



## SEIR and SERS of an Azobenzene Acid Monolayer on Silver Island Films

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### INTRODUCTION

There is increased interest in the use of organized molecular assemblies for investigating fundamental questions and practicable applications. Understanding the preparation techniques, Langmuir–Blodgett (LB) and self-assembly (SA), as well as the methods for investigating the structure, orientation, and chemical and/or physical properties of thus created monolayers, is becoming more and more important.<sup>1–3</sup> The conventional LB technique is to transfer mono- or multilayers of amphiphilic molecules from an air/water interface onto solid substrates, while self-assembly is to prepare monolayers on the basis of special interaction between the adsorbate and substrates, such as organosulfur molecules on gold, carboxylic acids on silver, aluminum oxide and silicon on metal surfaces, etc.<sup>1,2</sup> For the preparation of alkyl acid monolayers on silver surface, both the LB and the SA techniques might be valid due to the hydrophobicity of the acid and the special nature of the silver substrates.<sup>1,2</sup> However, direct comparison of monolayers on silver substrates which were fabricated by the SA and LB techniques has not yet been provided.

Surface-enhanced Raman spectroscopy (SERS) has

long been recognized as a powerful analytical technique for adsorbates on surfaces.<sup>4–6</sup> It is also one of the most powerful tools for *in situ* observation of interfacial reactions because of its high sensitivity and selectivity.<sup>7</sup> Recently, surface-enhanced infrared (SEIR) spectroscopy has been developed as a novel surface analytical technique,<sup>8,9</sup> but few reports can be found. Both of these techniques are based on a phenomenon whereby the Raman or infrared intensity is notably increased when molecules interact with specific metal surfaces.<sup>9,10</sup> As with SERS, the enhancement of SEIR depends greatly on the types of molecules, metals, and substrate materials on which the metal is evaporated, and also on the experimental conditions such as the average thickness of the island films.<sup>11–17</sup> Up to now, the process and its enhancement mechanism have not been completely clarified, although it has been accepted by many researchers that at least two mechanisms are responsible for SERS and SEIR: *electromagnetic* (EM) and *chemical*.<sup>11,16</sup>

Structural investigation by both SERS and SEIR might be valuable and reliable, if we can integrate these two powerful tools into the structural investigation of the same sample. We will be able to acquire much detailed structural information on monolayers.

In this paper, we investigate the structure of ABD (see below) monolayers on silver, created by the SA and LB techniques, respectively, using SERS and SEIR.

### EXPERIMENTAL

The amphiphilic azobenzene derivative 4-octyl-4'-(3-carboxytrimethyl-ene-oxy)-azobenzene (referred to as ABD) was purchased from Dojindo Laboratory (Kumamoto, Japan).

Plates of CaF<sub>2</sub> (20 × 10 × 2 mm) and silicon wafers (10 × 10 mm) were used as substrates for spectroscopy and atomic force microscopy (AFM) studies. Prior to the evaporation of the silver film, the CaF<sub>2</sub> plates were carefully cleaned with acetone and chloroform, and the silicon wafers were cleaned in “piranha solution” (3:7 H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub>, v/v) at 90 °C, followed by rinsing with milli-Q water and absolute ethanol. Thin island silver films were deposited on one face of the plates in a vacuum evaporator below 4 × 10<sup>-5</sup> Torr. Thickness was measured with a quartz thickness gauge; the deposition rate was kept at 0.1 nm/s.

