Surface-Enhanced Infrared Absorption (SEIRA) and Its Use in Analysis of Plasma-Modified Surface

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ABSTRACT: A thin film (<10 nm) of fine metal clusters (silver or gold) with an island form was deposited on a CaF₂ salt plate by slow vacuum thermal evaporation. Molecular layers of stearic acid, *p*-nitrobenzoic acid, and *m*-nitrobenzoic acid (*p*- and *m*-NBA) were prepared on the thin metal film. The system was then examined by infrared spectroscopy attenuated total reflection (IR–ATR). It was found that through the interaction between the metal islands film and the electric field of the incident IR beam the infrared absorption of the molecule layers adsorbed on the islands was enhanced by a factor of 17. The surface-enhanced IR absorption (SEIRA) also presents a selection rule. This method was then used to study the surface modification with O₂ and NH₃ plasma and the plasma polymerization of allylamine. This is the first time that SEIRA has been used in plasma investigations. A model is provided to explain the interactions between the metal islands film and the electric field of the incident IR beam in the SEIRA. The in-plasma-built functional groups can be further used to graft biofunctional molecules for the biomedical industry. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1231–1237, 1999

Key words: plasma; IR; surface-enhanced infrared absorption (SEIRA); surface modification

INTRODUCTION

Modification of polymer surfaces by means of plasma treatment is a very important and useful technique in biomedical material areas.¹⁻⁴ Plasma-modified or deposited layers are usually, however, very thin (nanometer range), thus making it very difficult to chemically analyze these layers.

For example, IR–infrared attenuated total reflection (ATR), a routine surface analysis technique (micrometer range), is not sensitive enough for plasma-treated surfaces.⁵ X-ray photoelectron spectroscopy (XPS), in contrast, has a greater sensitivity to the surface atomic composition (with the exception of H) and can be used to analyze the chemical structures of the polymer surface by curve-fitting procedures of the C_{1s} spectral envelope. However, for plasma-modified polymer surfaces, it often produces curve-fitting results which are ambiguous.^{6,7} Therefore, it is necessary to seek a suitable analysis technique for plasma-modified polymer surfaces. One possible technique is surfaceenhanced infrared absorption (SEIRA), which was

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Figure 1 The plasma processor system: (1) plasma chamber; (2) control system; (3) quadrupole mass spectrometer; (4) forepump; (5) stream meter; (6) monomer source (for allylamine); (7) gas source; (8) quartz thickness monitor; (9) turbo molecular pump; (10) sample holder; (11) electrode; (12) thermal evaporator; (13) optic emission spectrometer.

used in this work to study plasma-modified polymer surfaces. With this technique, which involves the formation of a very thin film (10 nm) of fine metal (silver or gold) clusters with an island form on a CaF_2 salt plate by slow vacuum thermal evaporation,⁸ the infrared absorption of sample molecules, which are adsorbed on or in close contact with the islands, is enhanced by 1 or 2 orders of magnitude. This phenomenon was first discovered by Hartstein⁹ and was named by Kamata et al.¹ and Osawa et al.^{10,11}

EXPERIMENTAL

A CaF_2 plate was used as the substrate of the thin metal film. First, it was ultasonicated in ether and then subjected to Ar plasma cleaning in a plasma processor (UNIVEX 300 from LEYBOLD) (Fig. 1) at 6 Pa for 10 min. An affiliated vacuum evaporator in the plasma processor was used for the thermal evaporation. A 99.99% and 0.25-mmdiameter silver or gold wire was heated in a tungsten boat (12). The pressure was 10^{-3} Pa, and the deposition rate was kept at 0.02–0.03 nm/s. The film thickness was measured by a standard quartz thickness monitor (8). A raster electron microscope (BEETLE, Carl Zeiss, Jena, Germany) was used to investigate the morphology of the evaporated metal islands.

