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**Non-Destructive Characterization of Polyimide/Copper and
Polyimide/Gold Interphases Using Surface-Enhanced Raman
Scattering and Reflection-Absorption Infrared Spectroscopy**

by

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Scattering and Reflection-Absorption Infrared Spectroscopy**

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ABSTRACT

The molecular structure of interfaces formed by curing the polyamic acid of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) against copper and gold substrates was determined using surface-enhanced Raman scattering (SERS) and reflection-absorption infrared spectroscopy (RAIR). It was found that acid groups of the polyamic acid reacted with metal ions on the substrates to form carboxylate salts when the polyamic acid was spin-coated onto metal substrates. Formation of carboxylates on the copper surface extended several hundred angstroms into the polyamic acid films, while only trace levels of carboxylates were formed on the gold surface. Formation of carboxylate salts suppressed the curing of polyamic acid on copper substrates. However, the degree of curing of the polyamic acid was high on gold surfaces. These results were compared to our previous work concerned with the molecular structure of interfaces between PMDA/ODA polyimides and silver substrates. The extent of carboxylate formation on silver was intermediate between those on copper and gold. Results obtained from SERS and RAIR also indicated that cured polyimide films above the partially cured layers were oriented edge-on with the PMDA moieties perpendicular to the metal surface and the ODA moieties mostly parallel to the surface.

I. Introduction

Polyimides have generated an accelerated interest for use in microelectronic and composite applications. This is attributed to the fact that polyimides offer good 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 applications in microelectronics and composites. As a result, numerous studies have been performed to characterize and control interfaces between polyimides and inorganic materials in order to improve the adhesion of polyimides to other materials.

Most previous studies have focused on metal/polyimide interfaces formed by deposition of metals onto pyromellitic dianhydride-oxydianiline (PMDA/ODA) polyimide (1-17). Generally speaking, metals such as chromium and aluminum having strongly negative free energies of vapor phase oxidation formed an interfacial oxide with the carbonyl oxygen atoms on the polyimide. However, other metals such as copper, silver, and gold interacted only weakly with PMDA/ODA polyimides and tended to diffuse into polymer during deposition rather than react with functional groups on the surface.

Polyimide/metal interfaces have been less widely studied but have received more attention recently (18-28). This type of interface can be formed by spin-coating polyamic acid (PAA) onto a metal surface from solution and then curing to obtain the polyimide. An alternative is to co-deposit monomers of polyimide such as PMDA and ODA onto a metal surface and then thermally cure

the monomers to obtain the polyimide. Properties of polyimide/metal interfaces may be much different than those of metal/polyimide interfaces, since polyimide/metal interfaces involve interaction of the metal with a polyamic acid (18-26) or monomers of the polyimide (27,28), instead of a polyimide.

In order to obtain new insight into the interaction between polyimides and metals, we have been interested in using a novel technique known as surface-enhanced Raman scattering (SERS) for characterizing polyimide/metal interfaces. 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 to its value for normal Raman scattering. The enhancement for molecules more than a few molecular layers from the metal surface is negligible. As a result, SERS is surface-selective and can be used for non-destructive characterization of polyimide/metal interfaces 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 interface. Most other analytical techniques which have been used to investigate polyimide interfaces, such as XPS and RAIR, required that either the polyimide film or the substrate be very thin or that they be separated.

Several reports have appeared indicating that SERS may be used as a probe for interfaces between polymers and metals (29-33). Boerio et al (31) investigated SERS from poly(α -methylstyrene) (PMS) spin-coated onto silver island films from methyl ethyl ketone (MEK) solutions having various concentrations. The

intensity of the observed bands was approximately constant even though the thickness of the PMS films varied from about 300 to 2000 angstroms, demonstrating that SERS was an interface rather than bulk effect.

Boerio and Hong (32) also used SERS to determine the molecular structure of interfaces between a silver island film and a model anaerobic acrylic adhesive system. The intensity of bands in SERS spectra of the neat adhesive were independent of the thickness of the adhesive films, indicating that the observed SERS signals were characteristic of the interface and not of the bulk films. 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 the 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.

Recently, we have used SERS to investigate the molecular structure of interfaces formed by curing the polyamic acid of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) (34) and the polyamic acid of PMDA and 2,2-bis[4(4-aminophenoxy)-phenyl]-hexafluoropropane (4-BDAF) (35) 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.

However, these two types of polyimide had different orientations when they were cured against silver substrates. For

the case of PMDA/ODA polyimide, PMDA moieties were adsorbed onto the silver surface edge-on with the carbonyl bonds perpendicular to the surface, while the ODA moieties were oriented mostly parallel to the silver surface. For PMDA/4-BDAF polyimide, the planes of the PMDA rings were parallel to the surface. The planes of the carboxylate groups were perpendicular to those of the PMDA moieties and the silver surface. Approximately half of the C_6H_4 rings in the 4-BDAF moieties were parallel to the surface but the planes of the COC groups were perpendicular to the surface.

The purpose of this paper is to report results we have obtained using SERS and reflection-absorption infrared spectroscopy (RAIR) to characterize PMDA/ODA polyimide/copper and PMDA/ODA polyimide/gold interfaces. These results are also compared to those obtained previously on silver (34). Results obtained from SERS and RAIR indicated that relatively large amounts of carboxylate salts were formed on the copper surface, resulting in a partial cure of PAA films on copper substrates. However, PAA was highly cured on the gold substrate. The extent of carboxylate formation on the silver substrate was intermediate between those on the copper and gold substrates.

II. 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 blown dry with nitrogen again.

The clean glass slides were placed immediately in a vacuum chamber which was purged with nitrogen and pumped down to 10^{-6} Torr using sorption, sublimation, and ion pumps. Gold 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 0.2 angstrom/sec. The thickness of the gold island films was controlled at about 65 angstroms using a quartz crystal oscillator thickness monitor. Effects of the thickness and deposition rate of gold island films on the SERS enhancement were investigated in our laboratory. It was found that 65 Å thick gold island films which were evaporated at a rate of 0.2 Å/s produced the maximum SERS enhancement for this kind of SERS-active substrate.

A chemical etching process suggested by Wokaun et al (36) was used to prepare SERS-active copper substrates, because evaporated copper tended to form smooth films. Copper substrates were prepared by immersing high purity copper foils (Aldrich Chemical Co.) in vigorously stirred 20% nitric acid solutions for 20 minutes. The surface to be studied was oriented perpendicular to the direction of flow. After etching, the copper foil was rinsed using distilled-deionized water and dried in a stream of dry nitrogen. The etching conditions described above, including the concentration of nitric acid and the etching time, were also optimized in our laboratory in order to obtain the maximum SERS enhancement.

The polyamic acid of PMDA and ODA was obtained from DuPont Corporation (PI2545). Thin films of polyamic acid were deposited onto freshly prepared gold and copper substrates by spin-coating from dilute solutions in N-methyl pyrrolidone (NMP). These polyamic acid films were dried at 100°C for 15 minutes to remove the solvent. Some of them were then cured by heating at 200°C for an additional 30 minutes in nitrogen to form the polyimide.

SERS spectra were obtained 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 Vector 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 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 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 polyamic acid and polyimide were obtained from a small amount of polyamic acid (viscous liquid) supported in a glass capillary tube and a thick polyimide film, respectively, 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} .

Samples were prepared for reflection-absorption infrared (RAIR) investigations as described below. Thick gold films were prepared by thermally evaporating gold onto clean glass slides. Copper substrates were prepared by mechanical polishing. Commercially pure copper foil 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 μm alumina on Microcloths (Buehler, Inc.) using deionized water as the lubricant. The resulting mirrors were rinsed in deionized water ultrasonically and blown dry with a stream of nitrogen.

Polyamic acids were immediately spin-coated onto freshly prepared gold and copper substrates from dilute solutions in NMP. After that, specimens were dried at 100°C for 15 minutes to remove the solvent. In some cases, PAA films were further heated at 200°C in nitrogen for 30 minutes to produce polyimides.