As reported in Ref. 18, the LB film of ABD in its *trans* form was deposited onto the CaF<sub>2</sub>, silver film-coated CaF<sub>2</sub>, and silicon substrate by the conventional Lang-

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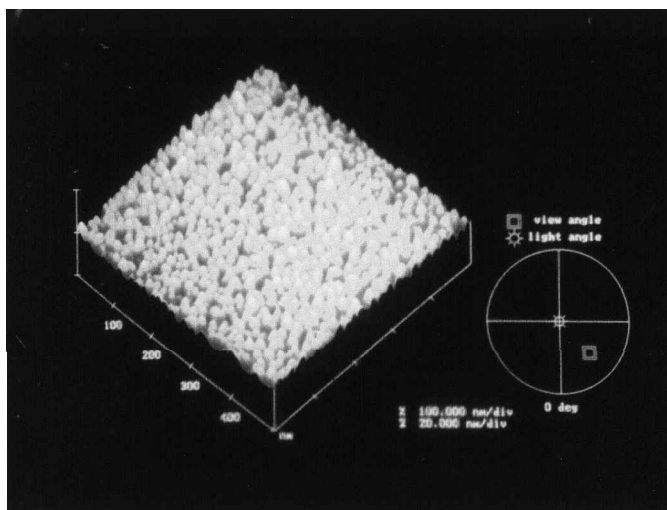


FIG. 1. A  $500 \times 500$  nm AFM image of silver island films on silicon wafer substrate.

muir–Blodgett technique using a commercial instrument (FACE, Japan) at a constant surface pressure of 20 mN/m. The subphase temperature was kept at 20 °C. The transferring ratio was nearly unity. The stable self-assembled monolayers (SAMs) were formed by immersion of the above-prepared substrates in 0.5 mM ABD ethanol solution over 24 h.

Raman spectra were recorded with a Renishaw System 1000 Raman imaging microscope (Renishaw plc, U.S.A.) and a 25 mW (632.8 nm) He–Ne laser (Model 127-25RP, Spectra-Physics, U.S.A.) and a Peltier-cooled charge-coupled device (CCD) detector. A  $50\times$  objective mounted on an Olympus BH-2 microscope was used to focus the laser onto a spot of approximately 1  $\mu\text{m}$  in diameter, and to collect the back-scattered light from the sample.

Transmission infrared spectra were acquired with a Perkin-Elmer System 2000 FT-IR spectrometer equipped with a liquid  $\text{N}_2$ -cooled MCT detector. All the spectra were obtained by referencing 100 sample scans to 100 bare  $\text{CaF}_2$  background scans at  $4\text{ cm}^{-1}$  resolution with strong apodization. The sample chamber was purged with dry  $\text{N}_2$  to eliminate the spectral interference from water vapor in air.

The AFM images were taken with a Nanoscope III atomic microscope (Digital Instruments, U.S.A.) in a tapping mode.

## RESULTS AND DISCUSSION

**The Morphology of the Substrate and the Preparation of ABD Monolayers.** It is well known that thin silver films evaporated on nonconductive substrates consist of small islands or particles in nanometer scale.<sup>11,14</sup> Atomic force microscopy was used to characterize the three-dimensional film and particle geometry and to obtain the particle shape and size distribution.<sup>19,20</sup> Figure 1 shows the  $500\text{ nm} \times 500\text{ nm}$  AFM image of the thin silver island film on Si substrate in three dimensions. Apparently, the silver film consists of well-separated silver islands with an average diameter of 18–23 nm and a height corrugation of about 2–3 nm. Because the size and shape of silver particles are remarkably small compared

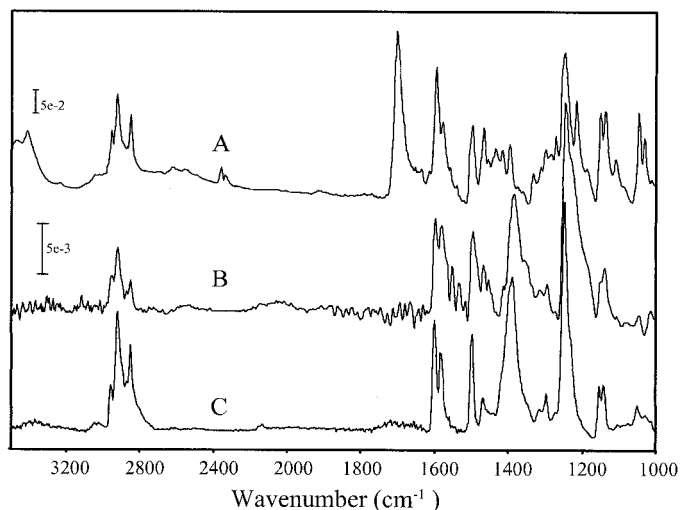


FIG. 2. The FT-IR spectrum of ABD molecules in KBr pellet (A) and the SEIR spectra of ABD monolayers on silver island film-coated  $\text{CaF}_2$  substrates; LB films (B) and SAMs (C).

