# The Use of Surface Enhanced Raman Scattering to Investigate the Surface Chemistry of Chromia Films

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Chromia surfaces have been physically modified by silver deposition to produce a large ($10^4$ times) enhancement of the Raman scattering cross-sections of surface species.

Since the initial reports of laser Raman microprobes,[1,2] the diffraction limited performance of micro-sampling has been exploited in the fields of microelectronics,[3] geology,[4] polymer chemistry,[5] and corrosion[6] to provide chemical analysis and phase information with 1—2 micron spatial resolution. The limitation of Raman microscopy as a tool for surface analysis is its lack of surface specificity. The probe depth can only be controlled to within ±0.1 μm, by manipulating the incident beam parameters and by a careful choice of objective lens. It is mainly determined by the components of the complex refractive index of a particular sample. This is a problem because although equipment is now sensitive enough to detect monolayers of surface species, there is no easy means of sampling only the first 1—10 Å of a thick sample. Therefore if surface effects are to be studied by Raman spectroscopy another approach must be adopted. Since its discovery in 1974 by Fleischman *et al.*,[7] the surface selectivity of surface enhanced Raman scattering (S.E.R.S.) has been used to distinguish aqueous solution species from metal electrode adsorbates in many electrochemical systems. It has also been reported that S.E.R.S. can be obtained from adsorbates on thin silver films.[8,9] In this case, it is necessary to control the silver deposition rate so as to generate silver islands of a particular size and shape. Another method is to control the morphology of the surface onto which the film is deposited.[10]

Here we report the first observation of S.E.R.S. from phonons of the substrates (as distinct from vibrations of adsorbates on the substrate) onto which silver has been deposited. Two different types of substrate were used, either oxidised chromium metal coupons or radio frequency (R.F.) sputtered layers of chromia on fused silica discs. Silver was deposited onto the oxidised samples by simple evaporation. The thickness was varied between 400 and 900 Å. R.F. sputtering was used to produce the second type of samples, both silver-on-chromia and chromia-on-silver films were prepared. In either case the R.F. sputtered layers were composed of 200 Å silver and 200 Å chromia. Film thicknesses were measured by ellipsometry, but it was found that the silver deposited onto the oxidised chromium coupons was too rough to make accurate measurements, therefore their approximate thicknesses were calculated from silver weight loss values.

Figure 1 shows the excitation dependence of the Raman spectrum of the surface of an oxidised coupon after 900 Å of silver had been deposited. No Raman scattering could be detected from the surfaces of other samples with thinner silver layers. The spectra show a single broad band at 878 cm$^{-1}$ which shifts position with excitation frequency. The intensity of the band deviates from the normal $\lambda^{-4}$ scattering rule (all photon count values have been normalised for detector responsivity), indicating that either S.E.R.S. or resonance Raman scattering of some silver compound is occurring. Chemical reaction of silver with chromia to form silver(I) chromate is not expected on thermodynamic grounds at the available $O_2$ partial pressure $p[O_2] = 0.2 \times 10^{-5}$ bar, and it is believed that S.E.R.S. is taking place because scattering was observed only from the oxide surfaces with the thickest deposited silver films. This is not surprising because surface morphology is known to be a crucial factor in generating S.E.R.S. Furthermore, scanning electron microscopy (S.E.M.) showed the 900 Å layer to have a 'rippled' appearance. The periodicity of this rippling was estimated to be between 0.25 and 0.5 μm. Figure 2 shows the excitation dependence of Raman spectra from a layer of chromia sputtered onto silver, which was initially sputtered onto fused silica. No Raman scattering could be detected from silver sputtered onto chromia samples. The results show two Raman bands at 814 and 782 cm$^{-1}$. Both bands shift appreciably with excitation wavelength. Again, the intensities of the bands deviate from the normal $\lambda^{-4}$ scattering rule. S.E.M. showed the R.F. sputtered films to be very flat in all cases, but a weak surface rippling was observed on the chromia-on-silver film which gave S.E.R.S.