RAIR spectra of the polyamic acid films before and after curing were obtained using a Perkin-Elmer Model 1800 Fourier-transform infrared (FTIR) 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} . Two hundred and fifty six 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 PAA and polyimide were obtained using the same spectrophotometer. Specimens of PAA were prepared by placing a small amount of liquid between two KBr pellets. Samples of polyimide were prepared by curing a small amount of PAA onto KBr pellets.

The thickness of the polymer films deposited on gold and copper substrates was determined by ellipsometry. Polymer films were spun onto thick gold films and polished copper substrates from the same solutions and at the same speeds as were used to prepare the RAIR specimens. The thickness of the films was measured using a Rudolph Research Model 436 ellipsometry to examine the metal substrates before and after deposition of the organic films.

III. Results and Discussion

Normal Raman and transmission infrared spectra obtained from the polyamic acid (PAA) and polyimide of PMDA/ODA are shown in Figures 1 and 2, respectively. Band assignments of the observed bands had been described in our previous work (34). For the purpose of convenience, they are summarized in Table I and II. Basically, we used the Wilson numbering system (37,38) to assign the modes of the substituted benzene rings in both Raman and infrared spectra. The Raman assignments for acid and amide groups were based on the work of Varsanyi (38), Mack et al (39), and Colthup et al (40), while Raman assignments for imide groups were given by Ishida et al (41) and Tsai et al (42). The

assignments of the infrared bands are similar to those proposed by DiNardo et al (43) for PMDA/ODA polyamic acid and polyimide and by Ishida et al (41), Dine-Hart et al (44), and Silverman (45) for PMDA/ODA polyimide.

The normal Raman spectrum of polyamic acid (see Figure 1A) was characterized by strong bands near 1623 and 1340 cm^{-1} and medium intensity bands near 1698, 1574, 1177, 940, and 761 cm^{-1} . Bands observed near 1698, 940, 761 cm^{-1} in the normal Raman spectrum of polyamic acid were assigned to the modes $\nu(\text{C}=\text{O})$, $\pi(\text{OH})$, and $\beta(\text{C}=\text{O})$ of the acid functional groups, respectively. Bands near 1574 and 1340 cm^{-1} were attributed to modes of amide groups. When the polyamic acid was cured at 100°C for 15 minutes and 200°C for an additional 30 minutes in nitrogen, bands due to acid and amide groups near 1698, 1574, 1340, 940, and 761 cm^{-1} disappeared. Bands assigned to the C=O stretching, CNC axial stretching, and CNC transverse stretching modes of imide groups appeared near 1802, 1403, and 1135 cm^{-1} , respectively, indicating that imidization had occurred under the above curing condition.

In the transmission infrared spectrum of the polyamic acid before curing (see Figure 2A), bands near 1720, 1303, and 1407 cm^{-1} were assigned to the C=O stretching, CO stretching, and COH in-plane bending modes of acid groups, respectively. Bands near 1663 and 1542 cm^{-1} were assigned to vibrational modes of amide groups. Bands related to amide and acid groups all disappeared after curing, while bands characteristic of imide groups were observed near 1778, 1730, 1378, 1169, and 726 cm^{-1} (see Figure 2B). These results again indicated that the polyamic acid was

imidized to form the PMDA/ODA polyimide using the thermal curing process described above.

The SERS spectrum obtained from a thin PAA film spin-coated onto an etched copper substrate spin-coated from a 4% solution in N-methyl pyrrolidone (NMP) is shown in Figure 3A. The SERS spectrum obtained from a thin PAA film spin-coated onto a gold island film from a 1.25% solution is shown in Figure 3B. The observed bands and their assignments are summarized in Table I. The thickness of these PAA films on copper and gold substrates was about 420 and 130 Å, respectively. When these two spectra were compared, some differences were observed. For example, the band near 1420 cm^{-1} appeared strong in the SERS spectrum of PAA on copper, while it was very weak in the SERS spectrum of PAA on gold. This band was assigned to the symmetric stretching mode of carboxylate groups, indicating that relatively large amount of acid groups in PAA were adsorbed dissociatively onto copper substrates to form carboxylate salts. However, only trace levels of carboxylates were formed on the gold substrate. A shoulder near 1698 cm^{-1} related to the carbonyl stretching mode of acid groups was still evident in Figure 3B but it almost disappeared in Figure 3A, further supporting the above results. The asymmetric stretching mode of carboxylates was combined with the tangential ring stretching mode $\nu(8a)$ of the benzene rings and appeared strong in the SERS spectrum of PAA deposited onto copper substrates.

Comparing these results to those obtained previously on silver (34), it was found that the amount of carboxylates formed

on the silver surface was intermediate between those on copper and gold substrates. This was evidenced by the observation of the medium intensity band near 1415 cm^{-1} which was due to the symmetric stretching mode of the carboxylate.

It should be noted that there were four bands near 1575, 1500, 967, and 725 cm^{-1} in the Raman spectrum obtained from a bare copper substrate. It was first considered that those bands were related to contaminants adsorbed on the copper substrate during the etching process. However, in some cases, these bands were also observed in the normal Raman spectra obtained from some polyimide model compounds such as N,N-diphenyl pyromellitic diimide, indicating that they were not related to the surface contaminations. Instead, it is likely that they were artifacts related to the gratings and must be subtracted from the SERS spectra. The SERS spectrum of PAA on copper shown in Figure 3A was obtained after subtracting the artifacts but the subtraction was not complete.

Reflection-absorption infrared (RAIR) spectra obtained from thin PAA films spin-coated onto copper substrates from 10, 2.5, 0.5% solutions in NMP and then dried at 100°C for 15 minutes are shown in Figure 4. The thickness of these films was about 1700, 300, and 90 Å, respectively. As the thickness of the films decreased, it was observed that the band near 1720 cm^{-1} associated with the C=O stretching mode of the acid groups became much weaker. Bands near 1600 and 1405 cm^{-1} which were assigned to the asymmetric and symmetric stretching modes of carboxylates were overlapped with bands due to aromatic rings and amide

groups. However, these bands became stronger and broader as the film thickness decreased. These results again indicated that acid groups reacted with the copper substrate to form carboxylate salts. In the case of PAA films having a thickness of 300 and 90 Å (see Figures 4B and 4C), the carbonyl stretching band near 1720 cm^{-1} almost disappeared, indicating that formation of carboxylates extended several hundred angstroms away from the copper surface.

Significant differences were observed in RAIR spectra obtained from thin PAA films spin-coated onto thick gold films from 2, 0.4, and 0.08% solutions in NMP as shown in Figure 5. The thickness of these PAA films was 260, 45, and 15 Å, respectively. The band near 1720 cm^{-1} associated with the C=O stretching mode of the acid groups decreased in intensity somewhat as the thickness of the PAA films decreased, indicating that only trace amounts of carboxylates were formed on the gold surface. These results are consistent with those obtained from SERS described above. Considering the inert nature of gold and the catalytic effect of copper, it is quite reasonable to expect the extent of carboxylate salt formation on copper substrates to be much greater than on gold substrates.

The SERS spectrum of polyimide obtained after thermal curing (200°C for 30 minutes in N_2) of a PAA film spin-coated from a 4% solution onto a copper substrate is shown in Figure 6A. The observed bands and their assignments are summarized in Table II. Significant differences were observed between this spectrum and the normal Raman spectrum of polyimide (see Figure 1B). For

example, the band near 1802 cm^{-1} in the SERS spectrum of polyimide on copper became relatively weak. The broad band near 1620 cm^{-1} , which had medium intensity in the normal Raman spectrum, was the strongest band in the SERS spectrum of polyimide on copper. This band was attributed to a combination of the asymmetric stretching mode of carboxylate groups and the ring stretching mode $\nu(8a)$ of the benzene rings. The band near 1405 cm^{-1} assigned to the CNC axial stretching mode of imide groups was overlapped with the band assigned to the symmetric stretching mode of carboxylates and remained strong in the SERS spectrum of polyimide on copper. The band near 1345 cm^{-1} due to amide groups of PAA was evident in the SERS spectrum of polyimide on copper, but was not observed in the normal Raman spectrum of polyimide.