with the Raman excitation wavelength (632.8 nm) and the infrared wavelength ( $\mu\text{m}$ ), the prepared silver substrate is believed to be SERS or SEIR active.<sup>11,14,21</sup> This kind of substrate is suitable to prepare SAMs or LB films because, not only is it very stable in ethanol solution and characterized by a hydrophobic surface, but it also has a good enhancement factor.<sup>14–17</sup>

**SEIR of ABD Monolayers.** The SEIR of ABD monolayer films on silver island films was successfully obtained with a high signal-to-noise (S/N) ratio.<sup>14–16</sup> The spectra of ABD molecules in KBr pellet (A), ABD LB films deposited on silver island film-covered  $\text{CaF}_2$  substrate (B), and ABD SAMs on silver island film-covered  $\text{CaF}_2$  substrate (C) are shown in Fig. 2. Major band assignments and peak positions, in agreement with previous studies,<sup>22,23</sup> are given in Table I. As is clearly seen from Fig. 2, the SEIR spectra of ABD SAMs and ABD LB films greatly differ from those of ABD molecules in KBr pellet. There is a new strong and broad band at  $1390\text{ cm}^{-1}$  in Fig. 2 (B and C), which can be assigned to the symmetric  $\text{COO}^-$  stretching,  $\nu_a(\text{COO}^-)$ . The absence of  $\text{C}=\text{O}$  stretching expected to be observed around  $1710\text{ cm}^{-1}$  in Fig. 2 (B and C) results in the ABD being absorbed on the silver island films surface through the  $\text{COOH}$  group by releasing its proton, according to the following chemical reaction:  $-\text{COOH} + \text{Ag} \rightarrow -\text{COO}^- + \text{Ag} + \text{H}_2$ . In this case, the antisymmetric  $\text{COO}^-$  stretching [ $\nu_{as}(\text{COO}^-)$ ] band cannot be seen in the expected frequency region,  $1564\text{ cm}^{-1}$ .<sup>24</sup> It can be explained by the selection rule of surface-enhanced infrared spectra: *only the vibrations which give dipole changes perpendicular to the metal surface are infrared active, and their intensity is greatly enhanced* (shown in Scheme I).<sup>11,25</sup> We suggest that ABD on the silver island films appears as the model shown in Scheme I. The  $\text{COO}^-$  bond is almost perpendicular to the surface of silver particle, in which the dipole moment of the  $\nu_a(\text{COO}^-)$  is perpendicular to the surface of the silver particle, while the  $\nu_{as}(\text{COO}^-)$  is parallel to the surface of the silver particle. In general, the typical diameter of ABD is  $0.35\text{ nm}^2$ .<sup>16</sup> In comparison with the size and shape of the silver particle (18–23 nm), the ABD mole-

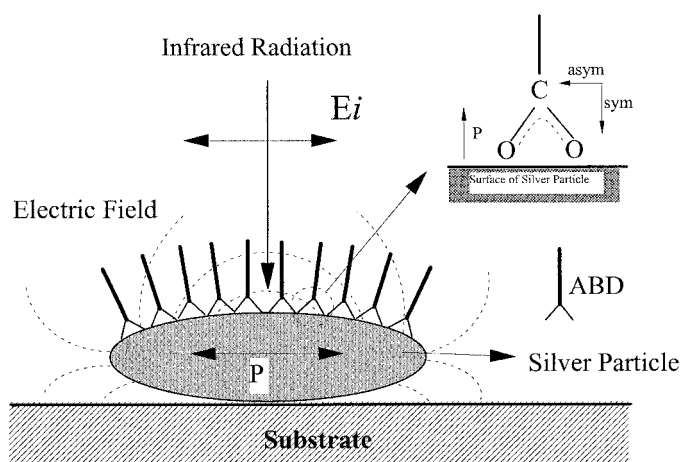
**TABLE I. Band assignments of FT-IR and Raman spectra.**

