results are in good agreement with SERS results.

Walczak *et al.*[17] investigated the structure and interfacial properties of spontaneously-adsorbed n-alkanethiolate monolayers on evaporated Ag and Au substrates. It was found that the adsorption behavior of n-alkanethiolate was different on Ag and Au due to different surface morphology and electronic properties of the substrate. Therefore, it was considered that metal substrates might have an important effect on the chemical curing of the model systems. In order to determine this, a SERS spectrum was obtained from a PA/m-ATP/Au sample cured in a mixture of acetic anhydride and triethylamine for 24 hours. This spectrum showed that bands near 1700 and 1230 cm^{-1} were much stronger than bands near 1800 and 1380 cm^{-1}, indicating that isoimide was still the

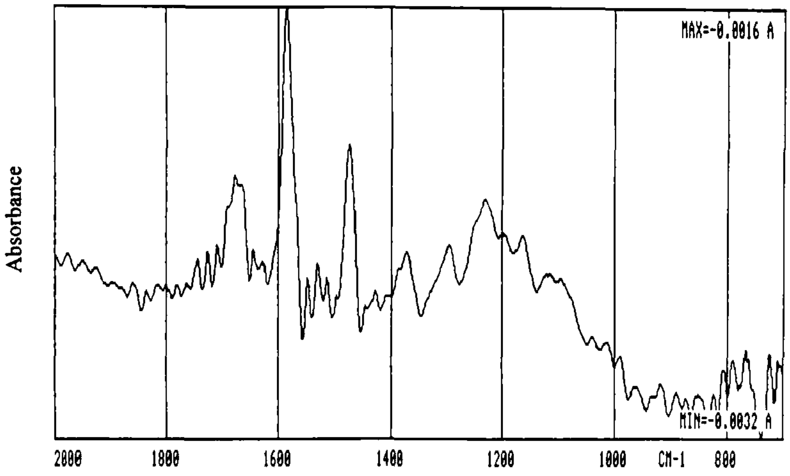

FIGURE 9 RAIR spectrum obtained from a sample prepared by immersing a m-ATP pretreated silver substrate into a 0.1% solution of PA for 24 hours, rinsing with acetone, and then curing the films in a mixture of acetic anhydride and pyridine.

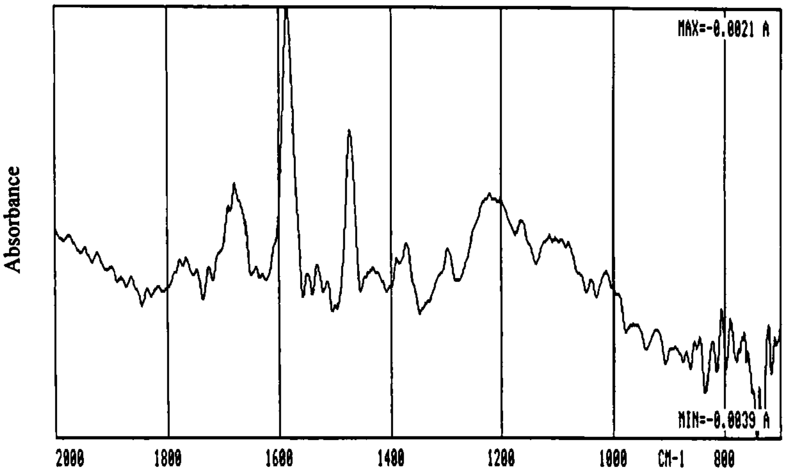

FIGURE 10 RAIR spectrum obtained from a sample prepared by immersing a m-ATP pretreated silver substrate into a 0.1% solution of PA for 24 hours, rinsing with acetone, and then curing the films in a mixture of acetic anhydride and triethylamine.

major product. This result demonstrated that the influence of metal substrate on the composition of curing products was not critical in the model systems.

