Simple Method for the Preparation of Surface-Enhanced Raman-Active Gold Films

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A simple method for the preparation of surface-enhanced Raman-active gold films is reported. The method involves sputter coating of gold to about 2000 Å thickness on oxidized aluminium foils which yield surfaces of sub-micrometre roughness. Self-assembled monolayers of thiols grown on these substrates yield good-quality Raman spectra. Monolayers with different functionalities have also been characterized by Raman scattering. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Since the discovery of surface-enhanced Raman spectroscopy[1,2] (SERS), numerous methods have been suggested for the preparation of active surfaces.[3] Among these, the electrochemical method of inducing roughness has become the most common.[1-3] Other methods include chemical etching, mechanical polishing and a host of other means.[4] Novel methods such as depositing films on filter-papers have been suggested.[5,6] Another important class of substrates is sols, both silver and gold.[7] In almost all of these methods, careful control of the experimental conditions is important for obtaining reproducibility and reliability. In this paper, we describe a reliable and reproducible one-step method for the preparation of active substrates, which in particular will be useful in the investigation of self-assembled monolayers (SAMs).[8]

While studying the chemical modification of SAMs by reactive ion beam collision in the gas phase[9] and in the solution phase,[10] it was decided to examine the effect of these transformations on the SER spectra of the monolayers. In our studies of SAMs we have been using thermally evaporated gold films on polished glass slides or on (100) polished silicon wafers. The conventional procedures for making active surfaces such as oxidation reduction cycles (ORCs) or mechanical polishing did not yield reproducible spectra of the monolayers.

It is well known that the experimental parameters are critical in the observation of SER spectra. For example, in the case of ORC, the number of cycles, the charge passed during the cycles, the characteristics of the elec-trolyte, the electrode potential, etc., have significant effects on the Raman enhancement.[11,12] In the case of sols, the chemical reduction of the adsorbant due to the excess reductant and the aggregation of the sol upon the addition of the adsorbate are two important causes of concern. For vapour deposition, the thickness of the film and the substrate temperature are two important parameters affecting the quality of the film.[11,12] For SERS to become an acceptable tool in microanalysis, especially for monolayers, it is important to develop reproducible and simple methods for the preparation of active surfaces. It was in this context that we decided to investigate the use of alternative routes for the preparation of active surfaces.

EXPERIMENTAL

There are several ways to induce roughness in a microscopic way. One is to evaporate metals of choice on already roughened surfaces. One of the simplest ways to induce microscopic roughness on a substrate is to oxidize it. The conditions employed will change the quality of the film formed. In our attempt to make SER-active gold films, we sputter deposited gold on oxidized aluminium foils. Commercial aluminium foil of 0.02 mm thickness, used for packaging, was employed for this purpose. The foils were oxidized by heating them at 500 °C in air for 5 h. These foils were coated with gold (99.9% pure) in an Edwards sputter coater used for the preparation of specimens for scanning electron microscopy (SEM). The evaporation was carried out at a pressure of 0.01 Torr of Ar (discharge conditions: 1.3 kV, 5 mA). The aluminium foil was sheeted on the substrate holder, which was 10 cm in diameter. After sputtering for about 30 min, a film of about 2000 Å thickness was formed. These films were cut to the appropriate size and used for the preparation of SAMs. Silver films for SERS work were also prepared similarly. SAMs were prepared by dipping the foil in 1 mM solutions of the thiols in absolute ethanol for 12 h. On

removal from the solution, the foils were washed in absolute ethanol and air dried.

Raman spectra were measured with a Bruker IFS 66v FT-IR spectrometer with a Fourier transform Raman attachment. The primary excitation source was Nd:YAG laser radiation at 1064 nm. A laser power of 70 mW was used for the 1,4-benzenedimethanethiol monolayers. For other monolayers a laser power of 300 mW was used. The sample was held in a fixed position. Each spectrum was constructed from 1000 scans and the accumulation was complete in 50 min. No degradation was observed. The same monolayer could be used for variable-temperature measurements involving several measurements in the 25–200 °C. Variable-temperature measurements were performed with a laboratory-built heater and a programmable temperature controller.

In our measurements, it was found that the quality of the films was better when they were removed from the sputter coater soon after evaporation and immersed in the solution. In the case of foils kept in the vacuum chamber for long period, spurious peaks were observed. Nevertheless, all the foils gave the expected peaks upon monolayer formation.