Considering the presence of bands related to amide and carboxylate groups in the SERS spectrum of polyimide on copper (see Figure 6A) and the low intensity of bands related to imide groups, it was concluded that only partial curing of PAA to polyimide occurred at the copper surface. This cure inhibition probably resulted from the formation of carboxylate salts between acid groups of the PAA and copper ions of the substrates.

Cure inhibition was also observed in our previous work for thin PAA films cured against silver substrates (34). This was evident from the observation of the strong band near 1620 cm^{-1} assigned to a combination of asymmetric stretching mode of carboxylates and the benzene ring stretching mode, and the band near 1345 cm^{-1} assigned to amide groups of PAA in the SERS

spectrum of polyimide on silver. However, the band near 1345 cm^{-1} in the SERS spectrum of polyimide cured against silver substrates was weaker than the corresponding band in Figure 6A, revealing that the degree of curing of PAA films on silver substrates was higher than on copper substrates.

The SERS spectrum of polyimide obtained after thermal curing of PAA films spin-coated from a 1.25% solution onto a gold island film is shown in Figure 6B. The assignments of the observed bands are also summarized in Table II. The thickness of these polyimide films on gold was about 125 Å.

Generally speaking, the SERS spectrum of polyimide cured against gold island films was more similar to the normal Raman spectrum of polyimide (see Figure 1B) than SERS spectra of polyimide cured against copper and silver substrates. Bands characteristic of imide functional groups, including those near 1802 , 1403 , and 1135 cm^{-1} , were all strong in the SERS spectrum of polyimide on gold, implying that a high degree of curing of PAA films occurred on gold substrates.

It was concluded from the SERS results that the extent of carboxylate formation on the metal substrates was greatest on copper, intermediate on silver, and least on gold. The formation of carboxylate salts inhibits curing of PAA adsorbed onto metal substrates, resulting in a lower degree of cure. Therefore, the degree of curing of PAA films deposited onto these metal substrates was greatest on gold, least on copper, and intermediate on silver.

Orientation effects may also contribute to the differences between SERS and normal Raman spectra of the polyimide. Moskovits developed a theory of Raman scattering by molecules near metal surfaces (46). According to the theory, bands corresponding to vibrational modes involving atomic motions which are mostly perpendicular to the metal surface are expected to be relatively strong. Bands corresponding to vibrational modes involving atomic motions which are mostly parallel to the surface are expected to be relatively weak.

If the polyimide was adsorbed with an edge-on configuration in which the carbonyl bonds were approximately perpendicular to the surface, the band near 1802 cm^{-1} corresponding to the stretching mode of the carbonyl groups would be relatively strong in the SERS spectra. The band near 1403 cm^{-1} corresponding to the axial CNC stretching mode would involve atomic motions parallel to the surface and would be relatively weak in the SERS spectra.

In fact, this is exactly what was observed in the SERS spectrum of polyimide on gold (see Figure 6B). The band near 1802 cm^{-1} was approximately half the intensity of the band near 1403 cm^{-1} in the normal Raman spectrum of polyimide (see Figure 1B), while it had the nearly same intensity as the band near 1403 cm^{-1} in the SERS spectrum of polyimide on gold. These results indicated that the cured polyimide was oriented on the gold surface with an edge-on conformation in which the carbonyl groups were perpendicular to the surface. The band near 1135 cm^{-1} , which was assigned to the CNC transverse stretching mode, was

stronger in the SERS spectrum of polyimide on gold than in the normal Raman spectrum, confirming the above conclusion.

However, orientation effects were not observed in the SERS spectrum of polyimide on copper (see Figure 6A). As described above, carboxylate layers might extend several hundred angstroms away from the copper surface, while the SERS effect is restricted to the first few molecular layers from the metal surface. Therefore, the SERS spectrum of polyimide on copper as shown in Figure 6A was dominated by bands related to carboxylate groups and contained little contribution from orientation effects.

RAIR spectra obtained from thin polyimide films which were prepared by spin-coating the PAA onto copper substrates from 10, 2.5, and 0.5% solutions in NMP and then thermally curing the films at 200°C for 30 minutes in nitrogen are shown in Figure 7. Bands related to carboxylate groups near 1600 and 1405 cm^{-1} in the RAIR spectra became stronger and broader and the band assigned to the carbonyl stretching mode of imide groups near 1730 cm^{-1} decreased in intensity as the film thickness decreased. These results again indicated that curing of PAA films on copper substrates was largely inhibited by formation of carboxylate salts.

As mentioned above, the thickness of PAA films spin-coated from 10, 2.5, and 0.5% solutions onto copper substrates was about 1700, 300, and 90 Å, respectively. The thickness of these PAA films after curing was not measured because of the growth of copper oxide layers during heat treatment. It has been reported that thermal oxidative degradation of the poly(ester imide) films

which were cured against copper substrates in air at 200°C for several hours led to thinning of the films (47). However, we cured our PAA films in nitrogen for only a short time (30 minutes). Oxidative degradation was largely reduced using this curing process and the thickness of the cured polymer films was not expected to decrease significantly.

It is known that thermal degradation of polymer films can be accelerated in the presence of copper. Several authors investigated the degradation of PAA cured against copper substrates in air (23,24,48). Two bands characteristic of degradation products were found in the infrared spectra. A medium intensity band near 2186 cm^{-1} was assigned to nitrile groups and a strong band near 1570 cm^{-1} was assigned to a combination of carboxylate groups and fused aromatic rings. The band near 2186 cm^{-1} was very weak in our RAIR spectra of PAA after curing, indicating that oxidative degradation was largely reduced when PAA films were cured in nitrogen. It was thus considered that the band observed near 1600 cm^{-1} in our RAIR spectra (see Figure 7B and 7C) was mostly attributed to the carboxylate groups.

RAIR spectra obtained from thin polyimide films which were prepared by spin-coating PAA onto gold substrates from 2, 0.4, and 0.08% solutions and then thermally curing the films at 200°C for 30 minutes in nitrogen are shown in Figure 8. The thickness of these polyimide films was about 250, 40, and 10 Å. The spectra were all dominated by bands characteristic of the polyimide, such as those near 1730, 1500, 1380, and 1240 cm^{-1} ,

even for the spectrum of the thinnest film (see Figure 8C), indicating that PAA was highly cured on the gold surface.

Orientation effects of polyimides adsorbed onto metal substrates may also causes the changes in relative intensity of some bands in RAIR spectra. 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 appeared with reduced intensity.

Assuming that the PMDA moieties were adsorbed with the edge-on orientation, the band near 1730 cm^{-1} was expected to increase in intensity relative to the band near 1378 cm^{-1} as the polyimide film thickness decreased, since the transition moment for the C=O stretching mode would be perpendicular to the surface and that for the axial CNC stretching mode would be parallel. However, for cure inhibition described above, the relative intensity of the bands near 1730 and 1378 cm^{-1} were both expected to decrease as the film thickness decreased.

When the RAIR spectrum of thick polyimide films (1700 Å) on copper (See Figure 7A) and the transmission infrared spectrum of polyimide (see Figure 2B) were compared, significant differences were observed. These differences were considered mostly due to orientation effects, since contributions from cure inhibition were not considerable in RAIR spectra of such thick films. Bands near 1730 and 1378 cm^{-1} in the transmission infrared spectrum of the polyimide had approximately the same intensity. However, the band near 1730 cm^{-1} was much stronger than the band near 1378

cm^{-1} in the RAIR spectrum of polyimide on copper, implying that PMDA moieties of polyimides were oriented edge-on with respect to the copper surface. Bands near 1500 and 1240 cm^{-1} in the transmission infrared spectrum of polyimide also had the similar intensities as the band near 1730 cm^{-1} , while they were much weaker in the RAIR spectrum of polyimide (see Figure 7A). These two bands were assigned to the tangential ring stretching mode $\nu(19a)\text{-C}_6\text{H}_2$ and the COC stretching mode of the ODA moieties, indicating that the plane of the ODA rings was oriented mostly parallel to the surface.