However, the effect of substituents attached to the benzene rings of organosulfur compounds played an important role in the chemical curing of the model systems. As mentioned above, when amic acids were cured in a solution of acetic anhydride and triethylamine, imide was usually the predominant product. These imide groups were mostly produced by the rearrangement of isoimide to imide. The relative amounts of isoimide and imide depended on the curing conditions and also on the substituent on the benzene rings. Sauers *et al.*[18–19] investigated reactions of n-aryl-phthalamic acids with acetic anhydride and sodium acetate. It was found that the substituent (at the para position) on the benzene ring which was attached to the N atom had a significant effect on the composition of products and the reaction rate. The content of imide was greater for compounds having electron-withdrawing substituents such as Cl than for compounds having electron-donating substituents such as OCH_3. This is because the isoimide-imide rearrangement involved a transition state in which negative charges were developed on the N atom.[15,18–20] Electron-withdrawing groups at the para position attracted electrons from the N atoms, resulting in stabilization of the transition state. Therefore, imide was the favored product in this case. On the other hand, electron-donating groups at the para position might release electrons to the N atoms. Thus the transition state was destabilized and less imide was formed.

Similar behavior occurred in the case of curing PA/APDS/Au systems in acetic anhydride/triethylamine solutions. Amic acid molecules were chemisorbed on the Au surface through S atoms. The interaction of S lone-pair electrons with metal would result in electron withdrawal from the para-substituent (*i.e.*, the nitrogen atoms). Therefore, the isoimide-imide rearrangement was favored and imide became the predominant product. However, the chemisorbed bond (S-metal) would not cause electron attraction from a meta-substituent. Isomerization of isoimide to imide was not favored. Thus, curing PA/m-ATP/Ag samples in acetic anhydride/triethylamine solutions gave mostly isoimide.

Similar surface reactions regarding the substituent effect and the electron-withdrawing property of chemisorbed bonds were also found by other workers.[2-3,21] Bunding[21] reported SERS from p- and m-pyridinecarboxaldehyde (PCA) adsorbed onto silver electrodes. It was found that p-PCA interacted with water to form p-pyridylcarbinol at the surface but m-PCA did not. These results were explained by the interaction of the N lone-pair electrons with metal. A chemisorbed bond would lead to electron withdrawal from the p-substituent but not from the m-substituent. Similar reactions were also observed for p- and m-nitrobenzoic acid as described above.[2-3]

Some information concerned with the orientation of amic acid and isoimide moieties in PA/m-ATP/Ag systems was also obtained by comparing the relative intensities of bands in RAIR and SERS spectra. As mentioned above, in the difference spectrum obtained by subtracting the RAIR spectrum in Figure 4 from that in Figure 6, the band near 1673 cm^{-1} assigned to the C=O stretching mode of amide groups was stronger than the bands near 1317 and 1521 cm^{-1} assigned to the C—N stretching and N—H bending modes. This result indicated that amic acid moieties were adsorbed with amide C=O bonds largely perpendicular to the Ag surface (see Chart II).

In the RAIR spectra of PA/m-ATP/Ag samples after curing (see Figures 9 and 10), bands near 1685 and 1234 cm^{-1} assigned to the C=N stretching and asymmetric C—O—C stretching modes of isoimide were stronger than the band near 920 cm^{-1} due to the symmetric C—O—C stretching mode of isoimde. This result suggested that isoimide was likely oriented with the C=N bonds mostly perpendicular to the Ag surface (see Chart II).

IV. CONCLUSIONS

The molecular structure of a model polyimide/metal interphase, which was formed by depositing PA onto a silver substrate that was pretreated with m-ATP and then curing the films in a mixture of acetic anhydride and pyridine or triethylamine, was determined using SERS and RAIR. It was concluded that m-ATP was adsorbed dissociatively onto Ag substrates through the S atom with a tilted conformation. The tilt angle for m-ATP molecules adsorbed on the Ag surface was determined using RAIR to be approximately 39°, while no preferred rotational angle was observed. When PA was deposited onto m-ATP-treated Ag substrates, anhydride groups of PA reacted with amino groups of m-ATP to form amic acids. Chemical curing of these amic acids produced isoimide groups as the predominant product regardless of the use of pyridine or triethylamine catalyst. Differences in the relative composition of curing products between PA/APDS/Au and PA/m-ATP/Ag systems was attributed to the effect of substituents on the APDS and m-ATP benzene rings. It was again concluded that chemical linkages were formed between PA and Ag substrates through the organosulfur coupling agents. Formation of chemical bridges may lead to improved adhesion in polyimides/metal adhesive joints.

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