RESULTS AND DISCUSSION

Figure 1 shows the scanning electron micrographs of the thermally evaporated and sputter-coated gold films. It is evident that the sputter-coated film on oxidized aluminium foil [Fig. 1(a)] shows roughness of micrometre size. Previous SEM studies indicated the need for roughness of this order for Raman enhancement.[13] Thermal evaporation on polished glass [Fig. 1(b)] produced a more uniform film devoid of such roughness, although defects of sub-micrometre size are apparent. In order to understand the effect of oxidation, the micrograph of an unoxidized aluminium foil was also obtained [Fig. 1(c)]; this shows random defects, but the corrugations are not pronounced.

Figure 2 shows the Raman spectra of monolayers of 1,4-benzenedimethanethiol ($HSCH_2C_6H_4CH_2SH$) (BDMT) grown on gold-coated polished glass and oxidized aluminium surfaces. In order to compare the reliability of the spectrum, the spectrum of a monolayer grown on a silver film prepared similarly is also shown. The SERS spectrum of a BDMT monolayer on a silver sol has been studied by Lee et al.[14] Whereas the polished film does not yield any spectrum, the other two spectra are similar. The Ag monolayer spectrum is identical with that obtained from BDMT adsorbed on silver sol reported by Lee et al.[14] The complete absence of the S–H stretching mode on Ag indicates that the spectrum is only from the monolayer. The nearly complete disappearance of the aromatic C–H modes on Ag should be noted. This is explainable on the basis of SERS selection rules[15,16] and is indicative of an adsorbate geometry in which the benzene ring is lying flat on the surface.[14] In the Au monolayer, chemisorption occurs with only one of the sulphur atoms and the other thiol proton is retained. Therefore, an S–H stretching mode is observable at 2562 cm^{-1}. The presence of the thiol proton leads to the appearance of a C–S–H bending
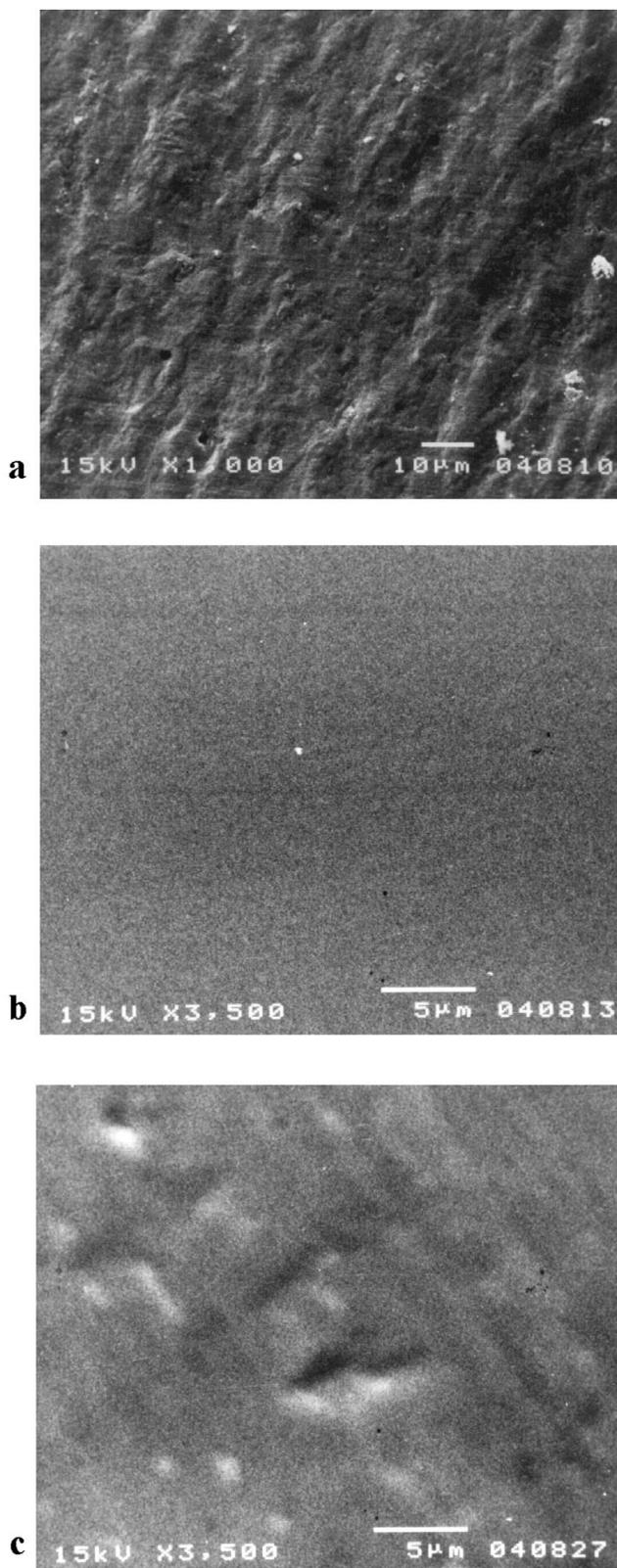

