

NOTE

A Versatile and Simple Method for the Preparation of Substrates for Surface-Enhanced Infrared Spectroscopy of Monolayers

Surface-enhanced vibrational spectroscopy involves the study of molecules adsorbed on surfaces that can enhance the absorption and emission of electromagnetic radiation. Surface-enhanced Raman scattering (SERS) is a well-investigated phenomenon and an established surface analytical tool (1). The surface enhancement of infrared spectra was first observed and investigated by Hartstein *et al.* in 1980 (2a), but it is still developing and has not yet matured into a reliable analytical technique.

Self-assembled monolayers (SAMs), especially alkanethiols on gold and silver surfaces, have been investigated intensely in the recent past (3, 4) for their potential applications in molecular technologies as well as for their importance in the fundamental understanding of interfacial properties. Essential tools for the characterization of monolayers have been methods of electrochemistry (4a), ellipsometry (4b), wettability (4c), reflection absorption infrared spectroscopy (4d–f), sum-frequency spectroscopy (4g), X-ray photoelectron spectroscopy (4h), rare gas atom scattering (4i), ion-surface collisions, scanning tunneling (4j), and atomic force microscopies (4k). Although each technique has focused on a few of the aspects of self-assembly, infrared spectroscopy has shed light on most of the issues concerning their structure. However, the poor sensitivity of the reflection absorption infrared spectroscopic technique in its normal mode of operation has substantially hindered its applicability to monolayers (4d–f). Both SERS (1) and surface-enhanced infrared (SEIR) spectroscopy (2), although surface sensitive, can be applied only to roughened surfaces. For these spectroscopies, preparation of reliable substrates is the most important requirement.

In earlier studies of surface-enhanced Raman scattering of SAMs carried out in our laboratory (5), we have successfully used a simple method for the preparation of surface-enhanced Raman active gold as well as silver films by sputter-depositing gold or silver on oxidized aluminum foils. The same method has been used here for the preparation of silver substrates for the surface-enhanced infrared studies. We also prepared silver surfaces where it was coated on a smooth silicon surface in order to compare the extent of enhancement of IR absorption.

Thin silver films on surfaces with nanometer scale roughness are known to be composed of silver islands (2), which can cause enhancement in the vibrational spectra of adsorbed molecules. Among the several ways to induce microscopic roughness on substrates, such as mechanical polishing, electrochemical etching, and ion sputtering, one of the simplest, particularly on a metallic specimen, is to oxidize it. Here, oxidized aluminum foils were used as substrates to coat the thin silver films. The conditions employed change the quality of the films formed. Commercial aluminum foils of 0.02-mm thickness, used for packaging, were employed for that purpose. The foils were oxidized by heating them at a temperature of 500°C in air for 5 h. These foils were coated with silver (99.9% pure) in an Edwards sputter coater used for the preparation of scanning electron microscopy (SEM) specimens. Evaporation was carried out at a pressure of 0.01 Torr of Ar (discharge conditions: 1.3 kV, 5 mA). The aluminum foil was sheeted on the substrate holder which was 10 cm in diameter. After sputtering for about 5 min, a film of about 300 Å thickness was formed. By keeping all other conditions the same, silver films of different thickness were prepared by varying the coating time from 5 to 35 min. Maximum enhancement was found in the IR studies when the coating was done for 5 min. These films were cut into appropriate size and used for the preparation of SAMs. Silver films on smooth silicon surfaces were also

prepared similarly. These films are labeled as Ag/Al and Ag/Si, respectively. SAMs were prepared by dipping the silver-coated samples in 1 mM solutions of the thiols in absolute ethanol for 12 h. The foils upon removal from the solution were washed in absolute ethanol and air-dried. IR spectra in the reflectance mode were measured with a Bruker FTIR IFS 66 V spectrometer equipped with a specular reflectance accessory. Generally, it is difficult to observe the infrared spectrum of a monolayer. For the reflection absorption, infrared studies of monolayer FTIR instruments equipped with highly sensitive detectors like N₂-cooled mercury cadmium telluride (MCT) detectors are required (2, 4d–f). We were able to observe the monolayer spectrum even with a room-temperature deuterated triglycine sulfate (DTGS) detector because of the surface enhancement. Samples were held static with an angle of incidence of 45°. Each spectrum consisted of 1000 scans and the accumulation was complete in 10 min.

