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Role of atomic-scale roughness in surface-enhanced Raman scattering

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The role of atomic-scale surface-roughness features ("adatoms") in the surface-enhanced Raman scattering (SERS) effect has been examined. We use a thin, low-temperature evaporation technique in ultrahigh vacuum to generate a surface with a high density of adatoms and fail to observe SERS signals from this surface. Only thicker films, with larger surface-roughness features, show SERS signals. This observation supports surface plasmon or electromagnetic mechanisms for SERS and demonstrates that adatoms play a limited role in the enhancement.

Numerous studies in the past several years have shown that the surface-enhanced Raman scattering (SERS) effect depends critically on the existence of surface roughness.[1–4] However, the size of the roughness features which are important has remained controversial. Theoretical models based on atomic scale roughness ("the adatom model")[5] have been put forth, along with experimental observations which are interpreted as supporting this roughness scale. These include the variation of light scattering intensities upon electrode cycling and evaporated film annealing temperature, and observation of short-range enhancement.[4–7] Other theoretical models, such as the electromagnetic[8–10] or surface plasmon[11] models, rely on roughness features 50–10 000 Å in size. Experimental observations supporting this scale of roughness include direct observation of such features on enhancing surfaces,[2] observation of long-range[2] and variable-range[12] enhancement, and correlation of optical absorption and SERS intensity.[13]

The major reason for the persistence of this controversy is the difficulty involved in detecting adatoms directly, such as with electron microscopy. This makes their existence or nonexistence on any surface difficult to determine, and their importance to SERS difficult to prove or disprove. In this paper, we use a carefully controlled evaporation technique which produces SERS signals which are clearly not due to the presence of adatoms. This evaporation technique eliminates the need for direct detection of adatoms in determining their role in the SERS effect.

It has been previously shown that evaporation of a relatively thick (≈ 1-μm) silver film onto a polished substrate held at between 100 and 180 K produces a surface with strong Raman-enhancing properties.[3,14,15] Room-temperature annealing removes this enhancement, demonstrating that surface roughness plays a crucial role in SERS, but determining the scale of the roughness from this observation alone is very difficult.[3,7] In the present work, the evaporated silver film thickness is carefully controlled, and the enhancement magnitude is examined for various thicknesses of evaporated silver. Adatoms can be generated by very thin (<1 monolayer $=3.6$ Å) evaporations onto cooled substrates, as has been shown by conductivity measurements on thin gold films.[16] Evaporation of a few monolayers of silver should produce a surface with as much atomic-scale roughness as evaporation of a much larger amount of material. Thus, such thin films should show as large SERS signals as thicker films if atomic-scale roughness is indeed the roughness responsible for SERS. If, on the other hand, larger-scale roughness features are necessary for enhancement, SERS signals should only become visible after evaporation of sufficient material to form these larger structures. Thus, information about the size of surface roughness features can be inferred indirectly from the thickness of the evaporated film, obviating the need for direct measurements of the adatom density.

The experimental procedures are similar to those which have been described elsewhere.[17] In this experiment, silver films were evaporated in ultrahigh vacuum (UHV) using a temperature-monitored crucible evaporator with liquid-nitrogen cryoshielding, similar to those used in molecular-beam epitaxy.[18] With this system, pressures less than 3×10^{-10} torr were maintained even during film evaporation. Film thicknesses and evaporation rates were monitored with a Sloan DTM-200 quartz crystal microbalance, which was mounted adjacent to the sample during evaporations. An evaporation rate of 4.2 Å/min was used, and this was maintained within 8%. Evaporations were done onto a polished oxygen-free high-conductivity (OFHC) copper substrate.