Cure inhibition became considerable when the thickness of the polyimide films on copper decreased (see Figures 7B and 7C). This was evident from the observation of a broad band near 1600 cm^{-1} and a shoulder near 1400 cm^{-1} , which were characteristic of carboxylate groups, and the decrease in intensity of the band near 1730 cm^{-1} due to the C=O stretching of imide groups. The intensity of the band near 1380 cm^{-1} assigned to the CNC axial stretching mode was also expected to decrease as the film thickness decreased. However, the relative intensity of this band did not change much in all of the RAIR spectra. This band overlapped with the band related to the carboxylate groups near 1405 cm^{-1} , resulting in the unexpected large intensity.

RAIR results described above indicated that formation of carboxylates suppressed the curing of PAA films on copper and carboxylate salts still remained in the interfacial region (few hundred angstroms) after curing. Above this partially cured interfacial zone, PAA was fully cured and oriented with an edge-

on conformation. This preferential orientation of cured PMDA/ODA polyimide may extend at least several hundred angstroms away from the copper surface. Russell et al (49) investigated the orientation of PMDA/ODA polyimide films formed by curing the polyamic acid onto quartz or pyrex substrates. They found that the long axes of the molecules were oriented parallel to the plane of the films and this orientation might extend several microns into the bulk polymer.

These results were also similar to our previous RAIR results concerning the molecular structure of the interfaces between PMDA/ODA polyimide and silver (34). It was found that a few molecular layers of carboxylate salts were formed adjacent to the silver surface and that the same orientation of PMDA/ODA polyimide as that on copper extended at least several molecular layers into the bulk polyimide.

The preferential orientation of cured PMDA/ODA polyimides on the copper surface was also observed on the gold surface. Since the curing of PAA was nearly complete on gold substrates, differences between RAIR spectra of polyimide cured against copper substrates (see Figure 8) and the transmission infrared spectrum of polyimide (see Figure 2B) were mostly due to orientation effects. The band near 1730 cm^{-1} was always much stronger than those near 1500 , 1378 , and 1240 cm^{-1} in the RAIR spectra, indicating that PMDA/ODA polyimide molecules were also aligned edge-on on the gold surface with the ODA moieties mostly parallel to the surface.

The results described in the present paper are generally consistent with those in the literature. As mentioned above, RAIR results obtained by Linde (20) indicated that PAA did not react with gold substrates. However, Russat (22) proposed that a thermally-activated chain cleavage or an unspecified interfacial interaction occurred between PAA and gold. Our results indicate that a trace level of carboxylate was formed on the gold surface, but the extent of curing of PAA was high on gold substrates.

Formation of carboxylate salts on silver and copper substrates was observed by Linde (20) who also found that heating PAA films on copper and silver substrates at 300-350°C in nitrogen for 8 minutes resulted in destruction of the films. However, no destruction of the PAA films occurred under the curing conditions used in the present study. These differences indicate that the structure of polyimide films cured against metal substrates depends strongly on the curing conditions.

IV. Conclusions

Results described above again demonstrate that surface-enhanced Raman scattering is a powerful technique for non-destructive characterization of polymer/metal interfaces. The structure of polyimide/metal interfaces strongly depends on the metal substrates used. When polyamic acid films were spin-coated onto metal substrates, it was found that formation of carboxylates on the copper surface extended several hundred angstroms into the PAA films, while few molecular layers of carboxylate salts were formed on the silver surface. The least amount of carboxylate formed on gold surfaces. Formation of

carboxylate salts inhibited the curing of polyamic acid, resulting in the lowest degree of curing of the polyamic acid on copper substrates and the highest degree of curing on gold substrates. The extent of curing of the polyamic acid on silver was intermediate between those on copper and gold.

Results obtained from SERS and RAIR also showed that cured polyimide films above the partially cured layers on gold, silver, and copper substrates were all oriented edge-on with the PMDA moieties perpendicular to the metal surface and with the ODA moieties mostly parallel to the surface. This preferential orientation may extend at least several hundred angstroms away from the metal surface.

V. Acknowledgements

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Table I. Tentative Band Assignments for PAA of PMDA/ODA

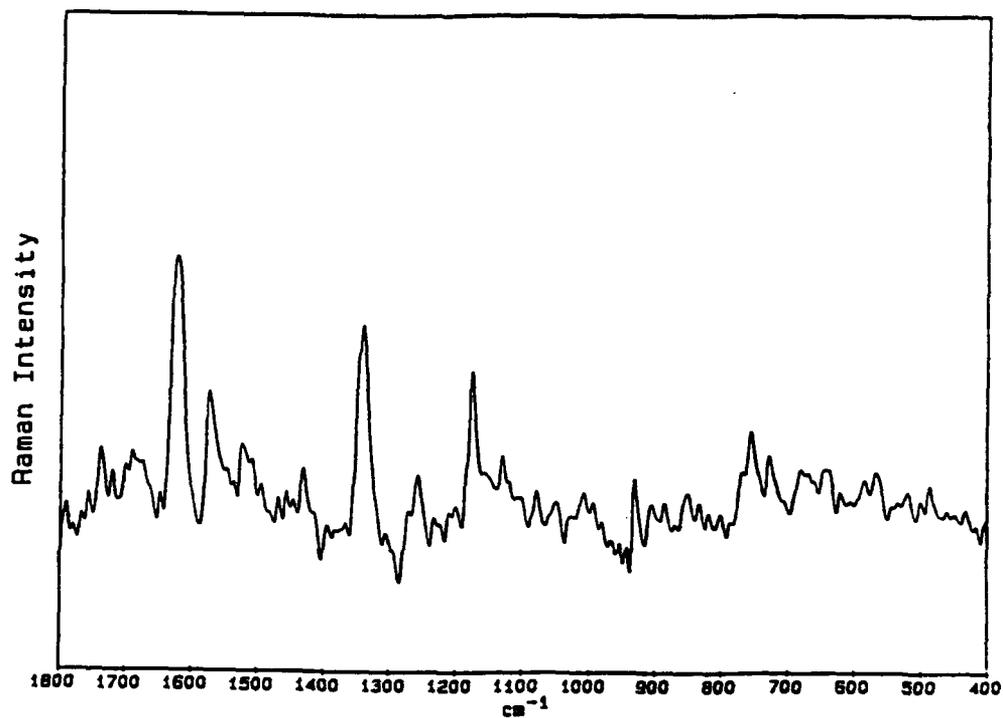
Raman	Frequency (cm ⁻¹)			Assignment
	SERS	IR	RAIR	
		3255(W)		ν (N-H)
		3205(W)		ν (20)-C ₆ H ₂
		2926(W)	2921(W)	ν (OH)
1698(W)		1720(S)	1722(W)	ν (C=O), acid
				ν (C=O), acid
1623(M)		1670(S)	1660(M)	ν (C=O), amide I
	1620(S)			ν (8a)-C ₆ H ₂ and C ₆ H ₄
		1610(W)	1609(W)	ν_{as} (COO ⁻) and ν (8a)
			1600(W)	ν (8a)
1574(W)	1576(W)			ν_{as} (COO ⁻)
				} ν (C-N-H), amide II
		1545(M)	1542(W)	
1450(W)		1499(S)	1500(S)	ν (19a)-C ₆ H ₄
	1420(W)			ν_S (COO ⁻)
		1410(M)	1405(W)	β (OH) acid and ν_S (COO ⁻)
1340(M)	1345(M)			ν (C-N)
		1303(M)	1304(W)	ν (C-OH)
1263(W)	1269(W)			ν (C-N-H), amide
		1237(S)	1240(W)	ν (C-O-C), ODA
		1216(M)	1219(W)	
1177(W)	1178(W)	1170(W)	1170(W)	ν (9a)-C ₆ H ₄ or ν (13)-C ₆ H ₂
		1113(M)	1110(W)	ν (18b)-C ₆ H ₄
1012(W)		1014(W)		ν (18a)-C ₆ H ₄
		987(W)		ν (17a)-C ₆ H ₄
940(W)				π (OH), acid
		872(W)		ν (17b)-C ₆ H ₂
	840(W)		833(W)	δ (COO ⁻)
761(M)		754(W)		β (C=O), acid
732(W)	733(W)			ν (1)-C ₆ H ₂
		661(W)		π (C=O), acid
636(W)				ν (6b)-C ₆ H ₄