SEIR spectroscopy has been applied successfully to the study of monolayers adsorbed on metal surfaces in reflection-absorption ATR as well as in transmission geometries (2). In spite of the application in various fields, the mechanism of SEIR is not fully understood. It is proposed that similar to SERS, the enhancement effect may have mainly two contributions, electromagnetic and chemical, which are independent (2). In the electromagnetic enhancement mechanism, it is the collective electron resonance, or in other words, multiple excitation of the surface plasmons that is responsible for the surface enhancement. Chemical enhancement mechanism is due to the change in the dipole moment of the chemisorbed molecules caused by the interactions such as charge transfer between the surface and the adsorbed molecules.

Figure 1a presents the comparison of two SEIR spectra of CH₃(CH₂)₇SH monolayers on silver in the high-frequency region, for the two different substrates taken in the reflectance mode. Figure 1b shows the corresponding low-frequency region. The difference in the enhancement of IR absorption by the two silver surfaces with different surface roughness is clearly manifested in the spectra. While all the important peaks of the monolayer are shown up in the spectrum from Ag/Al, only the highest intensity peak at 2917 cm⁻¹ is discernible above the noise level in the spectrum from Ag/Si. If the intensities of this band in both the spectra are compared, a fivefold enhancement is found for the spectrum from Ag/Al.

The frequencies observed and the assignments for the octanethiol monolayers are given in Table 1. Since the spectra of alkanethiols and thiolates have been discussed in detail in the literature (4d–f), we shall discuss only certain important regions pertaining to self-assembly. The C–H stretching region (2800–3000 cm⁻¹) shows four prominent peaks assigned to the characteristic aliphatic C–H stretching frequencies. Direct evidence of the cleavage of the S–H bond is seen in the spectrum; no S–H stretching mode, expected around 2570 cm⁻¹, is visible. Complete absence of this band suggests that thiols dissociate at the surface and adsorb in the thiolate form. This also suggests that only a monolayer exists at the surface and there are no physisorbed thiol molecules. The peaks observed at 1468 and 1423 cm⁻¹ can be assigned to methylene scissoring modes and the peaks at 1274, 1233, 1193, and 1067 cm⁻¹ are the progression bands which are due to the CH₂ wagging vibration. The CH₂ rocking region is characterized by one prominent peak around 722 cm⁻¹, which has contributions from C–S stretching vibration as well.

The ratio of methyl/methylene C–H symmetric stretching peaks is found to be 4.5, which is close to the value for octanethiol (4.66), indicating the absence

of impurities on the substrate. The methylene asymmetric and symmetric (d^+ and d^-) peaks are found at 2917 and 2847 cm^{-1} , manifesting the presence of ordering in the alkyl chain assembly. The methylene peaks characteristic of crystalline alkanes are at 2920 and 2849 cm^{-1} (6), which are close to the observed values for the 2D monolayers. Presence of wagging progression bands in the surface-enhanced spectrum is of particular importance because it is difficult to observe them in normal reflection measurements. In none of the early reports on the infrared spectroscopic studies of alkanethiol monolayers did wagging progression bands show up ($4d-f$).