Band assignment	FT-IR ( $\text{cm}^{-1}$ )			Raman ( $\text{cm}^{-1}$ )		
	Powder	SEIR of LB	SEIR of SAMs	Powder	SERS of LB	SERS of SAMs
$\nu_{\text{as}}(\text{CH}_3)$	2957	2957	2957	—	—	—
$\nu_{\text{as}}(\text{CH}_2)$	2925	2921	2920	—	—	—
$\nu_{\text{a}}(\text{CH}_2)$	2852	2851	2851	—	—	—
$\nu(\text{C}=\text{O})$	1703	—	—	—	—	—
$\phi$ Ring	1597, 1580, 1499	1601, 1584, 1499	1600, 1583, 1496	1602, 1313	1602, 1306	1602, 1310
$\nu_{\text{as}}(\text{COO}^-)$	—	—	—	—	1503	1499
$\nu_{\text{a}}(\text{COO}^-)$	—	1391	1386	—	—	—
$\delta(\text{CH}_2)$	1468	1468	1468	—	—	—
$\nu(-\text{N}=\text{N}-)$	—	—	—	1452, 1410	1458, 1410	1458, 1410
$\phi-\text{O}$	1249	1249	1247	1251	Weak	Weak
$\phi-\text{N}$	1152, 1139	1154, 1142	1154, 1141	1139, 1191	1141, 1187	1142, 1187

cules also can form a highly organized molecular packing on the silver island (shown in Scheme I).

In the higher frequency region, the C–H stretching vibration bands were observed clearly. The bands at 2954  $\text{cm}^{-1}$  can be assigned to the  $\text{CH}_3$  antisymmetric stretching mode, and the bands near 2920 and 2852  $\text{cm}^{-1}$  to the  $\text{CH}_2$  antisymmetric [ $\nu_{\text{as}}(\text{CH}_2)$ ] and symmetric [ $\nu_{\text{a}}(\text{CH}_2)$ ] modes, respectively. Considerable infrared research on SAMs has been devoted to these C–H stretching vibrations near 2800–3000  $\text{cm}^{-1}$ , since they can provide important information about the chain conformation, packing density, and orientation. Most importantly, the exact frequencies of the  $\nu_{\text{a}}(\text{CH}_2)$  and  $\nu_{\text{as}}(\text{CH}_2)$  stretching modes have been used to distinguish between *trans* (crystalline-like) and disordered (liquid-like) conformations of the alkyl chains.<sup>26,27</sup> Our infrared data on ABD monolayers, shown in Fig. 2 (A–C), confirmed this result and show the expected decrease of the  $\nu(\text{CH}_2)$  frequency with the change from LB films on bare  $\text{CaF}_2$  (2927  $\text{cm}^{-1}$ , 2852  $\text{cm}^{-1}$ ; spectrum not shown here) to LB or SA on thin silver island film-covered  $\text{CaF}_2$  (2920  $\pm$  1  $\text{cm}^{-1}$ , 2850  $\text{cm}^{-1}$ ). It is indicated that the monolayer (both LB films and SAMs) has an orientated structure. However, in comparison with a crystalline reference, all these peak positions are higher (2917, 2845  $\text{cm}^{-1}$ ).<sup>26,27</sup>

On the basis of the above consideration, we have demonstrated that stable, highly organized, and predictable ABD monolayers on prepared SEIRS-active substrates can be obtained by using SA or LB techniques. There is



SCHEME I. Model of ABD on silver island film.

no markedly different structure between LB films and SAMs.