Figure 1. Scanning electron micrographs of (a) the gold-coated oxidized aluminium foil, (b) gold-coated polished glass plate and (c) unoxidized aluminium foil.

mode at 785 cm^{-1} in Au which is completely absent in the Ag monolayer. The CH_2 wagging mode at 1253 cm^{-1} present in the Au monolayer is absent in Ag where the thiol proton is absent. Since only one sulphur is chemisorbing on the Au surface, the benzene ring lies
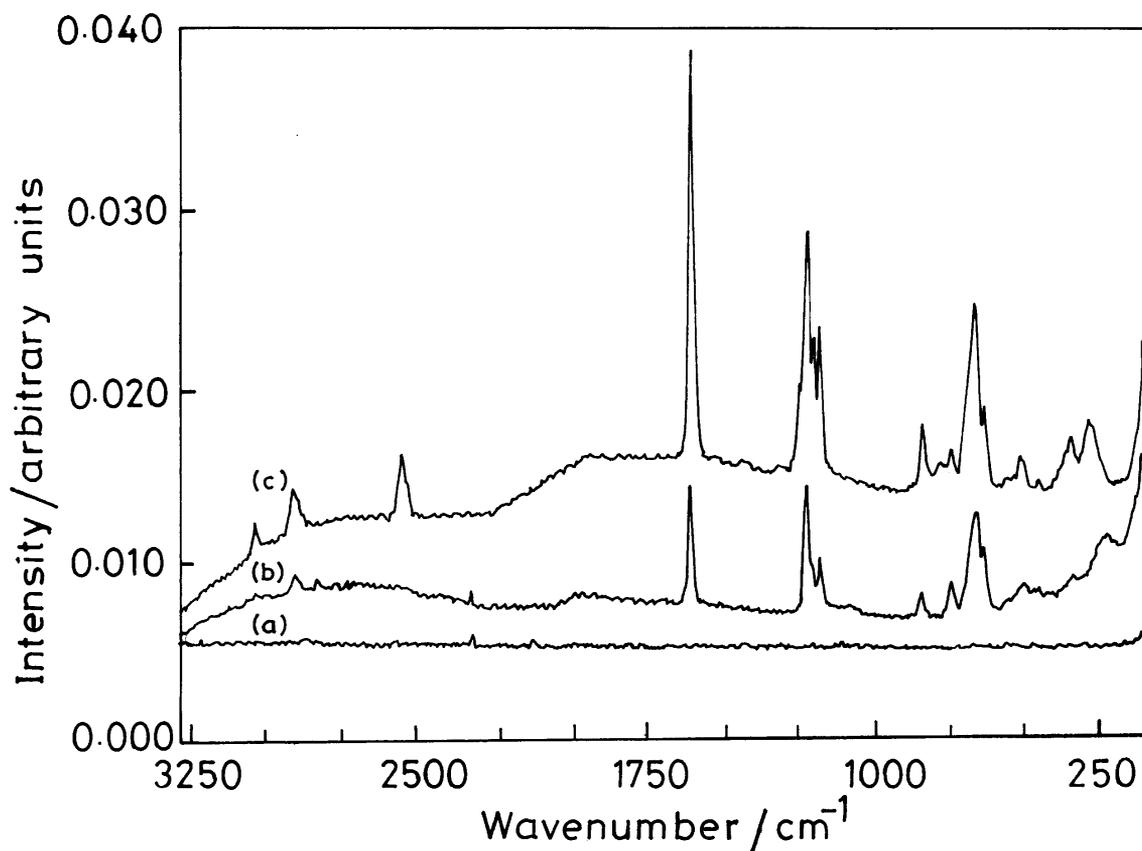
Figure 2. SER spectra of 1,4-benzenedimethanethiol monolayer on (a) gold deposited on polished glass, (b) silver and (c) gold deposited on oxidized aluminium foil.
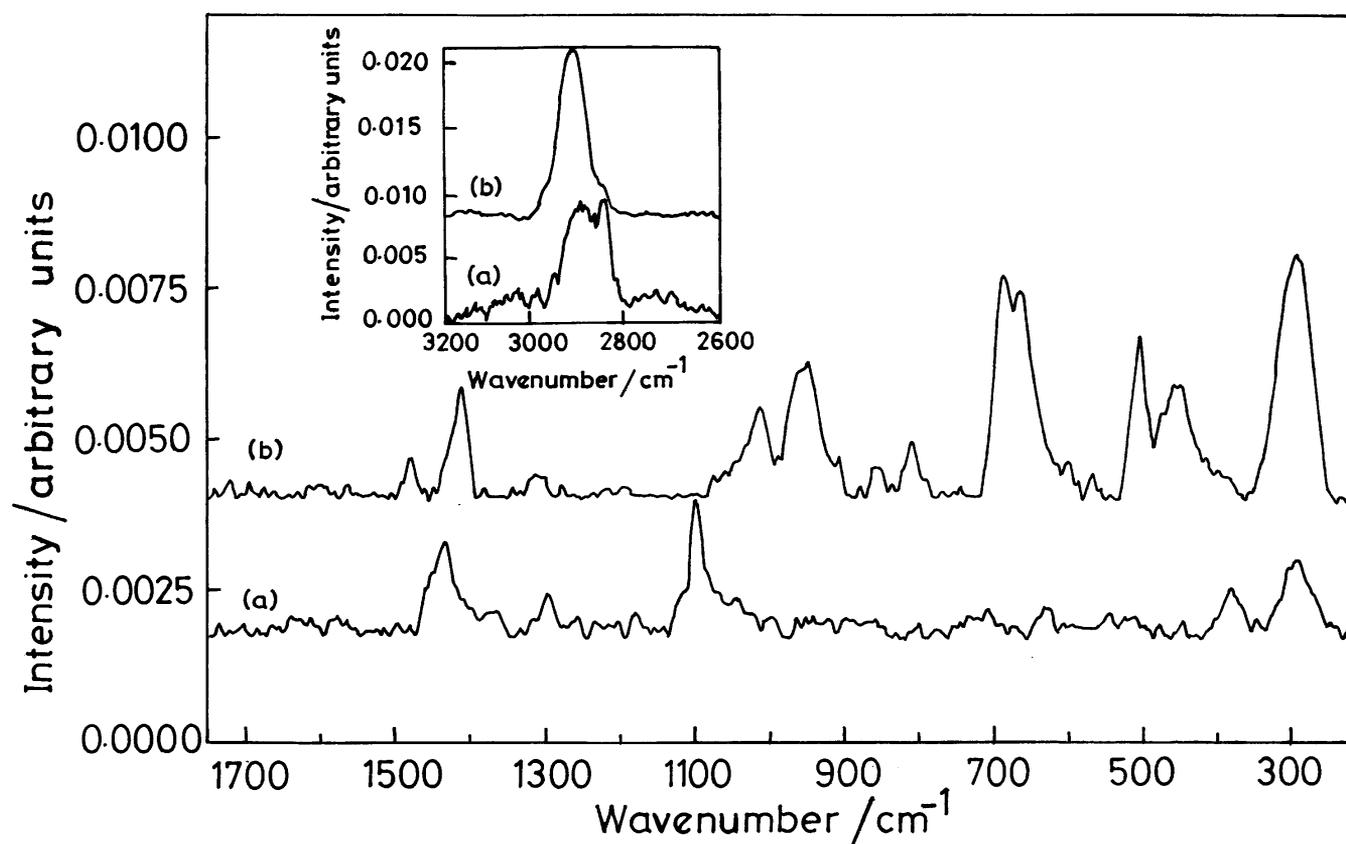

Figure 3. SER spectra of (a) mercaptoundecanoic acid and (b) mercaptopropionic acid monolayers on gold. The inset shows the C–H regions for the same samples.