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

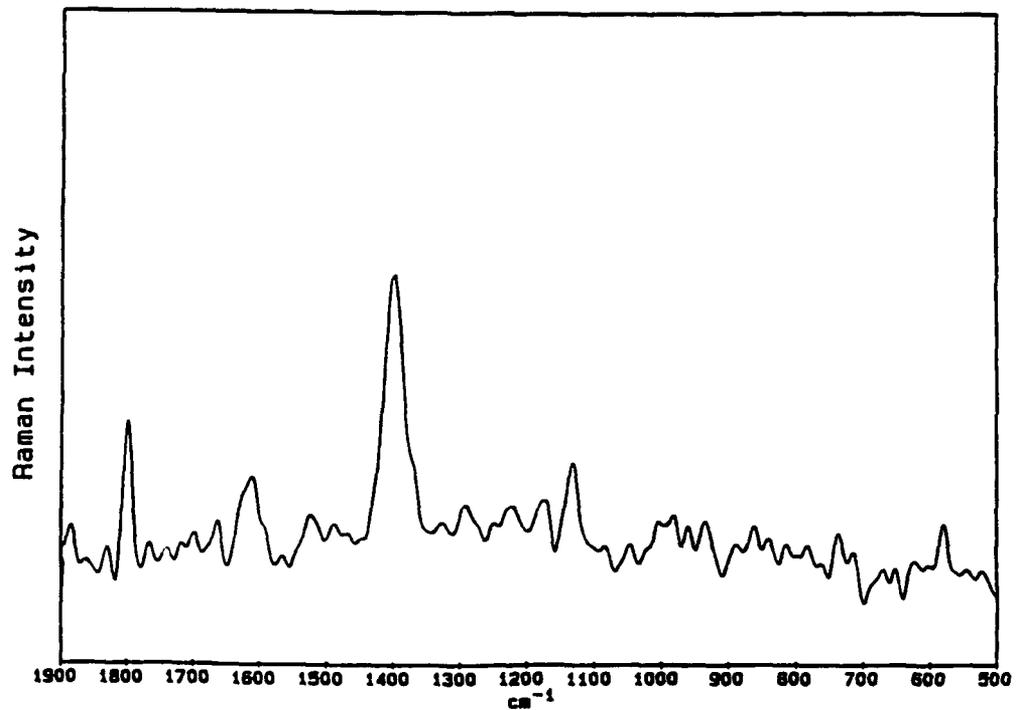
Table II. Tentative Band Assignments for polyimide of PMDA/ODA

Frequency (cm ⁻¹)				
Raman	SERS	IR	RAIR	Assignment
		3372(W)		
1802(M)	1798(M)	3073(W)		$\nu(20a)-C_6H_2$
		1777(S)	1778(W)	} $\nu(C=O)$, in-phase imide I
1623(M)		1725(S)	1730(S)	
	1620(S)			$\nu(C=O)$, out-of-phase
				$\nu(8a)-C_6H_2$
				$\nu(COO^-)$ and $\nu(8a)$
		1610(W)		$\nu(8a)$
1525(W)			1600(W)	$\nu(8a)$ and $\nu(COO^-)$
		1500(S)	1500(M)	$\nu(19a)-C_6H_4$
1403(S)	1408(W)	1456(W)		$\nu(19b)-C_6H_2$
			1405(W)	$\nu(C-N-C)$, axial, imide II
				$\nu(COO^-)$
		1378(S)	1379(W)	$\nu(C-N-C)$, axial, imide II
		1291(W)		$\nu(7a)-C_6H_4$
1180(W)	1176(W)	1239(S)	1240(W)	$\nu(C-O-C)$, ODA
				$\nu(9a)-C_6H_4$ or $\nu(13)-C_6H_2$
1134(W)	1142(W)	1169(M)	1169(W)	$\nu(CNC)-trans.$, $\nu(9a)-C_6H_4$
				$\nu(C-N-C)$, transverse imide III
		1116(M)	1116(W)	$\nu(18b)-C_6H_4$
		1093(W)	1096(W)	
		1015(W)		$\nu(18a)-C_6H_4$
865(W)		882(M)		$\nu(17b)-C_6H_2$
				$\nu(1)-C_6H_4$
		823(M)	825(M)	$\nu(17b)-C_6H_4$
		726(M)	726(W)	C-N-C, o.p.b.
				imide IV
736(W)				$\nu(1)-C_6H_2$
717(W)				$\nu(12)-C_6H_4$
625(W)	633(W)			imide ring, i.p.b.
		605(W)		$\nu(12)-C_6H_2$
586(W)	585(W)			$\nu(3)-C_6H_2$
		518(W)		$\nu(16b)-C_6H_4$

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

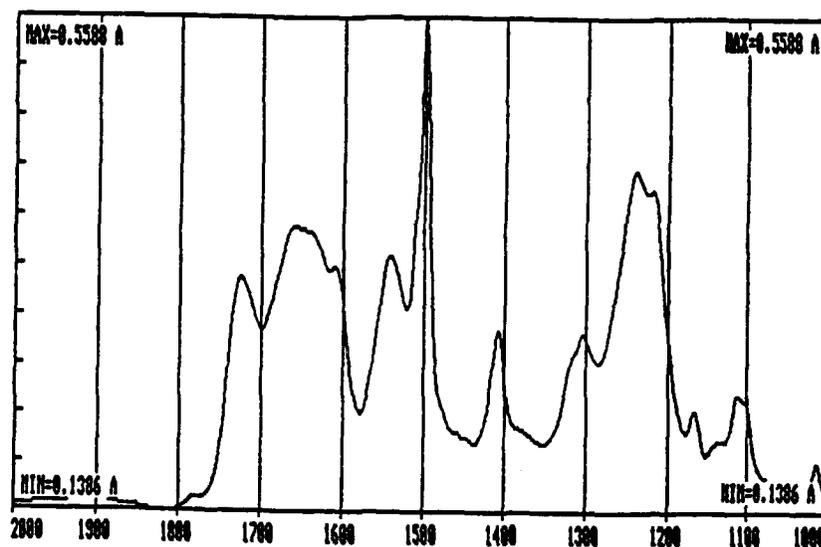


(A)

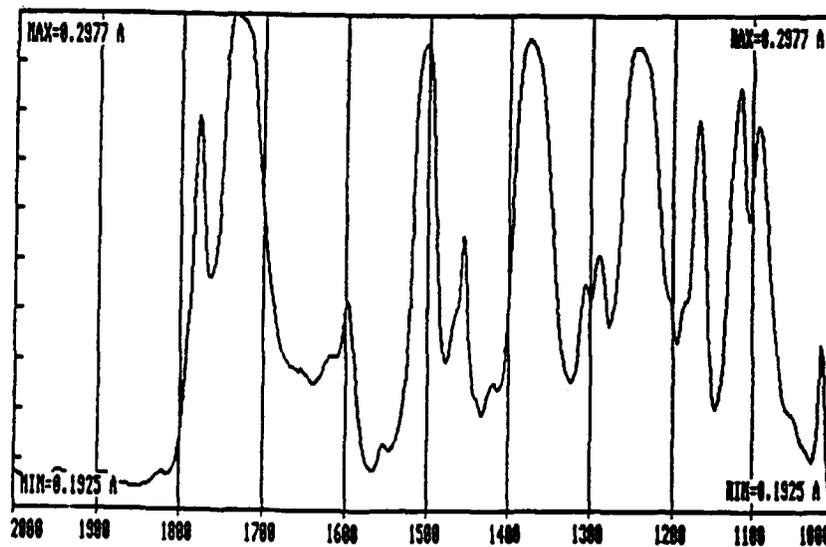


(B)

Figure 1. Normal Raman spectra of (A)-polyamic acid of PMDA/ODA and (B)-polyimide of PMDA/ODA.