The functions of thin metal islands films were investigated using molecular layers of stearic acid, p-nitrobenzoic acid and m-nitrobenzoic acid (*p*- and *m*-NBA) deposited on the thin metal film. Ten-microliter 0.1% w/v of the solutions (stearic acid in methyl alcohol, NBA in acetone) were deposited with a microsyringe on the CaF_2 plate covered with thin metal islands films. The solution was spread over an area of 1-3 cm². After slow evaporation of the solvent in the solvent atmosphere, the deposited solute builds multimolecular layers on the thin metal islands film. For preparation of a molecular monolayer, the CaF_2 plate was then washed with acetone to remove the physisorbed upper layers and only the chemisorbed first monolayer was left on the metal islands surface.¹¹ Figure 2 shows a possible structure of a CaF_2 substrate, the evaporated metal islands on the substrate, and the multimolecular layers adsorbed on the metal islands. Infrared transmission measurements of the prepared CaF₂ plate were made on an FTIR spectrometer of Nicolet Magna, Model 550, with a resolution 4 cm^{-1} .

A UNIVEX 300 plasma processor (Fig. 1) was used to treat the samples. The gases used for plasma treatment were Ar, O_2 , NH_3 , and allylamine. Each gas was used at a pressure of 6 Pa for plasma modification and polymerization.



Figure 2 A possible structure of a CaF_2 substrate, the evaporated metal islands on the substrate, and the multimolecular layers adsorbed on the metal islands.



Figure 3 Raster electron micrograph of 4-nm-thick gold islands film evaporated on a $\rm CaF_2$ plate; size: 226 \times 226 nm.

A quadrupole mass spectrometer (QMS 420, BALZERS) (3) was used to monitor the plasma waste gas. All the chemicals were reagent grade and were used without further purification.

RESULTS AND DISCUSSION

Figure 3 is a raster electron micrograph (BEETLE) of a 4-nm-thick film of gold islands evaporated on the CaF₂ plate. The well-separated metal islands are approximately 20–60 nm in diameter. From the metal islands morphology, a model is provided to explain qualitatively the principle of SEIRA in Figure 4. In the model, the metal islands are simplified as prolate ellipsoids placed side by side. The deposited molecular layers cover the ellipsoids' surface. The difference between the dielectric constants of the molecular layer and air is negligible, and the substrate (CaF₂) is not presented in Figure 4.

The metal islands film are polarized strongly in the electric field of the incident IR beam. They interact with the electric field and thus redistribute and reorient the electric field near the metal islands film. As a result of the interaction between the metal islands film and the electric field, two phenomena occurred as shown in Figure 4:

1. The electric field lines of the metal islands film are drawn together and this makes the

electric field strength very strong, especially in the gaps between the metal islands. This is the reason for the enhancement of IR absorption. This model can explain schematically the assumptions of Kamata et al.¹ and Osawa et al.¹¹ Figure 4 shows an IR transmission measurement situation: The incident angle of the IR radiation is 0° and the electric field of the IR beam far away from thin metal film is not disturbed and thus remained parallel to the thin metal film. The enhancement at this angle of incidence is the strongest. As the incident angle becomes larger (e.g., for reflection measure), the electric field lines (for *p*-polarization) are not parallel to the thin metal film, they are not drawn together, and the enhancement becomes weaker.

2. The electric field intersects the metal islands surface perpendicularly at every point. The first phenomenon causes the absorption enhancement while the second phenomenon can be used to explain the absorption selection rule.

Figure 5 shows the transmission spectra of stearic acid layers with a 4-nm silver islands film and without silver islands enhancement on a CaF_2 plate:

(a) is the spectrum of the multimolecular layers (before washing) without the metal islands. The absorption band at 1698 cm⁻¹ is assigned to C=O in COOH, and the bands at 2920 and 2850 cm⁻¹ are due to antisymmetric and symmetric CH₂ stretching, v_{as} (CH₂)



Figure 4 A model to explain the interaction between the metal islands film and the electric field of an incident IR beam.



Figure 5 Transmission spectra of stearic acid with and without enhancement of silver islands film on a CaF_2 plate: (a) multimolecular layers without metal islands film; (b) multimolecular layers with metal islands film; (c) monomolecular layers with metal islands film; (d) monomolecular layers without metal islands film.

and $\nu_s(CH_2)$, respectively. This is a typical stearic acid molecule spectrum.