The structure of the surfaces studied is shown schematically in the inset to Fig. 1. Each evaporation was done onto a thick silver film, which was deposited *in situ,* and had been annealed at room temperature to remove surface roughness. Although not perfectly flat, this surface was sufficiently smooth to show no detectable Raman enhancement. On top of this silver surface, an additional silver layer of variable thickness was evaporated while the substrate was

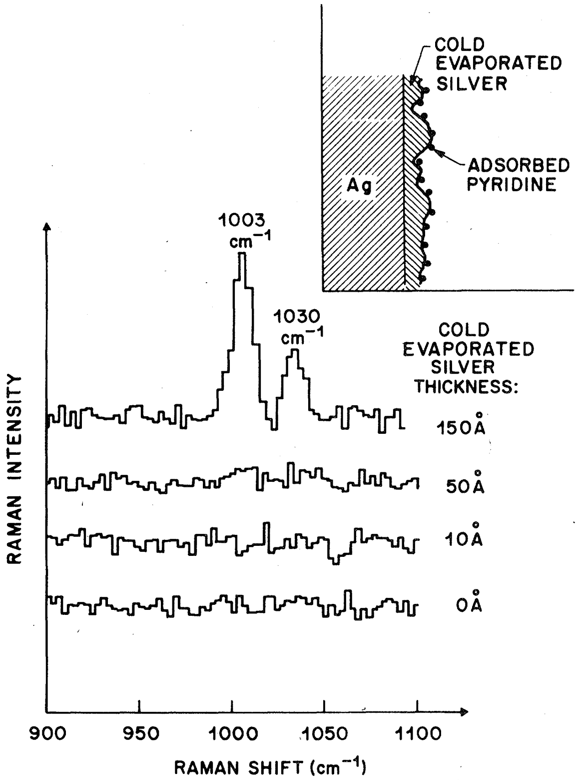

FIG. 1. Raman spectra from pyridine adsorbed on a thin, cold-evaporated silver film, as a function of silver film thickness. The inset shows the structure of the samples schematically: a thin silver layer is evaporated on top of a room-temperature-annealed silver surface while the sample is held at 180 K. This structure is then exposed to 2 L of pyridine, and the Raman spectrum is acquired. Spectra were taken with 300 mW of 4880-Å laser light, 5-sec dwell time, and 7-cm^{-1} spectrometer resolution.

held at 180 K. As shown previously,[3] the Raman enhancement arises from the surface roughness inherent in the process of deposition onto such a cooled substrate. A sample temperature of 180 K was found to maximize the SERS signals. After this thin "coldly evaporated" silver film was deposited, the sample was exposed to 2 L of pyridine,[19] and a Raman spectrum was acquired to measure the SERS properties of the surface. The sample was annealed briefly at room temperature to remove surface roughness before a new film of different thickness was coldly evaporated.

Figure 1 shows the Raman spectrum from pyridine adsorbed on silver films of four different thicknesses. The bottom curve, labeled 0 Å, is from a room-temperature-annealed silver film without any additional coldly evaporated silver. Subsequent curves are from cold-evaporated silver films of the indicated thickness. Contrary to the predictions of the adatom model, no SERS signals are observed from the 10-Å film. This failure means that any enhancement contribution from atomic-scale roughness mechanisms must be less than our detection limit, which is 10^3. Enhanced Raman signals do not appear until 150 Å of silver have been deposited. At this point, the two Raman lines at 1003 and 1030 cm^{-1} which have been previously reported for pyridine adsorbed on these silver films can be clearly seen.

Equally as many adatoms and atomic-scale roughness features should be present on the surface with a 10-Å low-temperature film as that with a 150-Å low-temperature film. If atomic-scale roughness were the cause of SERS, the enhanced Raman signals from the 10-Å silver film would be as strong as those from the 150-Å film. Figure 1 indicates that this is not the case; SERS signals are only observed from the 150-Å film. This indicates that the roughness features relevant to SERS are significantly larger than atomic scale, although a precise size cannot be assigned to them based on this experiment alone. Other measurements on these films, based on measurement of the enhancement range and the electromagnetic model, indicate that the relevant roughness feature are on the order of 50 Å in size.[12] Nevertheless, the current experiment shows conclusively that the role of atomic-scale roughness in SERS is a sharply limited one.

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[19] Exposure is expressed in uncorrected langmuirs, where 1 langmuir $\equiv 1$ L $\equiv 10^{-6}$ torr sec.