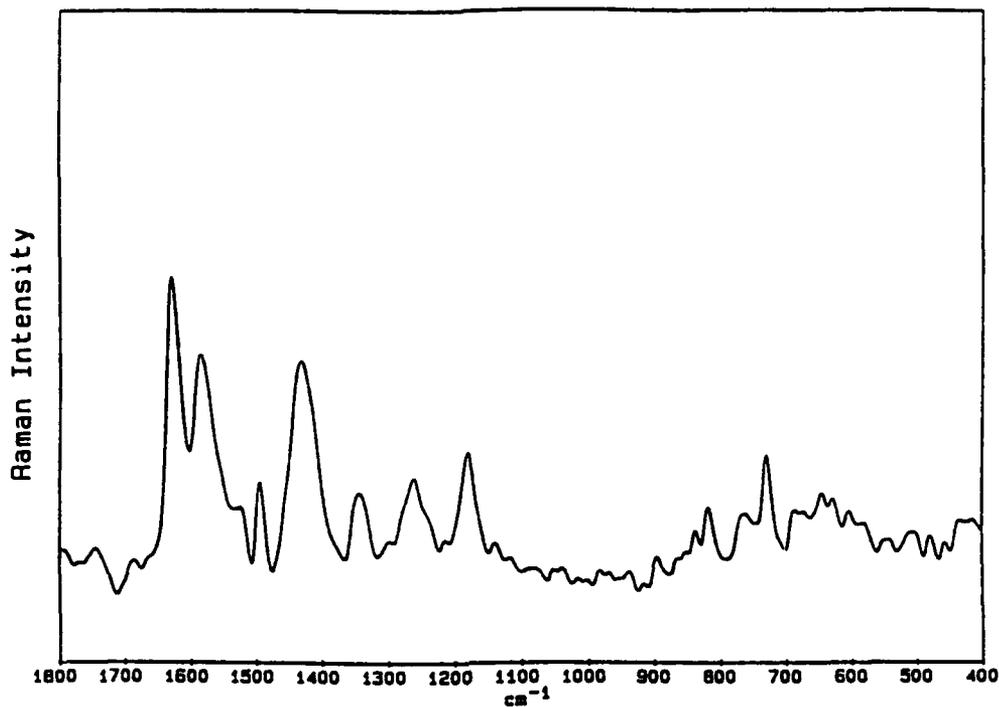


(A)

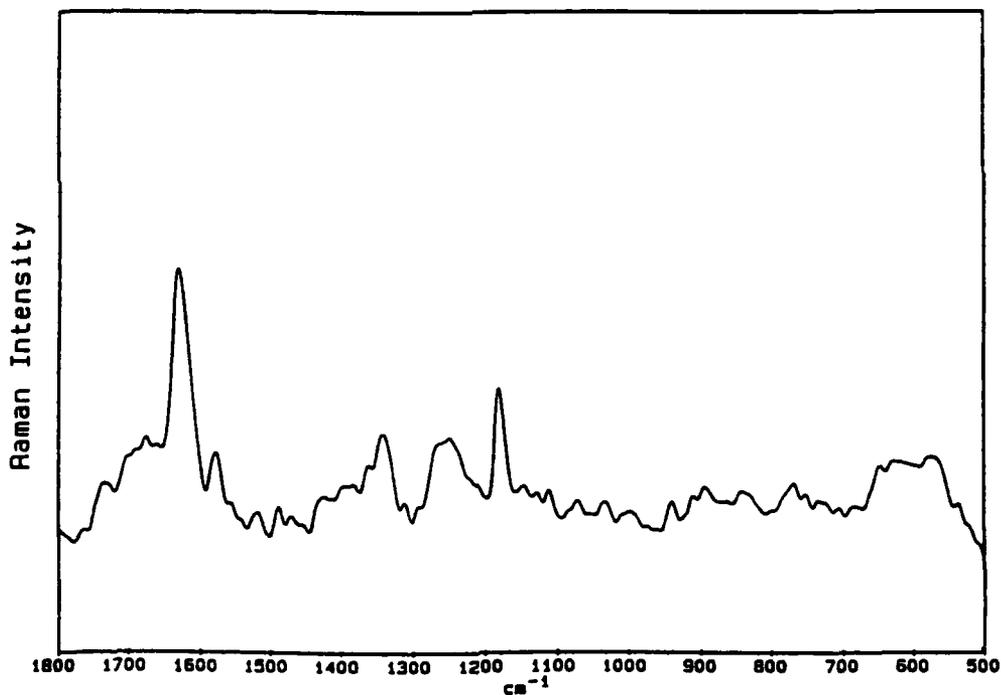


(B)

Figure 2. Transmission infrared spectra of (A)-polyamic acid and (B)-polyimide of PMDA/ODA.

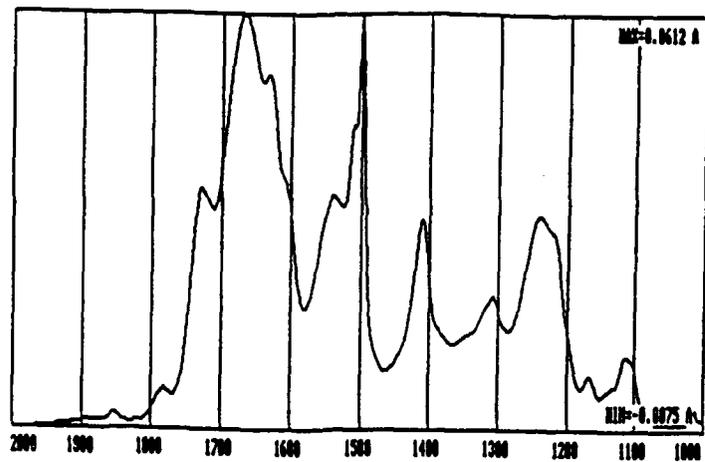


(A)

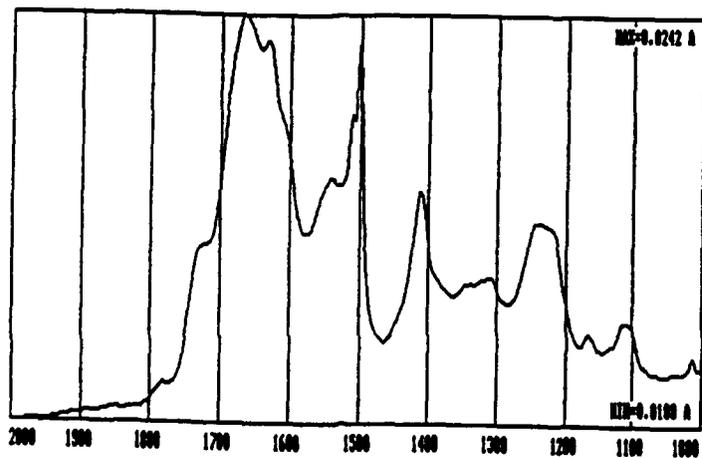


(B)

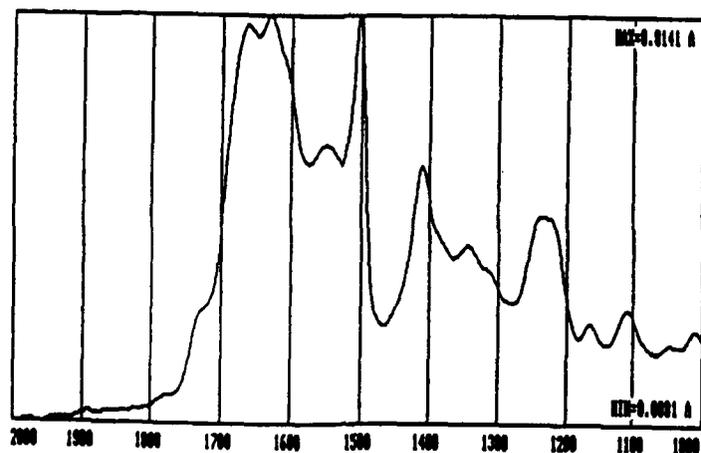
Figure 3. SERS spectrum obtained from polyamic acid of PMDA/ODA spin-coated onto (A)-an etched copper substrate from a 4% solution and (B)-a gold island film from a 1.25% solution in N-methyl pyrrolidone (NMP).