Table 1. Wavenumbers (ṽ) and assignments of bands in the normal Raman (OR) spectrum of BDMT and SER spectra of BDMT on gold and silver, together with the scaled[a] 6–31G* wavenumbers

BDMT solid OR $\tilde{\nu}$/cm^{-1}	BDMT/Au SER $\tilde{\nu}$/cm^{-1}	BDMT/Ag SER $\tilde{\nu}$/cm^{-1}	BDMT/Ag sol[b] $\tilde{\nu}$/cm^{-1}	Assignment	6–31G* Neu[c] $\tilde{\nu}$/cm^{-1}	Symmetry[d]
3056	3052	3050 (vw)	—	νCH(arom)	3053	A′
3035	—	—	—		3015	A′
3010	—	—	—		—	A′
2928	2924	2916 (w)	2928	νCH(CH$_2$)asym	2957	A″
					2956	A″
2840	—	—	—	νCH(CH$_2$)sym	2918	A′
					2917	A′
2553	2562	—	—	νSH	2626	A′
					2625	A′
1611	1609	1609	1604	νCC(ring str.)	1644	A′
1576	—	—	—	νCC(ring str.)	1592	A′
1430	—	—	1420	CH$_2$ def.	1467	A′
1254	1253 (sh)	—	1218	CH$_2$ wag.	1339	A′
	1224	1224	—	CH$_2$ wag.	1290	A′
					—	A′
1200	1201	1201	1200	Sub. sen. band[e]	1195	A″
					1184	A″
					1170	A′
1183	1181	1177	1180	β_{C-H}[f]	984	A″
978	—	—	—	γ_{C-H}[f]	941	A″
838	838	842	842	γ_{C-H}[f]	894	A″
792	785	—	—	δ_{CSH}[f]	850	A″
743	743	743	741	γ_{C-H}[f]	818	A′
676	668, 675	662	642	νC–S	731	A′
638	636	634	630	βCCC[f]	694	A″
					625	A′
—	515	500	515	—	496	A′
344	355	345	345	Sub. sen. band	326	A″
—	296	233	—	Metal–S vib.	—	—
—	—	—	—	CH$_2$ def.	286	A″
—	—	—	—	CS bend.	164	A′
					161	A″

[a] Multiplied by 0.9.
[b] Ref. 15 (the bands at 642 and 630 cm^{-1} have been assigned differently in Ref. 15).
[c] Neutral molecule.
[d] Symmetry notation.
[e] Substituent-sensitive band.
[f] γ, Out-of-plane vibration; β, in-plane vibration; δ, bending vibration.

perpendicular to the surface and surface selection rules[15,16] permit the observation of the aromatic C–H stretch at 3052 cm^{-1}. The S–H band at 2540 cm^{-1} completely disappears for a monolayer exposed to alkaline solution and the peaks at 785 and 1253 cm^{-1} also disappear, suggesting that the spectrum is from a monolayer itself. The monolayers were also characterized by X-ray photoelectron spectroscopy. The SER spectrum has been assigned (Table 1) on the basis of *ab initio* molecular orbital calculations and a detailed discussion will be presented elsewhere.[17]

In order to ascertain the reliability of the method, spectra of several monolayers of C$_n$H$_{2n+1}$SH (n = 3, 6, 8, 9, 10, 12 and 18) were also measured. The spectra were identical with those reported in the literature.[18] Various aspects of monolayer formation and their thermal stability were investigated using Raman spectroscopy and the results have been presented elsewhere.[19]

Figure 3 shows the spectra of the monolayers of mercaptoundecanoic acid and mercaptopropionic acid grown on gold films prepared on oxidized aluminium foil. This demonstrates the applicability of this method to systems with different functionalities. A detailed Raman study of these monolayers will be published separately.[20]

Although there have been attempts to make SER-active substrates by evaporation of Ag on materials such as PTFE and polystyrene[21] or latex spheres deposited on filter-paper,[22] no similar method has been reported for gold. There has been a preliminary report on the SER activity of oxidized surfaces.[23] It is important to note that it is relatively easier to obtain SERS from silver than gold. However, the method reported here has also been successfully tested with silver, where the spectra are identical with those from chemically prepared films. Although a study of different metal foils might lead to a better selection of the substrate, aluminium seems to be preferable owing to its easy availability and lower cost.

In conclusion, an inexpensive, simple, one-step method is suggested for the preparation of gold films active for SER scattering.

Acknowledgements

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