Thickness of the silver layer is also found to be an important factor in determining the enhancement. Many theoretical and experimental studies (2) have shown that the presence of silver islands on the surface is essential for the surface enhancement of the vibrational spectra of the adsorbed molecules by the electromagnetic enhancement mechanism. On sputter coating, the thin

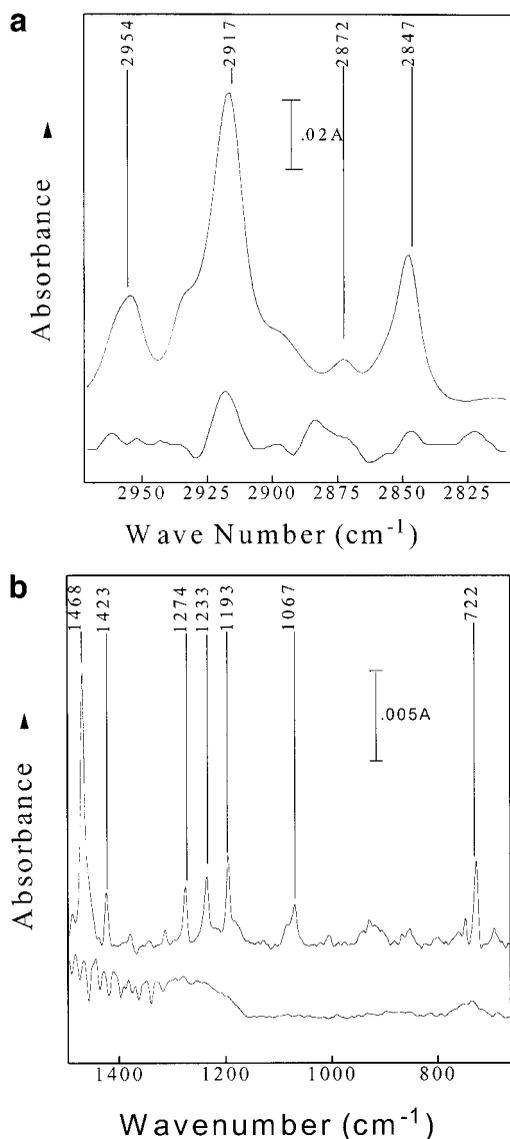


FIG. 1. SEIR spectra of $\text{CH}_3(\text{CH}_2)_7\text{SH}$ monolayers on the two different silver surfaces (a) in the high frequency region and (b) in the low-frequency region. The top spectrum is from Ag/Al and the bottom one is from Ag/Si (noise level is more in the bottom spectrum due to low intensity of reflected light in the specular reflectance geometry).

TABLE 1
Observed Frequencies and Assignments for the SEIR Spectrum of Octanethiol Monolayers Grown on Ag/Al

Frequency (cm^{-1})	Assignments
2954	$\nu_a \text{CH}_3$
2917	$\nu_a \text{CH}_2$
2871	$\nu_s \text{CH}_3$
2846	$\nu_s \text{CH}_2$
1468	CH_2 scissoring modes
1423	
1274	CH_2 wagging modes (progression bands)
1233	
1193	
1067	CH_2 rocking and $\nu(\text{C-S})_T$
722	

silver layer formed will essentially consist of silver islands due to the roughness of the underlying oxidized aluminum surface. Scanning electron microscopic investigation of the films has shown roughness in submicrometer dimensions on oxidized aluminum foils prior to and after silver sputtering (5a). When the coating time is increased, the islands come closer and as the thickness of the silver film increases on longer time coating, the islands aggregate and the surface loses its ability to enhance the IR absorption. By varying the time for coating, keeping all other parameters constant, we observed maximum enhancement for SAMs on silver films sputter-coated for 5 min, which corresponds to a thickness of 300 Å.

Thus, the present study reveals strong dependence of the surface-enhanced infrared absorption spectrum on the nature of the substrate and the surface roughness. The surprisingly high enhancement observed for the IR spectra for SAMs grown on Ag/Al suggests a simple method for the preparation of SEIR active substrates. Detailed vibrational spectroscopic study of SAMs on two-dimensional surfaces is possible this way by employing simple methodologies. It is also important to mention that spectra are acquired using standard detection systems in a commercial analytical spectrometer without additional preparation.

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