(A)

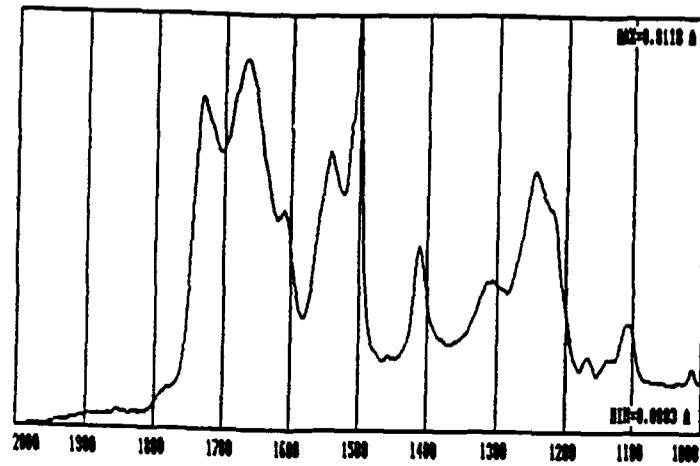


(B)

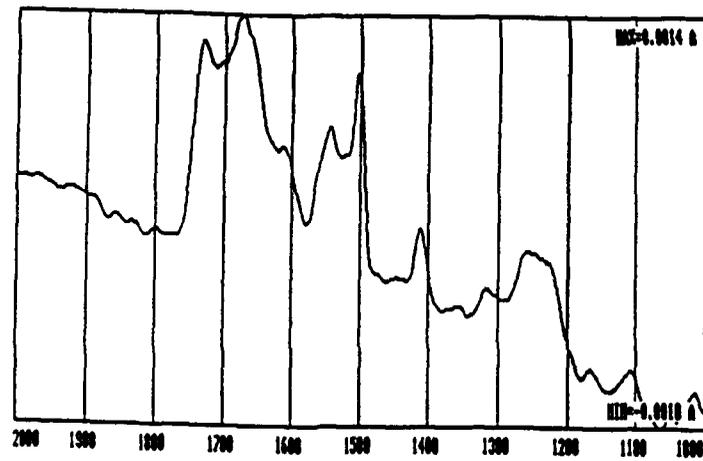


(C)

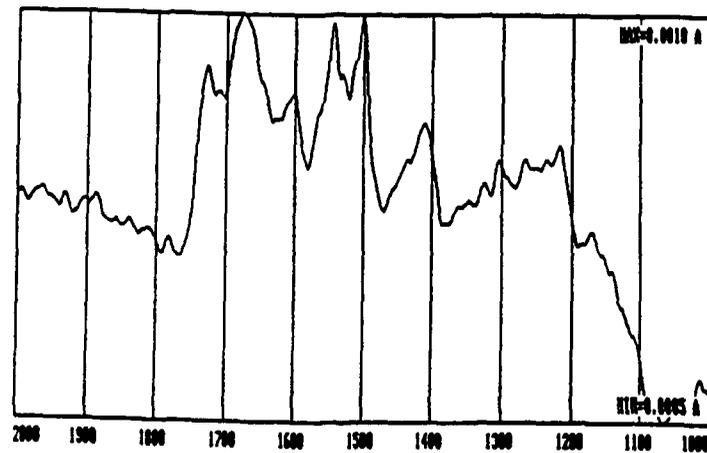
Figure 4. RAIR spectra obtained from polyamic acid of PMDA/ODA spin-coated onto copper substrates from (A)-10%, (B)-2.5%, and (C)-0.5% solutions in NMP.



(A)

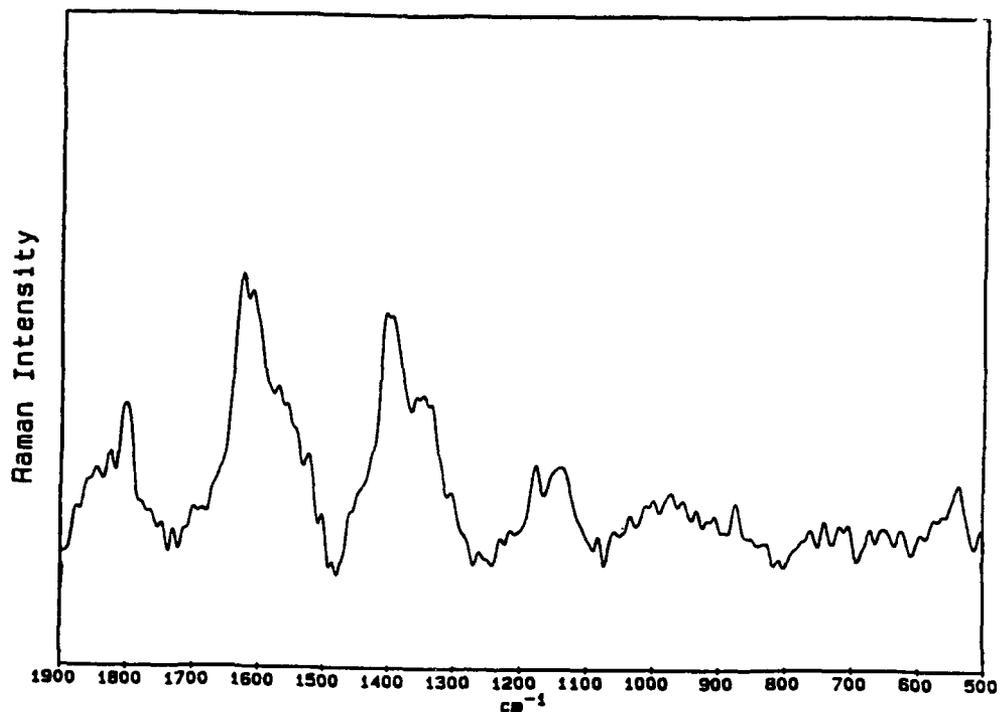


(B)

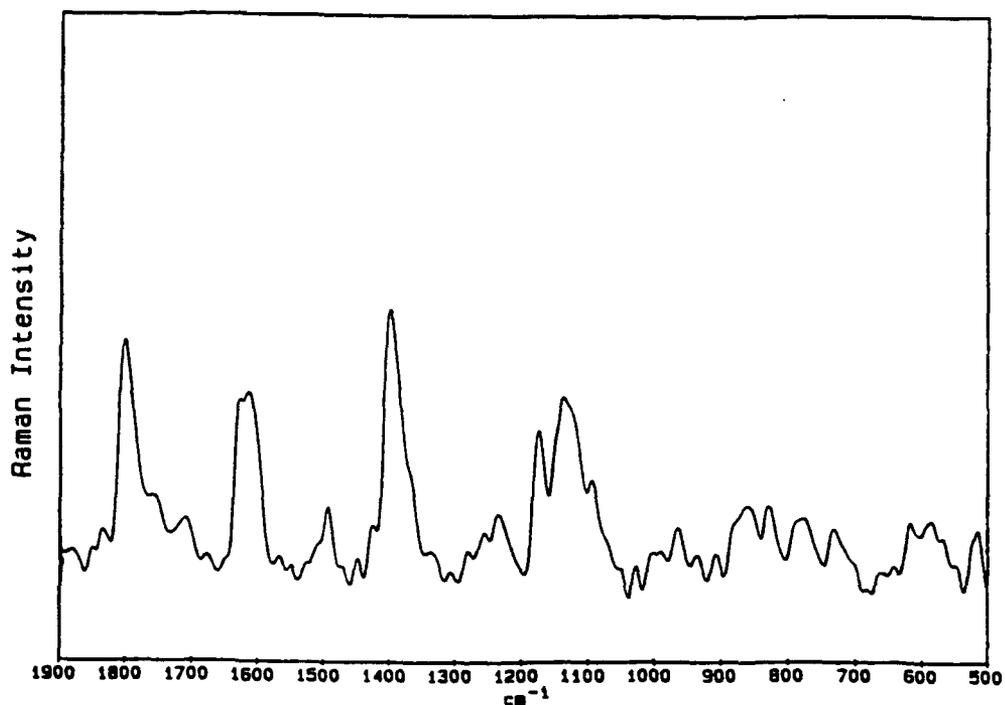


(C)

Figure 5. RAIR spectra obtained from polyamic acid of PMDA/ODA spin-coated onto thick gold films from (A)-2%, (B)-0.4%, and (C)-0.08% solutions in NMP.