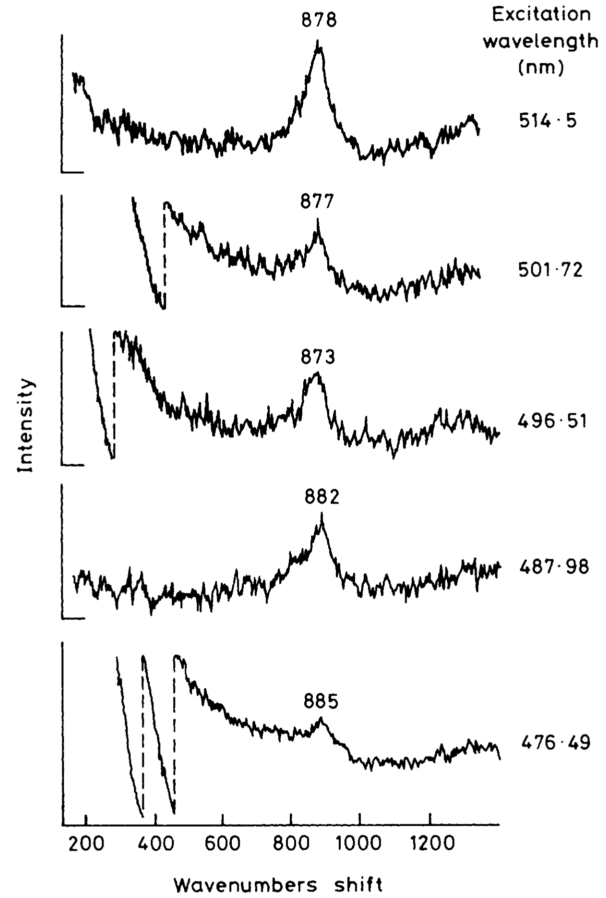

**Figure 1.** Excitation dependence of S.E.R.S. from an oxidised chromium metal coupon with a vapour deposited silver film. Spectra were obtained using 0.1 mW laser excitation and 160 s acquisition time in each case.

All spectra were recorded on a Raman microprobe with 2 μm laser spot diameter and 3 kW cm$^{-2}$ laser power density.

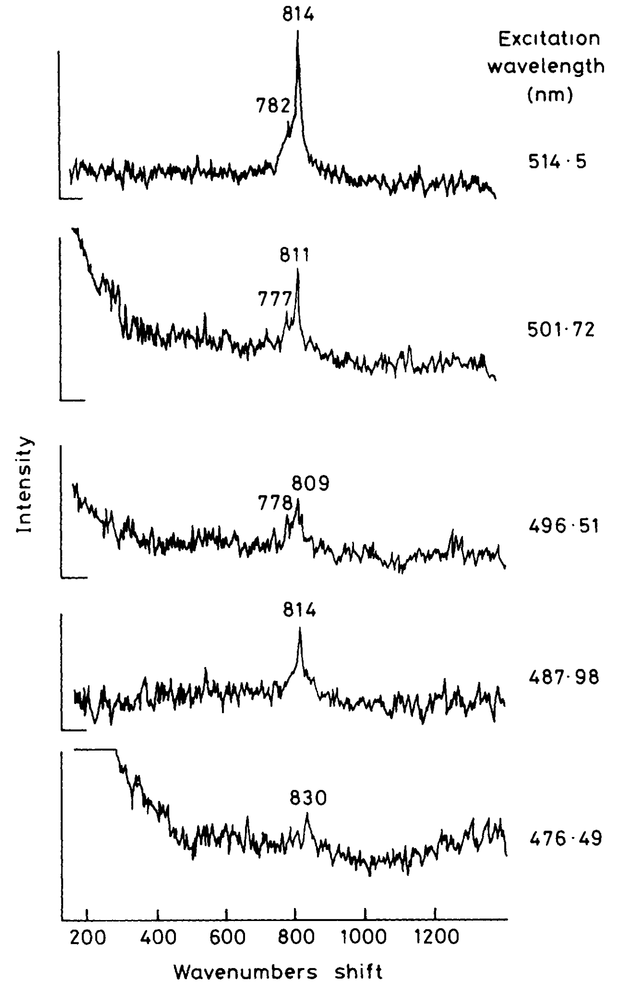

**Figure 2.** Excitation dependence of S.E.R.S. from R.F. sputtered chromia on silver thin films on fused silica. Spectra were obtained using 0.1 mW laser excitation and 160 s acquisition time in each case.

Spectra were found to be representative of the surface as a whole and no laser induced damage was observed at these power densities. An intensified diode array detector allowed spectra to be rapidly recorded and no loss of S.E.R.S. intensities were observed during the course of experiments.

S.E.R.S. is a surface selective phenomenon and therefore the Raman spectra obtained will represent only the first few atomic layers of chromia. Comparison of these results with previously published Raman spectra[11—15] shows that the spectra are markedly different from bulk chromia,[11] but similar to $Cr^{VI}$ oxyanions.[12] The important implication of this is that the chromia surfaces investigated here are composed of higher oxidation state chromium sites, allowing charge compensation by $O^{2-}$ or $O_2{}^{2-}$ adsorption.

There is every reason to suppose that the technique of silver modification can be extended to other substrates, providing that the surface morphology of the silver can be accurately controlled.

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