

Reply to "Comment on 'Role of atomic-scale roughness in surface-enhanced Raman scattering'"

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Otto argues that my original data can support his model for the importance of atomic-scale roughness (ASR) in surface-enhanced Raman scattering (SERS) if a process which he proposes for low-temperature film growth is used. This process is not supported by the resistivity data which he cites. Although several enhancement mechanisms probably do contribute to SERS, the conclusion of the original experiment, that enhancements due to ASR contribute less than 10^3 of the effect, remains valid.

The key disagreement is over the size of the surface roughness feature responsible for surface-enhanced Raman scattering (SERS). The original experiment¹ was the first effort to determine directly the relative importance of atomic-scale ($\sim 3 \text{ \AA}$) and larger scale (50–10 000 \AA) roughness to SERS in ultrahigh vacuum (UHV). Its conclusion was that atomic-scale roughness (ASR) features provided no more than 10^3 of the enhancement.

The experiment in question¹ involved depositing silver films on a "smooth," cooled substrate and measuring the Raman enhancement as a function of film thickness. No SERS signals were observed for films of 10 or 50 \AA , but large signals were seen for 150- \AA films. There is no disagreement on these results; the problem is in determining the microstructure of the film, given its average thickness.

The original analysis of this data was that the ASR density should saturate after several atomic layers had been deposited, and that subsequent evaporations only increased the roughness on a larger scale. Thus it was concluded from the data that ASR alone was not sufficient to produce observable enhancement in this experiment.

In order to support the thesis that ASR is primarily responsible for the enhancement, Otto argues that the surface density of ASR features increases with deposited silver thickness up to 150 \AA of additional silver thickness.² However, this interpretation is not consistent with the temperature-dependent resistivity data he cites as evidence for ASR.^{3,4}

Pariset and Chauvineau measured the increase in resistivity of thin, smooth metal films when additional layers of metal were deposited at low temperatures.^{3,4} Otto cites their measurements as direct evidence of the nature of ASR in deposited films.² Pariset and Chauvineau measured the growth in the excess resistivity as a function of the low-temperature deposition thickness for gold at 83 K. They found that this resistivity increase saturated at 12 \AA of additional gold deposit,³ so, within the context of Otto's

interpretation of their experiment, the "fuzzy step" density saturates at this thickness.

Thus the growth mode proposed by Otto, in which the "fuzzy step" density increases out to 150 \AA of silver deposition, is contradicted by the data of Pariset and Chauvineau, which shows the saturation of ASR at approximately 12 \AA . The original data analysis is supported by this resistivity data.

Otto points out that an experiment analogous to that of Ref. 1 was performed in an electrochemical cell and gave opposite results. When an average thickness of less than a monolayer of silver had been deposited, large SERS signals were observed.⁵ Indeed, this result was one of the original justifications for the adatom theory of SERS.⁶

These seemingly contradictory experiments obtained in different environments can be reconciled by understanding a complication present in the electrochemical cell. There are a number of factors which encourage deposition on preexisting surface protrusions in the electrochemical environment. Concentration of the dc applied growth field, enhanced diffusion, and Ohmic resistance of the solution all can cause greatly enhanced deposition in the region of an existing surface defect.⁷ Thus, for average silver deposition thickness of around one monolayer, one can deposit large amounts on a small fraction of the sample surface, complicating the interpretation of any experiment done in this environment. No such complications are present in UHV, where the silver deposition is thermal, and not mediated by an applied electric field. Thus UHV provides a simpler, more direct environment in which to study this problem.

It is certainly likely that both electromagnetic and other mechanisms contribute to the SERS effect. Tsang *et al.*⁸ have recently repeated this experiment,¹ using silver gratings as a substrate instead of a flat surface. By using these grating structures, they were able to observe the enhanced Raman spectrum from pyridine both in the absence and in the presence of a 20- \AA silver low-temperature film. This thin film,

which presumably introduced ASR, did produce an additional short-range enhancement, but the enhancement it contributed was on the order of a factor of 20–100.

The conclusion of the original work was that atomic-scale roughness contributed less than 10^3 of the observed enhancement. In view of Otto's com-

ments, and the recent experiments of Tsang *et al.*, this remains correct.

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