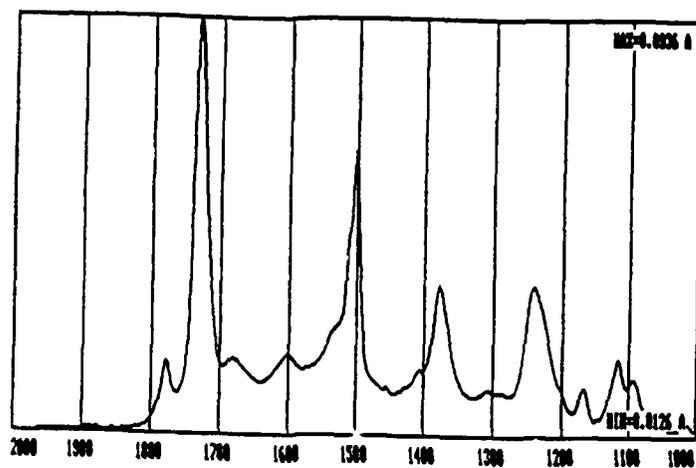


(A)

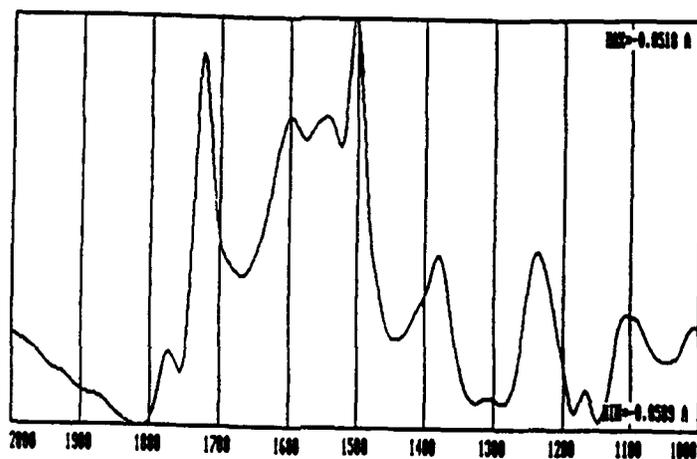


(B)

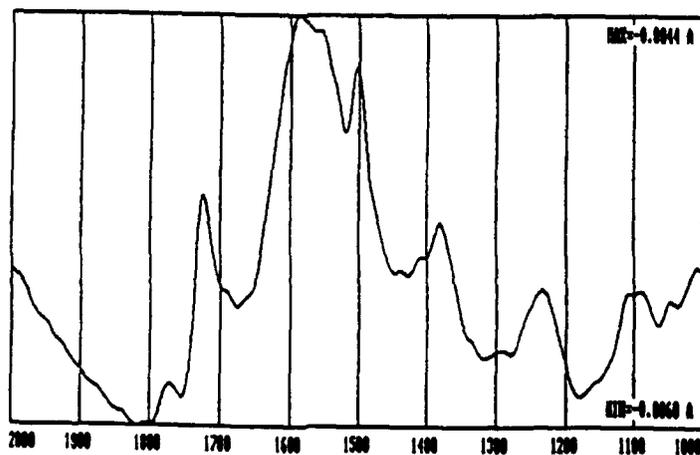
Figure 6. SERS spectra obtained after curing of polyamic acid of PMDA/ODA spin-coated onto (A)-an etched copper substrate from a 4% solution and (B)-a gold island film from a 1.25% solution in NMP.



(A)

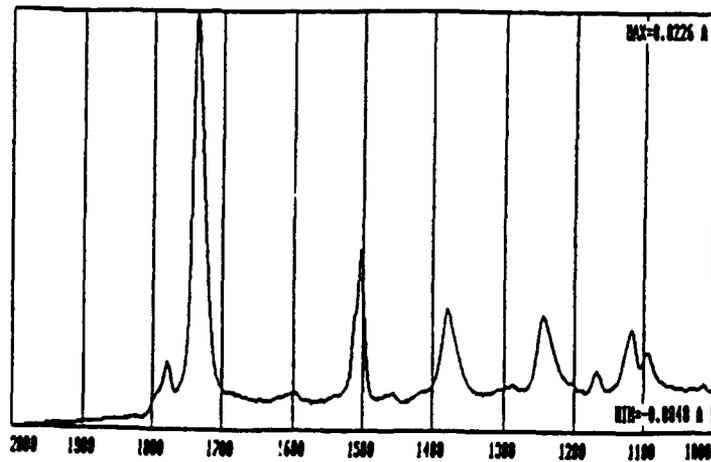


(B)

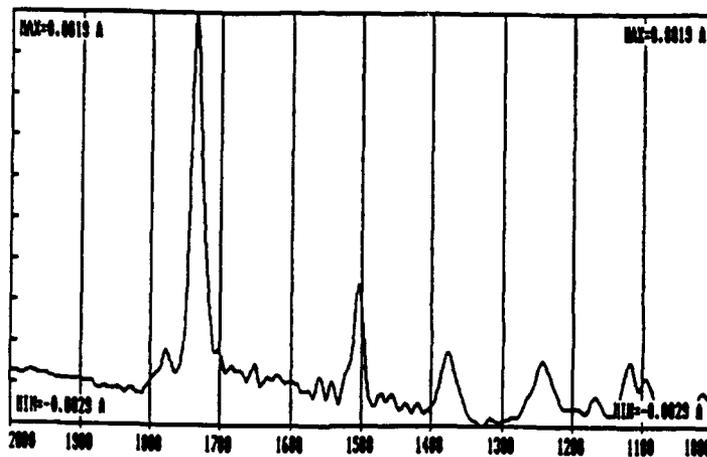


(C)

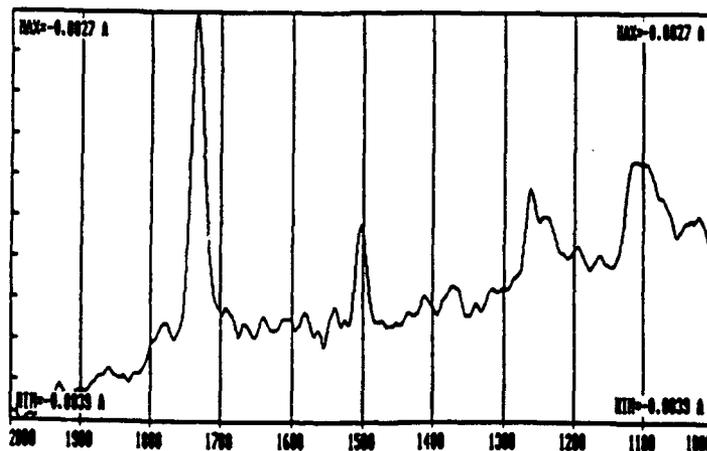
Figure 7. RAIR spectra obtained after curing of polyamic acid of PMDA/ODA spin-coated onto copper substrates from (A)-10%, (B)-2.5%, and (C)-0.5% solutions in NMP.



(A)



(B)



(C)

Figure 8. RAIR spectra obtained after curing of polyamic acid of PMDA/ODA spin-coated onto thick gold films from (A)-2%, (B)-0.4%, and (C)-0.08% solutions in NMP.

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