- (b) is the spectrum of multimolecular layers (before washing) on 4-nm silver islands film. The new band at 1395 cm⁻¹ is assigned to a symmetric COO⁻ stretching, ν_s (COO), which indicates that the first stearic acid layer was chemisorbed onto the silver islands surface through the carboxyl group with dissociation of a proton,¹⁰ the upper layers consisting of physisorbed molecules (see Fig. 1) which contribute to the band of COOH.
- (c) is the spectrum corresponding to the first monolayer chemisorbed onto the silver islands surface (after removing the upper layers). The free COOH bands from the upper layers at 1700 cm⁻¹ as seen in (a) and (b) disappear and the symmetric COO⁻ stretching, ν_s (COO⁻), is the same as in (b). The C—H bands are weaker than in (b), but still strong enough to be identified.
- (d) is also the spectrum of stearic acid monolayer without silver islands and without an enhancement factor; therefore, all bands are weak. The intensity enhancement fac-

tor for $\nu_s(CH_2)$ at 2850 cm⁻¹ is 17, which is ratio of the band in (c) to the band in (d).

SEIRA presents an absorption selection rule: Only the molecular vibrations, which have dipole-oscillation contributions perpendicular to metal islands surface, are IR active. This rule is identical with the absorption selection rule of reflection-absorption spectroscopy (RAS), but SEIRA has a much higher sensitivity than has RAS. With the absorption selection rule, SEIRA can be used to study the molecular orientation of monomolecular layers, for example, self-assembling layers or LB layers adsorbed on a metal islands surface, which is difficult to do using RAS.

p-NBA and *m*-NBA are structure isomers. They were used here to explain the absorption selection rule of SEIRA. Figure 6 shows the molecular orientations of the chemisorbed first layer of (a) *p*-NBA and (b) *m*-NBA on the metal islands surface. Their long axes are perpendicular to the metal islands surface and the electric field Ei's near the metal islands surface are also perpendicular to it. In Figures 7 and 8, both spectra (a) demonstrate bands of multimolecular layers (before washing) of *p*- and *m*-NBA on 3-nm silver



Figure 6 Molecular orientation of a metal islands surface chemisorbed first layer of (a) p-NBA and (b) m-NBA; Ei is the electric field.

islands film. The $\nu_{s}(COO^{-})$ at 1400 cm⁻¹ belongs to the first p- and m-NBA layer, which chemisorbed on the silver islands surface through the carboxyl group, and the C=O bands at 1700 cm⁻¹ belong to the free COOH of the upper p- and m-NBA layers. The spectra (b) in Figures 7 and 8 show only absorption of the first *p*- and *m*-NBA layer chemisorbed on the silver islands surface. Since in the first layer the symmetric dipoleoscillations of $\nu_s(\text{COO}^-)$ of *p*-NBA and *m*-NBA at 1400 cm^{-1} and the symmetric dipole–oscillation of $\nu_{\rm s}(\rm NO_2)$ of *p*-NBA at 1350 cm⁻¹ are parallel to the electric field, these three oscillations are IR active. The symmetric dipole-oscillation of $\nu_{\rm s}({\rm NO2})$ of *m*-NBA, although not totally parallel to the electric field, nevertheless possesses a component in the direction of the electric field and



Figure 7 Absorption of *p*-NBA on the silver islands surface: (a) multimolecular layers; (b) only the first layer.



Figure 8 Absorption of *m*-NBA on the silver islands surface: (a) multimoleculer layers; (b) only the first layer.

therefore it is also IR active. So, chemisorbed p-NBA and m-NBA monolayers both have $\nu_s(\text{NO2})$ and $\nu_s(\text{COO}^-)$ bands [Fig. 7(b) and Fig. 8(b)]. The antisymmetric dipole–oscillation of $\nu_{as}(\text{NO2})$ of p-NBA is completely vertical to the electric field; therefore, in Figure 7(b) at 1531 cm⁻¹, there occurs no absorption, but in (a) at the same position, there is absorption. Since the physisorbed upper layers are not so strictly oriented as is the chemisorbed first layer, their antisymmetric dipole–oscillation, $\nu_{as}(\text{NO}_2)$, possesses a parallel component parallel to electric field. In Figure 8(b), there is a band for m-NBA at this wavenumber, since $\nu_{as}(\text{NO}_2)$ of m-NBA has a parallel component to the electric field.