**SERS of ABD Monolayers.** The Raman spectra were successfully obtained with a high S/N ratio on the same silver island film-coated substrates that were used for SEIR, and it was believed to be SERS.<sup>28</sup> The SERS of ABD LB films on silver island film-coated  $\text{CaF}_2$  (A), ABD SAMs on silver island film-coated  $\text{CaF}_2$  (B), and the powder of ABD (C) in the region 900–1800  $\text{cm}^{-1}$  are shown in Fig. 3. Major bands assignments and peak positions are also listed in Table I. As we know, the multiple bands in these spectra, assigned to  $\phi$ -N stretching (1141  $\text{cm}^{-1}$ , 1189  $\text{cm}^{-1}$ ), N=N stretching (1452  $\text{cm}^{-1}$ , 1410  $\text{cm}^{-1}$ ), and benzene ring vibrations (1601  $\text{cm}^{-1}$ , 1313  $\text{cm}^{-1}$ ), are characteristic of the azobenzene moiety.<sup>29</sup> Comparing these spectra, several important features should be noticed: (1) Fig. 3A and 3B are very similar, with no frequency change, indicating that the monolayers we prepared using the two different techniques have a similar structure. (2) There are some differences between the SERS and the bulk spectra; there is a new peak (very weak) near 1500  $\text{cm}^{-1}$  in Fig. 3A and 3B, which can be assigned to the  $\nu_{\text{as}}(\text{COO}^-)$ , demonstrating the monolayers on silver island films by  $\text{COO}^- \text{Ag}$  linkage and thus created stable monolayers as shown in Scheme I. This vibrational mode cannot be observed in SEIR because of the selection rule. In this sense, SERS gives us more

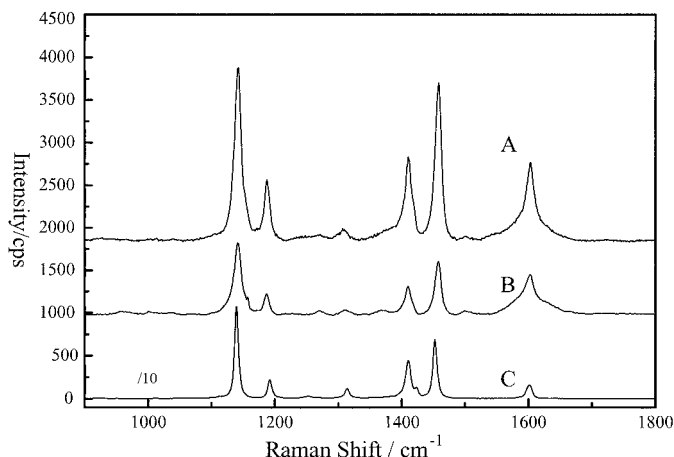


FIG. 3. The Raman spectrum of ABD powder (C) and the SERS of ABD monolayers on silver island film-coated  $\text{CaF}_2$  substrates; LB films (A) and SAMs (B).

evidence to confirm the mode shown in Scheme I. (3) The band at  $1452\text{ cm}^{-1}$  was shifted from  $1452\text{ cm}^{-1}$  in bulk to  $1458\text{ cm}^{-1}$  in SERS, which can be assigned as one of the stretching vibration of  $-\text{N}=\text{N}-$ . Another stretching vibration of  $-\text{N}=\text{N}-$  is  $1410\text{ cm}^{-1}$ , which has not changed (these two bands are attributed to the Fermi resonance of  $-\text{N}=\text{N}-$  and  $\text{ph}-\text{N}$ ). It also indicates that highly organized films have been realized.

## CONCLUSION

The SEIR and SERS spectra of SA and LB monolayers of azobenzene acid deposited onto silver island films have been investigated. Indirect evidence for chemisorption with the formation of the  $\text{COO}-\text{Ag}$  bond is presented.

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