It is the first time, to our knowledge, that SEIRA was used as a tool in plasma investigation: The long aliphatic chain of stearic acid seems to be a polyethylene molecule; therefore, on the silver islands surface, a chemisorbed stearic acid monolayer (after washing away the upper layers) was used with its aliphatic chain to simulate the reactions of a polyethylene surface with plasma, which showed a higher sensitivity. Figure 9 shows the spectra of O₂ plasma oxidation with the stearic acid monolayer as a function of time (0-30)s). At t = 0, the sharp bands at 2920 and 2850 $\rm cm^{-1}$ are due to the $\nu_{as}(\rm CH_2)$ and $\nu_s(\rm CH_2)$ of the aliphatic chain. The band at 1400 cm^{-1} is due to symmetric stretching of the chemisorbed carboxyl group, $\nu_{\rm s}(\rm COO^-)$; there is no free COOH band. After several seconds of plasma oxidation, the stearic acid molecules were oxidized and etched, the oriented structures were disordered, and all the peaks of CH₂ became weaker. Mass spectro-



Figure 9 Spectra of O^2 plasma oxidation of a stearic acid monolayer as a function of time (0-30 s).

graph measurements demonstrated that CO_2 , CO, H₂O, and H₂ are plasma-degradation products of aliphatic chains, which existed in the plasma waste gas. Since 12-s C=O bands emerged at 1715 cm^{-1} , it is more evidence of the oxidation of the stearic acid aliphatic chains. After 30-s oxygen plasma treatment, the stearic acid layer was almost exhausted and all the bands became very weak. Besides the C=O group, other function groups can also be formed in O_2 plasma, for example, the hydroxyl group, which can only be identified with SEIRA in IR spectra after derivation with trifluoracetic anhydride (TFAA).^{6,12,13} The formation of oxygen-function groups in oxygen plasma are widely used to modify polyolephin surfaces, for example, to improve the hydrophilic property and to enhance its biocompatibility.^{14,15} The rapid oxidation function and etching function of oxygen plasma can also be used for surface cleaning and for chip manufacturing in the semiconductor industry.

Ammonia plasma is another important plasma. A stearic acid monolayer adsorbed on the silver islands surface (after washing away the upper layers) was also used to simulate the ammonia plasma reaction with polyethylene. Figure 10 demonstrates the spectra of the NH₃ plasma reaction with the stearic acid monolayer as a function of time (0–120 s). At t = 0, the band at 1400 cm⁻¹ belongs to the symmetic COO⁻ stretching, ν_s (COO⁻); there is no free COOH band. Bands at 2920 and 2850 cm⁻¹ are due to ν_{as} (CH₂) and ν_s (CH₂). Even after a 120-s reaction, these three bands are still strong, meaning



Figure 10 Spectra of NH_3 plasma oxidation (0-120 s) of a stearic acid monolayer as a function of time (0-120 s).

that the reaction of ammonia plasma with stearic acid is weaker than with an oxygen plasma, but some amine groups can be introduced onto the monomolecular layer, which can modify intensively the surface characteristics and can also be identified by its derivation product with pentafluorobenzaldehyde (PFBA) in the IR spectra.^{6,13}





Figure 11 Spectra of plasma-polymerized allylamine (PAA) thin films with and without silver islands films on CaF_2 : (a) 7-nm PAA without silver islands film; (b) 20-nm PAA without silver islands film; (c) 7-nm PAA on 5 nm silver islands film; (d) 20-nm PAA on 5 nm silver islands film.

For the surface modification of polyrzhylene surfaces, many organic "monomers" with specified function groups can also be plasma-"polymerized" on the surface. This extremely thin plasmapolymerized film can also be analyzed by SEIRA. Allylamine (CH₂=CH-CH₂-NH₂) was polymerized by plasma to form a thin film on a CaF_2 substrate surface. To avoid the destruction of the function groups of amine by plasma, the substrate was placed downstream of the plasma zone. Figure 11 shows the spectra of plasma-polymerized allylamine thin films (with thickness of 7 and 20 nm) with and without silver islands films. In (a) and (b), which are without silver islands films, there is almost no absorption, but (c) and (d), with silver islands film, have very clear bands: At 3300 and 1650 cm^{-1} , they should be due to NH stretching, and at 2160 cm^{-1} , to CN stretching. The in-ammonia plasma-built amine and nitrile groups can be further used to graft biofunctional molecules, for example, proteins, enzymes, and antibodies for the biomedical industry.

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